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TREATING KERATOKONUS DISEASE WITH CROSS-LINKING METHOD
TRAJTIMI I KERATOKONUSIT ME METODEN E CROSS-LINKING

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ABSTRACT
Keratokonus is a degenerative disease, starting generally at 14- 25 years old and causing progressive thinning of the cornea. Because of these thinning, corneal shape is reduced into a conical one, causing also distortion of vision. Clinically, keratokonus presents progressive changes of the refraction, principally of astigmatisms, the patient frequently change the glasses but don't feel comfortable with them. Extreme advancement of the keratokonus can cause corneal perforation, destroying the vision. To avoid this, corneal transplant is required to save the eye. Considering the young age of the patients, high cost of the of the corneal transplantation, and the risk of transplant reject, high priority is given to the early diagnose and halting treatment. Nowadays, cross-linking is the only procedure used to halt the natural progression of keratokonus, Studied and applied for the first time at Dresden University, a great number of clinical studies supported its efficacy in halting the progression of keratokonus.

PERMBLEDHJE
Keratokonusi është sëmundje degjenerative e kornesë, e cila fillon të evidentohet në moshën 14- 25 vjeç dhe shkakton hollim progresiv të saj.Për shkak të këtij hollimi, kornea merr formë konike duke shkaktuar deformim dhe dëmtim të shikimit.Klinikisht paraqitet me rritje progressive të korrigjimit optik,kryesisht të astigmatizmit,pacienti ndërron shpesh syzet por nuk ndihet komod me to.Ndërkaq mprehtësia e pamjes ulet progresivisht. Në stadet e deformimit te avancuar dhe të hollimit ekstrem, kur kornea tenton perforimin, transplanti I kornesë është e vetmja metodë që mund të shpëtojë syrin.Duke pasur parasysh faktin se prek kryesisht moshat e reja,koston e lartë të transplantit të kornesë si dhe pasojat invalidizuese për shikimin në rastin e flakjes së këtij të fundit, rëndësi të veçantë merr diagnostikimi I hershëm dhe trajtimi me metodën e cross-linking. Cross-linking është për momentin e vetmja metodë e njohur që vitet e fundit po përdoret gjerësisht në frenimin e ecurisë progressive te keratokonusit. E eksperimentuar dhe aplikuar për herë të parë në Universitetin e Dresdenit, studime të shumta kanë mbështetur efikasitetin e saj në trajtimin e keratokonusit.

Key words: keratokonus,keratometri,pakimetri,cross-linking,kornea

INTRODUCTION

The cornea is a transparent interface covering the front of the eye. It has the function of protecting the eyeball and also is a powerful refracting surface, providing 2/3 of the eye's focusing power. The adult cornea has a thickness of 500 µm and is comprised of 5 layers: epithelium, Bowman's membrane, stroma, Descemet's membrane and the endothelium. The stroma is the thickest layer composed of collagen fibrils oriented parallel to each-other. It has also transversal fibrils which bond the parallel ones to each-other, giving to the cornea its natural strength. This phenomenon is known as natural cross-linking and it is responsible for the cornea's resistance against deformation.Keratoconus is a bilateral non-inflammatory disease which causes progressive corneal thinning, leading to protrusion, distortion, and scarring of the cornea1 It is a naturally occurring ocular condition which leads to steepening of the central cornea, increasing myopia, irregular astigmatism, and

loss of best spectacle-corrected visual acuity. Corneal thinning normally occurs in the infero-temporal or in the central cornea2. Exceptional case of superior localizations have also been described3,4.Keratokonus becomes evident normally during puberty6 , although the disease has also been found to develop earlier5 and latter in life6.It potentially progresses until the fourth decade of life, when it usually stabilizes6. A study has determined that 50% of non-affected eyes of subjects with unilateral keratoconus will develop the disease in 16 years7. If left untreated, keratokonus frequently progresses to formation of descement's tears (known as Vogt's stries) and corneal perforation, seriously threatening the vision. At this point,corneal transplantation is required to restore useful vision and saving the eye. Corneal Collagen Cross-linking is a treatment for keratoconus and other corneal ectasia which was developed first at the University of Dresden in 19988. In this procedure ultraviolet (UV) light and riboflavin (vitamin B2) drops are used to strengthen the cornea's structure, to slow or halt the progression of keratoconus, preventing deterioration of vision and the need for corneal transplantation. Firstly experimented in porcine and rabbits corneas, the results showed that riboflavin soaked and UVA irradiated corneas were stiffer and more resistant to enzymatic digestion. Investigations also proved that the treated corneas contained high molecular weight polymers of collagen due to fibril cross-linking11.Others, in vitro investigations, on human and porcine corneas examined the best treatment parameters for standard cross-liking, such as riboflavin concentration, intensity, wavelength of UV-A light, and duration of treatment.9 Also it has been proved that UVA irradiation is not harmful for the endothelium, if the corneal thickness is above 400 µm 10 After the laboratory, clinical results were also encouraging. The pilot study included 16 patients with progressive keratokonus that were treated with cross-linking. All of them showed stopped progressing after treatment.70% had flattening of the steepest keratometry, decrease in average and maximum keratometric values and 65% had visual acuity improvement. No complication reported 8

After that, cross-linking became a worldwide used technique. Generally is applied by using Dresden protocol8 requiring the removal of central 9 nm of corneal epithelium layer, followed by 30 minutes of riboflavin administration, subsequently, UVA light is applied for 30 minutes. The corneal epithelial layer is generally removed to increase penetration of the riboflavin into the stroma.[11] During the UV light illumination, riboflavin acts further as a shield during irradiation to the cornea, protecting deeper ocular structures such as the endothelium, lens, and retina from UV-A irradiances that are too high(12) Another important role of riboflavin is to prevent corneal dehydration during exposure(13) The combination of riboflavin and UV-A light creates 80–95% absorption into the cornea during cross-linking depending on the concentration and the corneal thickness (12) Given the simplicity and minimal costs of the treatment, cross-linking treatment is also well-suited for developing countries(8) Later and latest study16, as the Siena Eye Study14, investigates long-term effects of standard cross-linking. Three hundred and sixty-three eyes were treated and monitored over 4 years, producing reliable long-term results proving the efficacy of the procedure in terms of long-term stability of the cornea by halting the progression of keratokonus, and proving the safety of the procedure14

In our hospital, cross-linking technique is applied from 2009. The patient presented with complains such as: progressive changements in refraction, changing frequently the glasses and not feeling comfortable with them, high astigmatism and myopia, are suspected for keratokonus. These patients are advised to undergo topographic examination with Pentacam instrument which is based on the Scheimpflug working principle, taking 12–50 images of the cornea at different angles using a rotating camera. Anterior and posterior corneal elevations are then measured using topographic analysis, providing useful information in keratokonus diagnostic and grading the severity of keratokonus15 IV-th grade of keratokonus with pachymetry lower than 360µm, Vogt's striae or corneal hydrops are immediately advised to undergo corneal transplant procedure. The patients, diagnosed in stage 1-3 of keratokonus, with no corneal changements are followed for 6 month to check the evidence of keratokonus progression and in this case, are advised to undergo cross-linking procedure. Others, already

presenting clear evidence of progression in comparison of earlier topographic examination are immediately advised to the cross-linking procedure. The results of follow-up are collected and discussed in "Results and Discussion" showing evidence of flattening the cornea and stopping the progress of keratokonus.

PATIENTS AND METHODS

81 eyes with progressive keratoconus were included in the study. Average age was 23.5 years (the youngest 15 years old and the oldest 38 years old). A rotating Scheimpflug camera (Pentacam HR, Oculus) is used to diagnose and follow-up the keratokonus before and post cross-linking treatment. Corneal elevation, pachymetry and keratometry were the parameters measured. The inclusion criterias were: progression of keratoconus resented as an incresing in maximum keratometry (steepest keratometry) at least 0,5 D in 6 months, preoperative corneal thickness above 400 µm, no corneal scar, no previsious corneal surgeries.Patients underwent cross-linking procedure according to Dresden protocol.After cross-linking procedure the patients were followed with three dimensional corneal topography (Pentacam HR Oculus) and the parameters followed were: keratometry steepest, flattest, average,corneal pakimetry average and thinnest, uncorrected and best-corrected visual acuity. The follow-up time was 12 months.

RESULTS AND DISCUSSION

The values for each parameters are recorded after 1 month, 3 month, 6 months and 12 months after cross-linking. The average value is recorded for each variable for each period of time and compared using the Willcoxon test to obtain the values of z and p.The results are recorder in the tables below:

Table 1 Values of flattest keratometry

Tiime	Value	Test Wilcoxon
Before cross-linking	46.6	
1 Month after treatment	46.9	Z=2.29 P = 0.0254
3 Months	46.2	Z= 0.59 P = 0.5799
6 Months	45.6	Z= 3.88 P = 0.0023
12 Months	44.8	Z= 3.71 P = 0.0005

Table 2 Values of steepest keratometry

Time	Value	Testi Wilcoxon p
Before cross-linking	50.6	
1 Month after treatment	51.1	Z=2.6 P = 0.0117
3 Months	50.5	Z= 0.04 P = 0.969
6 Months	49.9	Z= 2.399 P = 0.0164
12 Months	49.2	Z= 3.85 P < 0.001

Table 3 Values of average keratometry

Time	Value	Test Wilcoxon
Before cross-linking	48.3	
1 Month after treatment	50.0	Z=3.8 P = 0.0001
3 Month after treatment	48.3	Z= 0.54 P = 0.585
6 Month after treatment	47.6	Z= 2.83 P = 0.004
12 Month after treatment	47.1	Z= 2.8 P < 0.001

Table 4 Values of UCVA (uncorrected visual acuity)

Time	Value	Test Wilcoxon
Before cross-linking	0.68	
1 Month after treatment	0.21	Z=1.15 P = 0.24
3 Month after treatment	0.29	Z= 0.63 P = 0.524
6 Month after treatment	0.31	Z= 1.88 P = 0.05
12 Month after treatment	0.65	Z= 2.1 P =0.74

Table 5 Values of BCVA (best corrected visual acuity)

Time	Value	Testi Wilcoxon
Before cross-linking	0.54	
1 Month after treatment	0.46	Z = 017 P = 0.2455
3 Month after treatment	0.55	Z= 0.9 P = 0.3547
6 Month after treatment	0.61	Z= 2.8 P < 0.001
12 Month after treatment	0.64	Z= 2.8 P < 0.001

As we see in table 1,2 and 3 , keratometry value of the first month after cross-linking, have the tendency to be higher than before . The remodeling of the keratokonus area is not yet started. The real reduction in keratometry results become evident after 6 months and progressively continuing after 12 months. From table 1 and 2 is noted that after 1 year :

- flattest keratometry reduced of 1.8 D
- steepest keratometry reduced of 1,4 D (statistically significant Z= 3,85 p< 0,001)
- average keratometry reduced of 1,2 D (statistically significant Z=2.8 p< 0,001)

Tables 3 and 4 presents the values of UCVA and BCVA, measured with Snellen chart, and their changements after 1,3,6, 12 months are recoreded. This values are lower 3 months after cross-linking mostly due to corneal haze after it. The visual acuity recovers 6 months after cross-linking and later changes as follow:

- UCVA remains the same 12 months after cross-linking
- BCVA improves 1 line 12 months after cross-linking (z=2.8 p<0,001)

The values of corneal thickness remains almost the same and never going down 400 µm. The reduce of 10 µm over 12 months is due to corneal shrinking induced from intensified collagen cross-linking process.

CONCLUSIONS

After collagen cross-linking, the modification in corneal shape and thickness and BCVA were found to be:

- Reduction in keratometry (flattest 1,8 D, steepest 1,4 D)
- Stabilization in corneal thickness
- Improving of BCVA (1line)

Therefore flattening and stabilizing the cornea, collagen cross-linking showed to be an efficient method in stopping keratokonus progression

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NEONATES IN INDUCTION OF LABOR COMPARED WITH EXPECTANT MANAGEMENT

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SUMMARY
The aim: To study the relationship between neonatal problems, induction of labor and determine whether there is an optimal delivery gestational age. Materials and methods: It is a study in Hospital of Obstetric Gynecologic "Geraldine Queen" in Tirana for neonates with history of premature rupture of membrane ≥18 hours for outcome of neonate in induction of labor compared with expectant management. Results: Were included 617 newborn. 213(37.4%) infants were premature. The labor was induction in 263(42.6%) cases. The incidence of neonatal infection was 11.53%, sepsis 9.27%. Mortality was seen in 8(1.3%) neonates. Conclusions: Induction of labor is protective factor in premature rupture of membranes. Key words: neonate, rupture of membranes, induction, expectant management

PERMBLEDHJE
Qëllimi: Të studiojë lidhjen ndërmjet problemeve të neonatit në lindjen e induktuar dhe përcaktimin kur është koha më e përshtatshme për lindje.Materialet dhe metoda: Është një studim në Spitalin Obstetrik Gjinekologjik "Mbretëresha Geraldinë" Tiranë për neonatët me histori të rupturës së parakohëshme të membranave ≥ 18orë për rezultatet e neonatit në lindjet e induktuar krahasuar me qëndrimin pritës. Rezultatet: 617 u përfshinë në studim. 213(37.4%) neonatë ishin prematurë. Lindja u induktua në 263(42.6%) raste. Incidenca e infeksionit neonatal ishte 11.53%, sepsis në 9.27%. Mortaliteti rezultoi 1.3%. Konkluzion: Induksioni i lindjes është faktor mbrojtës në rupturën e parakohëshme të membranave. Fjalë kyçe: neonat, rupturë e membranave, induksion, qëndrim pritës.

Background: Premature rupture of membranes is a spontaneous rupture of fetal membranes and leakage of fluid from the vagina before the onset of true labor. Premature rupture of membranes happens to full term infants (PROM) and to preterm infants (PPROM). (16, 18, 12) It has a risk for neonatal morbidity such as: infection, sepsis, birth asphyxia, respiratory distress syndrome, apnea, neurologic disorder (10, 12,16 18)
There are two options for managing of premature rupture of membranes, expectant management (a wait and see approach) or early planned birth. The infection is the main risk in management is expectant. This risk need to be balanced against the risk of iatrogenic prematurity if early delivery is planned. The use of prophylactic antibiotics, or corticosteroids, fetal lung maturity testing, and immediate delivery compared with expectant management are undefined aspects of management. (7, 19)
When PROM occurs at term, early delivery is associated with a lower incidence of maternal infection compared with expectant management.(2) At extreme preterm gestations, in the absence of maternal or fetal compromise, there is unanimity in that expectant management to allow further fetal maturation is desirable (13)

The aim: To evaluate the effectiveness of early planned birth compared with expectant management for neonates of women with PROM.

Materials and methods: It is a prospective descriptive study in University Hospital of Obstetric Gynecologic "Geraldine Queen" in Tirana Albania during a period 1 January 2009 to 31December 2012. We study the outcome of neonate with history of PROM in induction of labor compared with expectant management.

Entered into this study all neonates of mother with history of PROM ≥ 18 hours. Age of pregnancy is ≥28 years. Exclusion criteria were as follows: infants with congenital anomalies, multi fetal gestation, infantile was not born at our hospital. According to the gestational age neonates were classified into five groups: 28-30 weeks, 31-32weeks, 33-34 weeks, 35-36 weeks, up to 37 weeks.

Time of rupture of membranes from delivery was classified into the early birth group (will be delivered within 24 hours and the later birth group (will be delivered after 24 hours). Options for managing was classified into two groups: expectant management (a wait and see approach) and induction of labor (early planned birth) with intravenous oxytocin.

The infant outcome was neonatal infection, sepsis, neonatal major and minor morbidity, perinatal mortality, duration of stay in hospital, birth weight, Apgar. Maternal outcomes included: treated (antibiotics and glucocorticoids), induction of labor.

Neonatal infection defined as the presence of clinical signs of infection and a positive culture of a known pathogen from blood or cerebrospinal fluid. Clinical signs of infection include respiratory distress syndrome (RDS), apnea, lethargy, hypotension, poor perfusion, need for inotropic support or volume expansion, poor feeding and/or temperature instability.

Neonatal major morbidity was defined as presence of any of the following: RDS, intraventricular hemorrhage, need of artificial ventilation, bronchopulmonary dysplasia, sepsis, seizure, necrotizing enter colitis, pneumonia, meningitis, patent ducts arteriosis. Neonatal minor morbidity was defined as presence any of the following: jaundice, transient hypo or hyperglycemia.

A statistical calculation was performed by SPSS16. Was used chi square test, student t test, logistic regression analysis.

RESULTS: 27196 newborn infants were born alive during study period. 617(23.9%) infants had a maternal history of PROM >18 hours and included in the study. In 263(42.6%) cases the born were inducted. 231(37.4%) infants were born premature. 328(53.2%) infants delivered within 24 hours of PROM and 289(46.8%) infants delivered after 24 hours of PROM.

Table 1: Neonatal characteristics

Variable	Median	Deviation standard	Range
Apgar score (min 1)	8.16	±1.19	1÷10
Apgar score (min 5)	9.43	±0.91	3÷19
Birth weight (grams)	2938.9141	1588.5617	300÷3900
Duration of hospital stay	7.84	±5.77	1÷27

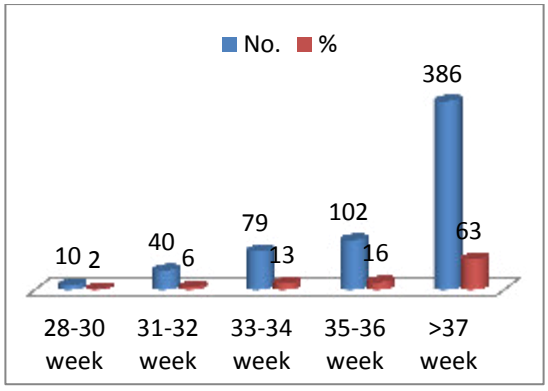

Figure 1: The classification of infants by gestational age

The incidence of infection resulted 11.54% (n=71). Infants in the induction group were less likely to have infection, than those in the expectant management group OR=0.26, 95%CI: 0.14-0.49, P<0.0001. The preterm infants had more likely to infection OR=9.56, 95%CI: 5.10-17.9, P<0.0001. Premature had greater risk for infection and the risk increases with decrease of the pediatric age P<0.0001.

Table 2: Correlates of infection with age of the pregnancy

Age (week)	Infection	Relative risk	95% Confidential interval	p value
28-30	7	20.67	10.57-40.44	P<0.0001
31-32	18	13.29	7.04-25.07	P<0.0001
33-34	22	8.22	4.33-15.6	P<0.0001
35-36	11	3.18	1.47-6.89	0.003
>37	13	reference		

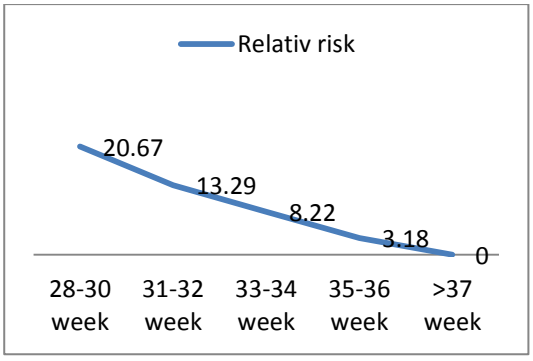

Figure 2: Relative risk of infection according to age of the pregnancy

After 24 hours of PROM, infantile were more likely to make infection OR = 3:32, 95%CI: 1.93-5.73, P<0.0001. There is high risk of infection after 48 hours and the risk increases with the latency period P<0.0001.

Table 3: Correlates of infection with the period of latency:

Time of PROM	Infection	Relative risk	95% Confidential interval	p value
18-24 hour	20	reference		
24-48 hour	14	1.2	0.62-2.32	0.5
> 48 hour	23	6.85	4.04-11.6	<0.0001
>7 hour	14	5.6	3.07-10.2	<0.0001

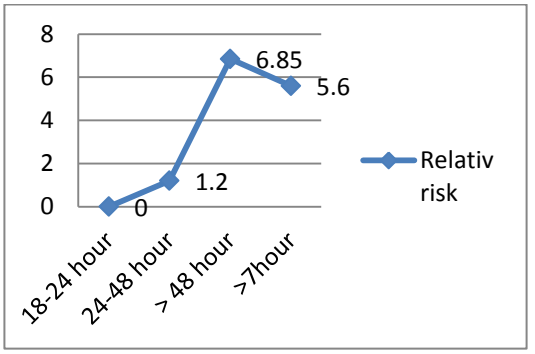

Figure 3: Relative risk of infection according to the period of latency

In induction of labor the newborn had less likely to occur sepsis. OR=0.19, 95%CI: 0.09-0.41, P<0.0001.

87(14.1%) neonates were born with asphyxia. Induction increased the chances of asphyxia, but without statistical significance. OR = 1.17, 95%CI: 0.74-1.84, P = 0.4. In prolonged latency period and premature infants were more likely to asphyxia respective: OR = 1:55, 95% CI: 0.98-2.46, P = 0.05; OR = 2.75, 95% CI: 1.73-4.37, P<0.0001.

Mortality was seen in 8(1.3%) neonates. Induction of labor reduced the chances of mortality, but not statistically significant. OR = 12:44, 95% CI: 0:08 - 2:21, P = 0.2.

The major composite morbidities were detected in 139(22.5%) infants. RDS was the most common major morbidity and resulted in 120(19:45%) infants. Preterm infant was more likely for major morbidity OR = 11.82, 95% CI: 7.44-18.7, P <0.0001. The major neonatal morbidity was significantly higher risk at 28-30 weeks of gestation p<0.0001

With increasing time of PROM infant had more likely major morbidity. Infants at greater risk were when latency period were >48 hours

162(26.26%) infants resulted with minor morbidity**.** Babies in the induction group were less likely to stay in intensive care units than in the expectant management group but not statistically significant. OR = 0:35, 95%CI: 0.07-1.72, P = 0:16.

Both maternal and infant length of hospital stay were significantly longer for cases of preterm PROM delivered at 34 weeks of gestation or less as compared with those who delivered after 36 weeks of gestation.

DISCUSSION

Overall incidence of PROM >18 hours was 23.9 % in our study. There is correlation to neonate problems with gestational age, delivery interval and whether labor was induced with oxytocin (42.6% N=263).

In our study resulted that neonatal outcome largely depends on fetal gestational age than PPROM itself. This finding is consistent with other studies. (15,17,20) Most preterm birth occurs after PPROM.(16)

Preterm labor before 34 weeks of gestation needs a course of antenatal corticosteroid.

In our study, infections, sepsis, mortality, respiratory distress syndrome, were high in study groups.

PROM results in loss of natural protection of fetus and intrauterine content. Both fetus and mother are at risk of infection. The incidence of neonatal infection of 11.54% in infants with maternal PROM >18 hours in our study was higher than previous studies (2.4-10%) (1, 4, 6) probably due to the difference in diagnostic and problems of our country conditions.

In our study the sepsis neonatal with history of preterm premature rupture of membranes (PROM) >18 hours resulted 9.27%. Although the risk of neonatal sepsis is reduced after intrapartum prophylaxis of mother with antibiotic therapy.

In our study the neonatal mortality resulted 1.3%. Approximately 5.3-20% of perinatal deaths are directly or indirectly attributable to PPROM. (1, 8)

The decision to abandon expectant management of women with preterm PROM in favor of delivery requires a close assessment of the potential risks related to development of intrauterine infection in those pregnancies expectantly managed compared with the gestational age–related risks for neonatal morbidity and mortality related to intentional delivery.

In our study resulted that infants in the induction group were less likely to have infection, sepsis, mortality than those in the expectant management group. Therefore induction of labor is protective factor for neonatal infection, sepsis, mortality. Same, randomized clinical trials have compared the maternal and neonatal outcomes related to immediate delivery compared with expectant management in women with preterm PROM between 30 and 36 weeks of gestation. (3,5,11,14)

Mercer et al (13) randomly assigned 93 women with PPROM between 32 and 36 weeks of gestation that had confirmed fetal lung maturity either to immediate delivery or to expectant management. These investigators demonstrated a trend toward decreased incidence of sepsis workups and confirmed sepsis, there were no significant differences in any of the evaluated major neonatal outcomes between the 2 study groups.

Cox et al(5) randomly assigned 129 women with PPROM between 30 and 34 weeks of gestation to either immediate delivery or expectant management. No fetal lung maturity testing, tocolytic, or corticosteroids were used in the study participants. No significant differences, however, were noted between the 2 groups with regard to any of the evaluated neonatal outcomes.

Naef et al (14) evaluated aggressive compared with conservative management of women with preterm PROM at 34 to 37 weeks of gestation. In this prospective investigation, 120 women with preterm PROM were randomly assigned to receive oxytocin induction or observation. No significant differences were noted in the incidence of major neonatal morbidities between the 2 groups.

Although these studies suggest that neonatal outcomes are similar between women who were managed expectantly compared with immediate induction, these investigations lacked sufficient statistical power to fully evaluate neonatal outcomes.

Despite the pivotal importance of accurate data regarding major and minor neonatal morbidities in pregnancies complicated by preterm PROM, few studies have attempted fully to characterize these morbidities in an attempt to identify an optimal gestational age for delivery of pregnancies complicated by preterm PROM.

Our findings are similar to those reported by Jothivijayarani et al.(9) These investigators characterized maternal and neonatal outcomes of 79 women with PPROM between 32 and 36 weeks of gestation

The basis of our results we recommend:

At gestations remote from term, expectant management is appropriate to allow fetal maturation. When PPROM complicates pregnancies closer to term the risks of prematurity are lower and the risk to the infant of sepsis becomes of greater significance.

This trial will provide evidence on the optimal care for women with PPROM close to term (34-37 weeks gestation). If it can be demonstrated that early planned birth in this clinical situation is associated with less maternal and neonatal morbidity

Induction of labor is protective factor for neonatal infection in premature rupture of membranes. Expectant management in labor at 34 weeks gestational age and beyond is of limited benefit

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THE DETERMINATION OF TREND INDICATOR IN A CESAREAN DELIVERY. A RETROSPECTIVE STUDY.

PËRCAKTIMI I TRENDIT TË INDIKACIONEVE NË NJË LINDJE CEZARIANE. NJË STUDIM RETROSPEKTIV.

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SUMMARY

Cesarean section is a major surgical procedure most commonly performed in women. In the last three decades it is increased all over the world and it is a major concern for many countries. Increasing number of cesarean delivery is occurring in countries with middle and higher income. Cesarean section might be an emergency procedure to save the mother/fetal life. Determination the incidence of cesarean deliveries, identifying contributing factors is the aim of this study. The study included all records from clinical charts, from January 2008 till December 2010. For statistical date is used SPSS 11.5 package and Chi-Square test. Accepted error is less than 5% ($p < 0.05$). The incidence of cesarean delivery is 35.4 %. Repeated cesarean delivery is the main factor in the rising incidence of Cesarean section from year to year.

Key words: Cesarean delivery, fetal complication, maternal indication, repeated cesarean delivery.

Introduction.

Cesarean delivery is a surgical procedure which applied in pregnant women who can not give vaginal birth. This procedure realized by an incision in uterine wall.

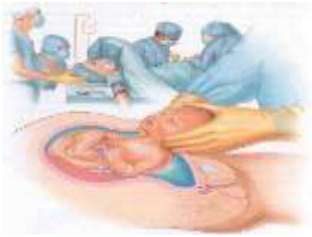


Fig.1 Cesarean delivery

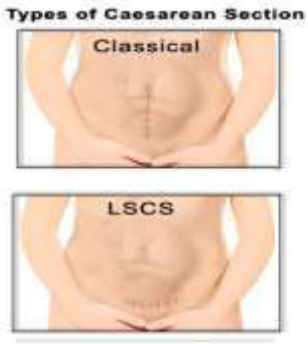


Fig.2 Types of cesarean section.

Cesarean section is a major surgical procedure most commonly performed in pregnant women[1].

In the last three decades it is increased all over the world[9] and this surgical porcedure is a major concern for many countries[7]. This technique, was born and developed time by time for the sole purpose of preventing the fetal and maternal complications. Increasing number of cesarean delivery is occurring in countries with middle and higher income[14]. But in the other side there are no scientific sources which show significant benefits for the mother and the baby. so this increasing of cesarean delivery is unjustified [4,5,12,15]. Cesarean delivery can be accomplished because the mother chooses it with her own decision[8], but it can also be performed as a result of unpredictable events [3,11]. This surgical delivery may be an emergency procedure to save the mother and / or baby. Such emergencies may include: fetal distress, abruption of the placenta, umbilical cord prolaps, placenta previa, active herpes etc. But this delivery has potential risks for the mother as well as the fetus if we compare it with vaginal delivery [2]. Because when applying this surgical procedure is necessary the incision of uterine wall, which is associated with blood loss, increased risk of damage to internal organs, especially the bladder and uterine vessels. It may also be necessary re hospitalization because of these women wound infection. Potential risk for maternal mortality as a result of complications from anesthesia, puerperal infection, thrombosis. Such complications have an incidence of about 3.6 times more than the vaginal delivery. While children born by cesarean section represent a potential risk for respiratory complications. These complications are the most common reason for transfer the babies in the neonatal intensive care unit.

But despite the complications that may be associated with cesarean delivery we see that the number of cesarean section is increasing[10].

Aim

Determination the incidence of cesarean deliveries for the years 2008-2010. Identification of contributing factors that affect the births by surgical procedure, but also determining the trend of these factors.

Methods

This is a qualitative, descriptive and retrospective study. In this study are included all records of clinical charts from obstetric department at Maternity Hospital " Koço Gliozheni " Tiranë, from January 2008 till December 2010. The data collection procedure consisted of surveying information available in clinical records.

For statistical date is used SPSS 11.5 package and Chi-Square test. Accepted error is less than 5% ($p < 0.05$). In this study are included only pregnant women which gave birth by surgical procedure. Have been calculated also demographic and obstetrical data from clinical charts.

Results

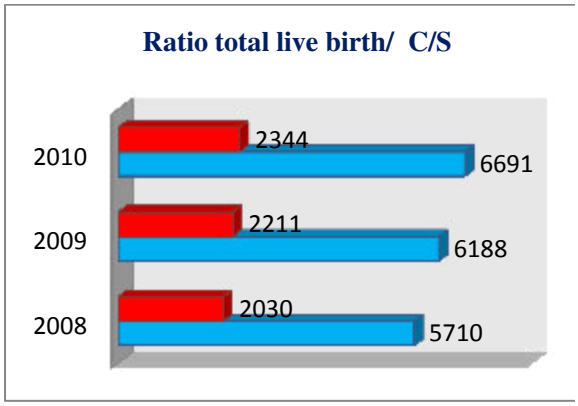
By analyzing the clinical charts for three years, results that were born 18 589 babies of which, 6585 were born by surgical procedure. So the rate or the incidence of cesarean section is 35.4 %. This mean that approximately 1 in 3 births is performed with cesarean section. In fact this incidence of cesarean births is very high, considering what WHO recommends for cesarean births. In 1985, the World Health Organization (WHO) determined that there is no justification for any region in the world to have cesarean childbirth rates over 10-15%, supporting the hypothesis that when this rate increases to more than 15%, the health risks overcome the benefits. Two decades later, however, the cesarean childbirth rates continue to contradict the WHO recommendation, in developed as well as in developing countries[12].

In 2008 have born 5710 and 2030 of them are born by cesarean section. In 2009, 6188 babies have born, and 2211 of them have born by cesarean section. In 2010 we see that the number of live births is increased and the same

thing we can say for the cesarean section with a ratio 6691/2344.

	2008	2009	2010
N. Total live birth	5710	6188	6691
N. C/S	2030(35.55%)	2211(35.73%)	2344(35.03%)

Table 1. Describe the percentage of cesarean section.



Graph.1 Show the ratio of total live births and cesarean section for years 2008-2010.

The table which is shown below explains some contributing factors that affect the cesarean delivery rate.

	2008- N 2030 C/S	2009- N 2211 C/S	2010-N 2344 C/S
P. Previa	3.1%	1%	2%
Multiple Gestation	2.1%	1.9%	3%
Preeclampsia	9.3%	6.8%	8%
Abnormal presentation of fetus	5.2%	3.9%	4%
Fetal distress	18.5%	18.4%	15%
Dystocia	6.2%	4.9%	6%
Premature rupture of membranes	14.4%	12.6%	10%
Previous cesarean section	34%	35.9%	38%
Others	7.2%	14.6%	14%

Table 2. expresses the % of the contributing factors of cesarean delivery in the years we studied.

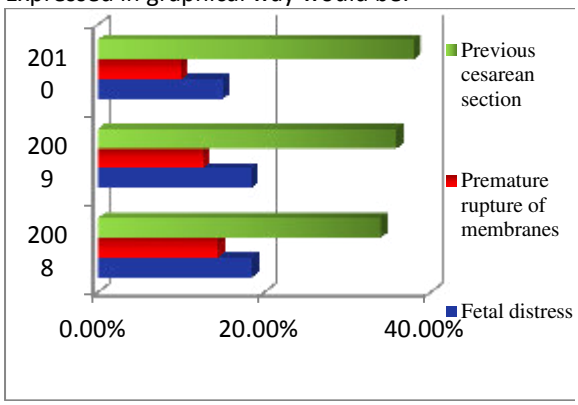
* Others = diabetes, serotine pregnancy, premature, fetal abnormalities, cervical cancer, active infection by herpes etc. * N- number of cesarean delivery.

In general the table shows the factors that contributed in the rising trend of cesarean delivery for each year. As we see, we realize that approximately a little decrease for each contributing factors in 2010, exept previous cesarean section that is increasing year after year.

Interpreting the table we realize that repeat cesarean delivery occupies a main place in the rising incidence of Cesarean section from year to year. So in 2008 the number of previous cesarean section was 665 (34%) of total cesarean section performance. In 2009 and 2010 the number of previous cesarean section increased from 815 (35.9%) to 897 (38%) in 2010.

But in the same time, premature rupture of membranes and fetal distress also have contributed in the rising trend of cesarean delivery from 2008 to 2010. The mean of fetal distress for this three years we studied is 378 or 17.3%, while for premature rupture of membranes as a factor contributing in rising trend of cesarean section is 277 or 12.3 %.

Expressed in graphical way would be:



Graph.2 Most important factors of C/S.

So, previous cesarean section changes with an average of approximately 36 % in the three years that we studied. While the mean of fetal distress is 17.3%, and premature rupture of membranes varies 12.3%.

In same studies which describe the reasons of rising trend of cesarean births in worlwide we realize that most contributing factors are: previous cesarean section, dystocia, transverse presentation of fetus and of course fetal distress [6] . As well as in our study we find some similar factors contributing in cesarean section rate as are: previous cesarean section, fetal distress and premature rupture of membranes.

Conclusions

In our study (for years 2008-2010), we found that the incidence of cesarean delivery is approximately 35.4%. The factors that contributed more in the rising trend of cesarean section are: previous cesarean section, fetal distress, premature rupture of membranes. In some cases we found the voluntary of woman making decision in favor of cesarean section. So it is important to provide detailed information about cesarean delivery before decision of the woman. Discussing for the complications that can accompany it, and high cost it has for maternity.

Based on some several studies conducted US, the increasing number of cesarean delivery is due to non-medicinal reasons(women who choose private medical service, the grate age of woman, educated women ect). While in our country the increasing number of cesarean delivery is due to medical reasons but followed very closely also by non-medicinal reasons. So, it is important to select carefully the patients if they really need a caesarean section or not.

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NUTRITIONAL SUPPORT OF ADULT PATIENTS IN INTENSIVE CARE UNIT

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SUMMARY
Background: In the patients of the ICU (intensive care unit), there is a delayed or inadequate nutrition support. The purpose of this study was to examine the relationship between energy balance and clinical outcome in critically ill patients. **Methods:** Prospective observational study conducted in 432 consecutive patients staying ≥ 4 days in the mixed ICU of the QSUT "Mother Teresa". Energy balance was calculated as energy delivery minus nutritional requirements. **Results:** Multiple regression analysis identified cumulated energy deficits as being independently associated with infectious complications, overall complications, the ventilator stay, ICU stay and with mortality. **Conclusions:** Negative energy balance cumulated during inadequate nutrition support was associated with a higher rate of infectious complications, mortality, longer ventilator stay and ICU stay. Our findings suggest the need for implementation of quality improvement measures by the healthcare team to enhance the provision of nutrition support to the patients of the intensive care unit.

Keywords: critically ill, nutritional support, enteral nutrition, parenteral nutrition, energy balance, morbidity and mortality.

INTRODUCTION

Over 2 millennia ago Hippocrates, Father of Medicine (460-377 BC), once said "If we could give every individual the right amount of nourishment and exercise, not too little and not too much, we would have found the safest way to health".

Traditionally, nutrition support in the critically ill population was regarded as adjunctive care designed to provide exogenous fuels to support the patient during the stress response. Nutrition care is considered to be a basic and mandatory (essential) element of modern intensive care treatment. Nutritional support influences morbidity and mortality rates in critically ill patients [1]. Administration of nutritional support is required in critically ill patients to limit the negative energy and protein balance observed in these patients [2,3]. Prevention of nutrient depletion during nutritional support can eliminate the excess morbidity and mortality associated with malnutrition.

Vincent has emphasized the importance of feeding the ICU patient in a simple but appealing pneumonic: 'FAST HUG" (Feeding, Analgesia, Sedation, Thromboembolic prophylaxis, Head end elevation, Ulcer prophylaxis, and Glucose control) [4].

Prolonged hypocaloric feeding is associated with clinical complications; energy balance should be calculated in the most ill patients. Underfeeding ICU patients for periods longer than a few days can cause unnecessary protein losses, may lead to further nutritional

deterioration, and consequent complications (increased nosocomial infections, poor wound healing and respiratory muscle dysfunction) [5]. Particularly in the patients of the ICU, there is a delayed or inadequate nutrition support [6,7,8]. The purpose of the present study was: 1. To evaluate the cumulated energy balance during ICU stay. 2. To examine the relationship between energy balance and clinical outcome in critically ill patients.

Material and methods

The study was designed as a prospective observational study, conducted in consecutive patients staying ≥ 4 days in the mixed ICU of the University Hospital Centre "Mother Teresa" of Tirana, Albania, collecting data during 2010 and 2012. As nutrition support may only be relevant to critically ill patients who remain in the ICU for a prolonged period of time, we examined the use of nutrition support in patients above 18 years old, who remained in the ICU longer than 4 days.

Data were made anonymous for analysis.

Patient data: Age, sex, weight, height, and BMI, diagnosis and Acute Physiology and Chronic Health Evaluation (APACHE II) prognosis score [9] were recorded upon admission to the ICU. Nutritional status on admission was assessed according to Nutritional Risk Screening 2002 [10]. The patient with a total score ≥ 3 was considered at nutritional risk.

Determination of energy requirements: Indirect calorimetry, despite being the gold standard for determination of energy requirements, remains unavailable in the vast majority of ICUs [11]. Predictive equations however over- or underestimate requirements [12]. Indirect calorimetry studies have shown that, in most situations, a value of 25 kcal/kg/day can be used to estimate energy requirements. This is also recommended by ESPEN [13,14]. As in our clinic is not available indirect calorimetry, energy target was set at 25 kcal/kg/day.

Energy delivery: total delivery includes energy from enteral and parenteral feeds, from non-nutritional sources (glucose and gluco-saline infusions used for drug dilution and fluid support).

Energy balance was calculated as energy delivery minus energy target, on daily basis. Data were collected on energy delivery, and cumulated energy balance on discharge from ICU. Cumulated energy balance was calculated on discharge. Five levels of energy balance were considered for analysis: 1: 0 to – 5000 kcal, 2: -5001 to -10000 kcal, 3: -10001 to -15000 kcal, 4: -15001-20000 kcal, 4: larger then -20000 kcal [8].

Clinical follow-up: Duration of ICU stay and length of ventilator stay, total complications, infectious complications and ICU mortality were recorded. Infectious complications were defined as sepsis or systemic inflammatory response syndrome [15], pneumonia, urinary tract infection, central venous catheter sepsis, and wound infection. Other complications were: post-operative (open abdominal wound, post-operative bleeding, anastomotic leak), neurological, respiratory, gastro-intestinal, cardiovascular, hepatic failure (by SOFA), renal failure (by SOFA) [16], and coagulation disorder. The duration of time in the ICU was defined as the time from admission of patients until they were ready for discharge. All patients were followed clinically until leaving the ICU or death and their outcome recorded.

Statistical analysis: Data are presented as the mean (SD: standard deviation) and ranges for numerical variables, as number (n) or percentage (%) for categorical variables.

Categorical data were analyzed using the Ch^2 test.

Multiple linear and logistic regression analysis was used to analyze the effect of cumulated energy balance on length of ICU stay, length of ventilator stay, total complications, infectious complications and mortality.

Statistical significance was considered at the level of $p \leq 0.05$.

All tests were two tailed. SPSS statistical package version 15.0 was used to analyze the data.

Results

Were studied a total of 432 patients that stayed in the ICU for more than 4 days. The mean age was 60.96 years old (16.20), with 56.48% (n = 244) being male. According to NRS 2002 the prevalence of malnutrition risk at the time of ICU admission was 63.6% (65.81% in the surgical patients and 57.98% in the medical patients, p = 0.16). The mean APACHE II score was 18.07 (5.54). ICU length of stay was 9.34 days (8.23); mechanical ventilation lasted 2.17 days (4.34). Cancer was present in 98 patients, 22.7% of the cases. 313 patients (72.45%) were post operative.

During ICU stay 143 patients (33.1%) have had ICU-acquired infections, 233 patients (53.9%) have had complications. ICU mortality was 28.7%.

The days without feeding were characterized by the unintentional delivery of 150-200 kcal from glucose infusions. All the study's patients were in negative balance at the end of their ICU stay.

Energy deficit was lower during combined enteral and parenteral feeding.

Energy delivery was lowest during the first week and therefore the largest negative balances were observed during the first week (figure 1).

Negative energy deficit was accompanied in all the patients by negative protein balance [- 68.9 ± 20.0 (71.5)] g protein/day. During their ICU stay patients received [16.5 ± 17.14 (19)] g protein/day, or 19.8% ± 20.9% (15%) of their protein daily requirements (the values are given as mean ± standard deviation and median).

The regression analysis identified cumulated energy deficits during the ICU stay as being independently associated with ICU-acquired infections: OR = 2.54; 95% CI: 1.98-3.26; p = 0.0000.

A cumulated energy deficit above -10000 kcal is associated with an increased risk for infections compared to the patients with cumulated energy deficit under -10000 kcal, RR = 1.87, 95% CI: 0.99-3.54, P = 0.05.

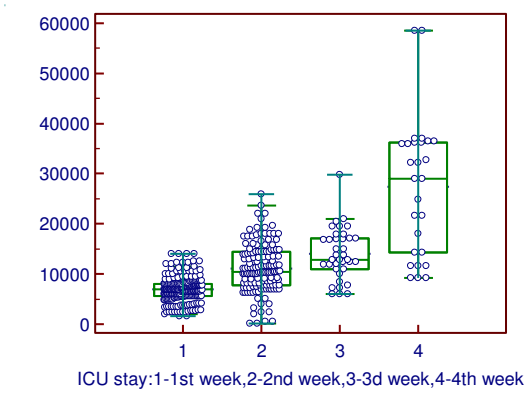

Figure 1. Cumulated energy deficit (in – kcal) according to the length of ICU stay in weeks

It did not find any association of negative energy balance with the total number of complications (OR: 1.17; 95% CI: 0.965 - 1.41; p = 0.10). For the values of cumulated energy deficit higher than -15000 kcal relative risk for complications was increased progressively.

The regression analysis identified cumulated energy deficits during the ICU stay as being independently associated with mortality: OR = 1.29; 95% CI: 1.05 - 1.58; p = 0.014.

Energy deficit during the ICU stay correlated with ICU length of stay: F = 580.09, P < 0.001; and the length of stay on mechanical ventilation: F = 116.95, P < 0.001 (table 1).

Table 1. Relationship between clinical outcome and cumulated energy deficit during ICU stay by regression analysis

Variable of outcome	**p**	**F**
ICU length of stay	< 0.001	580.09
Complications	0.197	1.66
ICU-acquired infections	< 0.001	85.59
Mechanical ventilation length of stay	< 0.001	116.95
Mortality	0.014	6.14

Discussions

This study investigated the nutritional support in 432 patients and showed that all patients were in negative balance at the end of their ICU stay. Our study showed that negative energy balance correlated with the infectious complications, longer stay on mechanical ventilation, longer stay on ICU, and mortality, but not with the total number of complications.

Some recent studies had shown that infectious are a classical complication of malnutrition and underfeeding [8,17]. The multiple regression analysis showed that the cumulated energy balance of the ICU stay was the strongest predictor of prolonged ICU stay. The present study as other studies [8], confirms that negative energy balance cumulated during inadequate nutrition support was associated with a higher rate of infections, complications, mortality, and longer ICU stay.

A recent study including 38 patients intubated at least 7 days suggested that large negative energy balance seems to be an independent determinant of ICU mortality in a very sick medical population requiring prolonged acute mechanical ventilation [18]. Also the present study showed that cumulated energy deficit is an independent risk factor on ICU mortality.

In our study we did not examine the relationship between the amount of protein administered and clinical outcomes, but all the patients had protein deficit and energy deficit was always associated with protein deficit. We have not studied the relation between caloric intakes and outcome, but from the results of the present study we can suggest that attempting to meet caloric targets may be associated with improved clinical outcomes in critically ill patients, as it was confirmed by some studies [19]. Another study including 200 medical ICU patients, observed a reduction in length of mechanical ventilation associated with improved nutritional support [20]. Based on these findings we can suggest that attempting to meet caloric targets may be associated with improved clinical outcomes in critically ill patients [19].

Conclusions

This study confirms that negative energy balance cumulated during inadequate nutrition support was associated with a higher rate of infectious complications, mortality, longer ventilator stay and longer ICU stay.

Our findings suggest the need for implementation of Guidelines for nutrition support in critically ill patients, in order to improve the clinical outcome of them. As the budget for the ICU is limited, a major problem remains underestimation of nutritional support and consequently an inappropriate nutrition support. Evidence of the impact of malnutrition and energy deficit in clinical outcome can encourage policymakers about the importance of investing on nutritional support.

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Conflict of interest statement

On behalf of all authors, it is hereby stated that there is no conflict of interest regarding this paper

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ISOLATION AND IDENTIFICATION OF SALMONELLA SPP., IN POULTRY FOR EGG PRODUCTION IN THE REGION OF SHTIME, LIPJAN AND FERIZAJ – KOSOVO

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PËRMBLEDHJE
Në këtë studim është hulumtuar prania bakterieve të gjinisë Salmonella spp. në shpendë për prodhimin e vezëve. Studimi është kryer në fermat dhe pularitë private në rajonin e Shtimës, Lipjanit dhe Ferizajit në Kosovë. Mostrat e prelevuar nga fecet, vezët dhe organet i janë nënshtruar metodës ISO 6579:2002, metodë standarde për zbulimin e Salmonella spp., ku me këtë rast janë hulumtuar gjithsej 312 mostra, ku 28 prej tyre ose 8.97% janë konfirmuar të jenë Salmonella spp. Përqindja më e madhe nga totali i shtameve të izoluara është paraqitur në rajonin e Lipjanit me 39.28%, në atë Shtimes 32.14% dhe Ferizajit 28.57%. Nga totali i shtameve të izoluara në këtë studim është konstatuar se numri më i madh është gjetur në mostrat e feceve, 18 shtame ose shprehur në përqindje 64.2%, ndërsa në vezë janë izoluar 7 shtame (25%) dhe në organe 3 shtame apo 10.7% ndaj totalit të izoluar.
Fjalët çelës: ekspozimi mjekësor, doza e hyrjes sipërfaqësore, TLD

SUMMARY
The study investigated the presence of bacteria Salmonella spp. gender in poultry for eggs production. The study was conducted in poultry and private farms in the region of Shtime, Lipjan and Ferizaj, Kosovo. Taken samples of feces, eggs and organs samples underwent in ISO 6579:2002 method, which is standard method for detection of the Salmonella spp., where 312 samples were investigated, 28 of them or 8.97% were confirmed to be Salmonella spp. The largest percentage of the total isolated strains is presented in Lipjan region with 39.28%, 32.14% in Shtime and 28.57% in Ferizaj. From the total number of isolated strains in this study, is illustrated that the largest number was found in feces samples 18 strains or 64.2% expressed in percentages, while in the eggs are isolated 7 strains (25%) and in organs 3 strains or 10.7 % of total isolation.

Key words: Salmonella spp, pathogens, poultry, serovars, strains

INTRODUCTION

Poultry in region of Shtime, Lipjan, Ferizaj and wider in Kosovo, is the line that is developing quickly, especially in the production of eggs and meat poultry. Modernization of poultry breeding industry has played a crucial role in not spreading and transmitting salmonella's infections in poultry (VELGA et al., 2005). Poultry and their products are often connected with the outbreak of salmonella's epidemics in animals and in humans around the world. Poultry and farms are the main reservoir of infections caused by species of Salmonella gender (Luiz et al., 2004). The infection enters through oral routes, causing in the most cases difficulty of inflammatory processes of the digestive tract. The Salmonella typically recognized as zoonotic species, induced pathogens and are intracellular parasites. The bacteria of Salmonella gender is belong to the Enterobacteriaceae family with 2400 serovars. In poultry the most known types of Salmonella spp serovars are: Salmonella enteritidis, S.typhi,

S.gallinarum, S.typhimurium, who also are the most significant agents of salmonellas food transited in humans (Popoff et al., 2004). Serotype is an important tool to understand the epidemiology of infections caused by species of Salmonella gender, which develops according to White Kaufmanns scheme(1920), and based on the discovery of H flagella antigen, somatic antigen O and the surface antigen Vi (Cabeli P., 2006).

Material and Methods

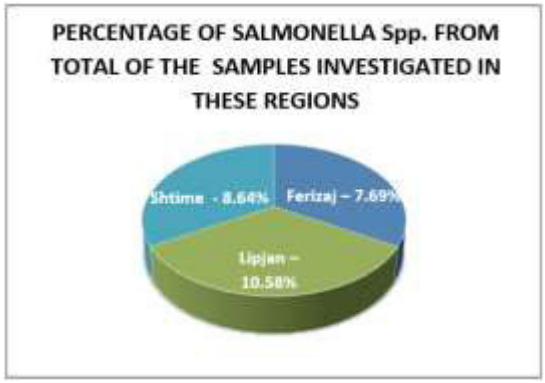
The samples for isolation and identification of species of the Salmonella gender were taken from organs, eggs, feces from poultry and private farms, during January-April 2014 in the region of Shtime, Lipjan and Ferizaj. Totally were taken: 63 feces samples, 189 samples from internal organs (liver, spleen, intestine and cloaca) and 60 egg samples. The isolation and identification is based on ISO 6579:2002 method, and was conducted at the Microbiological Laboratory of Food in the Food and Veterinary Agency of Kosovo. For diagnosis was used this material: BPW, RVS, BG-agar, XLD-agar, TSI-agar, Salmonella LATEX TEST - Oxoid England, Salmonella antiserum Siffin Berlin (Anti-Salmonella A-67 omnivalent, Anti-Salmonella I (A-E) and Anti-Salmonella F-67. 25 gr. of feces were taken for each sample and transferred into 225 ml of BPW. 25 gr. of each egg (white, vitelus and eggshell) were transferred into 225 ml BPW richen field. 25 g. of organs (liver, spleen, intestines and cloaca) were planted in 225 ml BPW. All cultures were cultivated in thermostat at 370C for 18-24 hours. After incubation, 0.1 ml of the cultures were transferred into tubes with 10 ml RVS (selective richen field) and incubated for 24 hours at 41.5-42 0C. Further crops were planted in the selected solid field BGA-agar and XLD-agar, than those were cultivated in the incubator for 24 hours at 37C. Five suspicious colonies were re-planted in Nutrien-agar and underwent biochemical confirmation tests using sugars, in TSI - agar 37C for 24 hours. Biochemical evidences were followed by serological tests such as Salmonella LATEX TEST-OXOID and use of antiserum as Anti-Salmonella A-67 omnivalent, Anti-Salmonella I (A-E) and Anti-Salmonella F-67.

Results and Discussion

From this study, after analyzing 312 samples from organs, eggs and feces of poultry for egg production, based on ISO 6579:2002 method, were isolated 28 strains of Salmonella gender or 8.97% of the total analyzed. The same results are also found in other researches that have been done in other countries of the world. While the same studies were conducted in Montreal Canadas, where about 264 samples were investigated, 8.7% of them were infected by Salmonella spp, whereas in the Mekong Delta Vietnam, from 302 samples inspected, 7.9% were infected with salmonella spp.

Chart.1. ***Percentage of Salmonella spp., from the total of investigated samples***

Region	Total sample	Salmonella *spp*.	Percetentage of the total number
Shtime	104	9	8.65%
Lipjan	104	11	10.58%
Ferizaj	104	8	7.69%
Total	312	28	8.97%



Graphic 1*: Percentage of Salmonella spp,, from the total of investigated samples.*

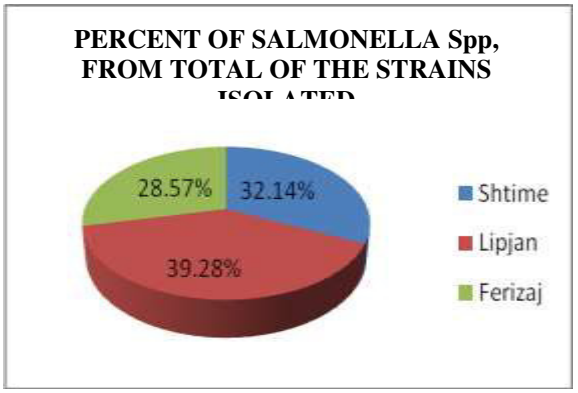
Region	Strains Total in Region	Feces		Egg (the white,vitelus and bark)		Organs (liver, spleen, intestine and cloaca)	
		Strains	%	Strains	%	Strains	%
Shtime	9	6	66.6 %	2	22.2%	1	11.1 %
Lipjan	11	7	63.6 %	3	27.2%	1	9.1%
Ferizaj	8	5	62.5 %	2	25 %	1	12.5 %
Total	28	18	64.2 %	7	25 %	3	10.7 %

Chart.2. Percentages of Salmonella spp. from the total of isolated strains

The above results show that from 312 feces samples, eggs and organs analyzed, 8.97 % of them belong to the species of Salmonella gender, indicating the presence of the infection in the three regions: Shtimje, Lipjan and Ferizaj.

In the chart and graphic below in percentages are given species of isolated Salmonella gender comparing with total number, analyzed in the studied regions.

Photo.1. *Salmonella spp.of in TSI-agar*



Graphic 2*: Percentages of Salmonella spp, from isolated strains*

As might be seen from the chart and graphic above, higher presence of cases is presented in Lipjan region with 39.28%, further Shtime region with 32.14% and 28.57% in Ferizaj.

In chart.3 are given the results of Salmonella spp expressed in percentages, in analyzed samples: feces**,** eggs and organs.

Chart.3. Percentages of *Salmonella spp,* in feces, eggs and organs

The above results indicate that from 28 isolated strains the highest percentage of samples are observed into feces, where 18 strains of Salmonella spp. are isolated or 64.2% of the total , in eggs are isolated 7 strains of Salmonella spp. or 25% of the total ,and in the organs are isolated only 3 strains of Salmonella spp. or 10.7%.

Region	Strains Total	Salmonella spp.	Percentage %
Shtime	28	9	32.14%
Lipjan	28	11	39.28%
Ferizaj	28	8	28.57%

This study will continue further by conducting of biochemical tests, which will be followed by serological tests such: Salmonella LATEX TEST-OXOID, and use of antiserums as Anti-Salmonella A-67 omnivalent, Anti-Salmonella I (A-E) and anti-

Salmonella F-67, which will facilitate further identification of the Salmonella gender species present in eggs**,** feces and organs samples in the poultry of Shtime, Lipjan and Ferizaj regions.

Conclusion

- From 312 analyzed samples by ISO 6759:2002 method, in three studied regions was found a prevalence of Salmonella spp, about 28 strains or 8.97% of the total analyzed samples.
- The highest prevalence of Salmonella spp, has the region of Lipjan with 39.28%, than Shtime 32.14% and 28.57% in Ferizaj to the overall total.
- The highest percentage is found in feces, where18 strains were isolated or 64.2%, in eggs were isolated 7 strains or 25% and in organs were isolated 3 strains with 10.7%
- Comparing the presence of Salmonella spp, with the total number of isolated strains, results that obtained feces from Shtime region has a higher percentage with 66.6%, followed by Lipjan 63.6%, and finally Ferizaj with 62.5 %.
- Comparing the presence of Salmonella spp, with the total number of isolated strains, comes out that in eggs, the percentage of salmonella infection in Lipjan region is the highest with 27.2%, than in Ferizaj with 25%, and Shtime 22.2%.
- The comparison of the Salmonella spp, presence with the total number of isolated strains in organs show that samples taken from Ferizaj have the highest percentage with 12.5%, followed by Shtime with 11.1% and Lipjan 9.1%.

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EVALUATION OF LUSHNJA AQUIFER GROUNDWATER THROUGH THE USE OF ENVIRONMENTAL ISOTOPES
VLERËSIMI I UJËRAVE NËNTOKËSORE TË AKUIFERIT TË LUSHNJËS NËPËRMJET PËRDORIMIT TË IZOTOPEVE MJEDISORE

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PËRMBLEDHJE
Akuiferi i ultësirës së Lushnjës midis lumenjve Shkumbin e Seman është studiuar për shfrytëzimin e ujërave nëntokësore për furnizimin e popullsisë me ujë të pijshëm. Zhvillimi i zonës dhe ndryshimet klimaterike që kanë ndodhur gjatë viteve të fundit e kanë bërë të domosdoshëm rivlerësimin e këtij akuiferi. Në këtë artikull bëhet një vlerësim mbi prejardhjen e ujërave nëntokësore të akuiferit te Lushnjës nëpërmjet matjes së izotopeve stabël mjedisore. Përveç përcaktimeve hidrokimike të përdorura deri më sot për studimin e zonës, u kryen edhe përcaktime të raporteve izotopike të oksigjenit-18 dhe deuteriumit. Për këtë qëllim u morën mostra uji nga pus shpime, puse të ndërtuara nga individë privatë dhe mostra reshjesh. Intervali i përbërjes izotopike për δ^2H varion nga -53.11‰ deri -12.58‰ dhe për δ^{18}O intervali i përbërjes izotopike të mostrave varion nga -8.30‰ deri -1.22‰.
Fjalët çelës: Hidrogjeologji, hidrologji izotopike, oksigjen-18, deuterium, ujëra nëntokësore.

SUMMARY
The aquifer of the Lushnja lowland which lies between the river Shkumbin and the river Seman has been studied in order to evaluate the use of groundwater in supplying the population with drinking water. Due to the changes that this region has been through, it is necessary to expand the study of this aquifer. In this paper it is discussed about the origin of the Lushnja aquifer groundwater by environmental isotopes measurements. In addition to the hydrochemical analyses, were determined the isotopic composition of the stable isotopes of hydrogen and oxygen. This study was conducted on water samples collected from boreholes, private wells and precipitations. The isotopic composition interval of the measurements of δ^2H ranges from -53.1 ‰ to -12.58 ‰ and for δ^{18}O the isotopic composition interval of the measurements ranges from -8.30‰ to -1.22 ‰.
Key words: Hydrogeology, isotopic hydrology, oxygen-18, deuterium, groundwater

INTRODUCTION

Environmental isotopes are very important for the investigation of the hydrological cycle. They offer information concerning the origin and movement of groundwater.

The isotopic ratios of oxygen and hydrogen in water are unique and often considered as “fingerprints”, thus due to different proportions of oxygen and hydrogen isotopes that constitutes water.

The stable isotopes ratios ^{2}H and ^{18}O in water samples are expressed in terms of so called δ-values and reported in permil (‰) relative to VSMOW2 (Vienna Standard Mean Ocean Water) water standard (0 ‰) [1; 2]:

$$\delta_{(VSMOW)} = \frac{R_{sample}}{R_{VSMOW}} - 1 \qquad (\times 1000‰)$$

Where R_{sample} = $^{2}H/^{1}H$ or R_{sample}= $^{18}O/^{16}O$ [3; 4]. The data obtained from measurements of deuterium and oxygen - 18 are plotted in a graph where is given the relationship between $\delta^{2}H$ and $\delta^{18}O$ relative to the VSMOW standard. Average annual values of $\delta^{2}H$ and $\delta^{18}O$ in precipitations collected from stations around the world give us a graph described by the relation:

$$\delta^{2}H = 8\delta^{18}O + 10$$

This graph shows the Global Meteoric Water Line (GMWL) [5; 6]. The difference of precipitations' isotopic composition from one station to another depends on various factors, including the origins and track of rainfall air masses, intensity and amount of precipitation, atmospheric temperature, condensation and evaporation [7; 8]. The GMWL provides a baseline to compare the isotopic composition of surface waters and groundwater. In this way it is possible to get information on groundwater recharge patterns, the origin of waters in hydrologic systems and mixing of ground water and surface water.

In this paper it is discussed the recharge pattern of the Lushnja aquifer by the use of environmental isotopes, oxygen-18 and deuterium. The goal is to delineate the sources of groundwater aquifer recharge by identifying the trends on the isotopic composition of the collected samples.

MATERIALS AND METHOD

Area of Investigation – The study area is situated in west Albania (Figure 1) and includes the city of Lushnja and its surroundings, covering an area of 256 km^{2}. The area is bounded in north by Shkumbin River, east from the hills of Thanasaj - Lushnjë - Karbunarë – Kosovë e Madhe; south from Seman River and west from the Divjakë-Ardenicë hills (Figure 1).

The development of the area, population growth and the variation use of the water in intensive farming during the last years have increased the demand of water brought into light the necessity to re-evaluate the aquifer of Lushnja. Also, the water of this aquifer is used as water supply of the population of Lushnja.

Figure 1. General view of Lushnja aquifer location

The first studies have initiated in 1965. Till now, the studies were based only on geological and hydrochemical analysis.

During a sampling campaign in 2010 were collected 48 water samples for isotopic ratios of deuterium and oxygen-18 measurements. The samples were collected from rain water and deep groundwater at various depth and location. 50 ml polyethylene bottles, double capped, were filled from the source. They were filled to the brim to exclude air [9]. Neither sample filtration, nor chemical treatments were necessary [10]. Determinations of both hydrogen and oxygen isotope ratios are measured on the same bottle of water.

The 48 water samples were analyzed for $\delta^{18}O$ and $\delta^{2}H$ at the IDES laboratory Orsay, France by a Dual Inlet Thermo Finnigan Delta Plus isotope ratio mass spectrometer (IRMS) coupled with a Finnigan equilibration unit (CO_2, H_2). Deuterium and oxygen isotope composition were measured using the classic CO_2-H_2O equilibrium method [11; 12]. A gas (H_2 for δD/H and CO_2 for $\delta^{18}O/^{16}O$) is brought into contact with the water sample and after a suitable equilibration time, the gas

acquires the isotopic signature of the sample. It is then transferred to the source of the mass spectrometer and compared to a reference gas [13]. The measurements were performed using three in-house standards, which were calibrated directly versus Vienna-Standard Mean Ocean Water (VSMOW), Greenland Ice Sheet Project (GISP), and Standard Light Antarctic Precipitation (SLAP2) [14; 15]. The results are reported in δ-notation, permil relative to the VSMOW international standard. Analytical precision for the measured water samples was ± 0.2 ‰ for $\delta^{18}O$ and ± 2 ‰ for $\delta^{2}H$.

48 samples were collected from groundwater and 7 samples were rain water $\delta^{18}O$ and for $\delta^{2}H$ values of which are used to plot the Lushnja Local Meteoric Line (presented elsewhere).

Results of water samples are given in Table 1 and the values are expressed in δ ‰ VSMOW.

RESULTS AND DICUSSION

In the following table it is possible to see the isotopic ratios of $\delta^{18}O$ and for $\delta^{2}H$ of the samples collected on Lushnja aquifer (Table 1). As it can be noticed from the table, the measured stable isotopes ratios range from -8.303‰ to -5.28‰ for $\delta^{18}O$ and for $\delta^{2}H$ vary from -53.11‰ to -33.13‰. The results of this investigation are plotted in a diagram, which shows the relationship between $\delta^{18}O$ and for $\delta^{2}H$ in the groundwater samples of Lushnja aquifer. In order to comprehend better the origin of the aquifer, the Global Meteoric Water Line (GMWL) is also included in the graph (Figure 2)

Sample Name	$\delta^{2}H$ Reportable Value (permil)	$\delta^{18}O$ Reportable Value (permil)
JLM-AL-10-01	-52.76	-8.30
JLM-AL-10-02	-45.59	-6.97
JLM-AL-10-04	-38.02	-6.14
JLM-AL-10-05	-37.36	-5.72
JLM-AL-10-06	-38.31	-5.69
JLM-AL-10-07	-38.98	-5.96
JLM-AL-10-08	-44.47	-6.78
JLM-AL-10-09	-43.07	-6.57
JLM-AL-10-11	-41.06	-6.28
JLM-AL-10-12	-38.73	-6.12
JLM-AL-10-13	-38.93	-6.06
JLM-AL-10-14	-40.99	-6.34
JLM-AL-10-16	-33.13	-5.32
JLM-AL-10-18	-43.98	-6.63
JLM-AL-10-19	-46.09	-6.97
JLM-AL-10-20	-37.64	-5.88
JLM-AL-10-21	-53.11	-7.35
JLM-AL-10-22	-38.15	-5.74
JLM-AL-10-23	-40.35	-6.16
JLM-AL-10-24	-38.62	-5.87
JLM-AL-10-25	-42.27	-6.69
JLM-AL-10-26	-46.95	-7.17
JLM-AL-10-27	-35.65	-5.75
JLM-AL-10-28	-39.30	-5.94
JLM-AL-10-29	-42.33	-6.49
JLM-AL-10-30	-41.12	-6.03
JLM-AL-10-31	-41.08	-6.17
JLM-AL-10-32	-33.58	-5.28
JLM-AL-10-33	-34.46	-5.35
JLM-AL-10-34	-38.45	-5.86
JLM-AL-10-35	-39.63	-6.19
JLM-AL-10-36	-38.94	-6.05
JLM-AL-10-37	-38.58	-5.94
JLM-AL-10-38	-35.90	-5.41
JLM-AL-10-39	-37.52	-5.71
JLM-AL-10-40	-37.44	-5.76
JLM-AL-10-41	-38.27	-5.85
JLM-AL-10-42	-38.66	-6.06
JLM-AL-10-43	-40.76	-5.92
JLM-AL-10-44	-35.15	-5.45
JLM-AL-10-45	-37.85	-6.07

Table 1. Results of isotopic analyses of local runoff and groundwater

The isotopic $\delta^{2}H$ and $\delta^{18}O$ data of the collected water samples show that most samples cluster near the GMWL, which suggests that the main recharge of the aquifer is of meteoric origin. This is the first source of the recharge of the aquifer. The groundwater samples collected on the north part, near the Shkumbin River, shows that the isotopic composition of the underground water is more depleted, which indicate that the aquifer is partially recharged from the Shkumbin River. The third source of recharge is from the Seman River

(see Figure 2). While the samples collected on the west part of the aquifer exhibit an enriched isotopic composition of oxygen-18 and deuterium near to the isotopic composition of the sea. This points out to the probability of having seawater intrusion. Furthermore, on the graph it is possible to see that the isotopic composition of only two samples is very low which suggest the presence of old water (palaewater). The chemical analyses of these samples show high salinity concentration. Moreover, these samples were collected on boreholes drilled in the old bed of the Seman River and (the second one) in the former Tërbufi marsh. Thus, it can be said that we are dealing with brine waters originated from Seman palae riverbed and former Tërbufi marsh.

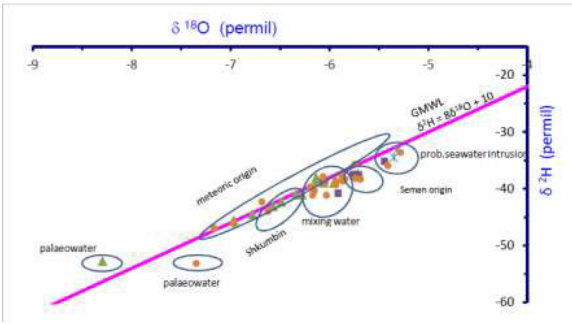

Figure 2. Isotopic composition of the sample values vs. the Global Meteoric Water Line and Lushnja Local Meteoric Line

CONCLUSIONS

The water samples measured during this study determine the range and patterns of stable isotope of hydrogen and oxygen in the groundwater of Lushnja. The application of the environmental isotopes (deuterium and oxygen-18) has provided with a better understanding of the hydrogeological conceptual model of the aquifer.

The aquifer of Lushnja is a complex coastal aquifer. Studying the isotopic composition of its groundwater sample, it is possible to detect four different recharge sources: fresh water from rain falls, fresh water from the two boundary rivers (Shkumbin and Seman) (mixing waters), seawater intrusion from the Adriatic Sea and also, the presence of palaewater.

Stable isotopic signature of water expressed as $\delta^{18}O$ and $\delta^{2}H$ are most commonly used environmental isotopes because the sample collection is easy and costs of analyses are moderate.

In this study are established the first pillars for a new monitoring system, which is compared with classic system of chemical and physical parameters.

ACKNOWLEDGEMENTS

The study of aquifer in the area of Lushnja could not be accomplished without the help of many colleagues.

First, we should thank the colleagues of the Albanian Geological Survey who collected the samples.

Also, special thanks should go to the colleagues of Laboratoire Hydrologie Isotopique, Université Paris-Sud, France for the opportunity to use the equipment for the measurements.

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THE APPLICATION OF SPECTROSCOPIC TECHNIQUE FOR THE STUDYING OF CONTROLLED RELEASE OF 2,4-D HERBICIDE FROM AAm/DMAEMA/DEG HYDROGELS

ZBATIMI I TEKNIKËS SPEKTROSKOPIKE PËR STUDIMIN E LËSHIMIT TË KONTROLLUAR TË HERBICIDIT 2,4-D NGA HIDROXHELET AAm/DMAEMA/DEG

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SUMMARY
The 2,4-D herbicide is one of the widest used herbicide in many countries and its uncontrolled application in agriculture is contributing on the contamination of the soil and the underground waters. Our contribution in this paper is the developing of new, effective and cost-efficient cross-linked AAm/DMAEMA/DEG hydrogels for removal of 2,4-D herbicides from contaminated waters. The hydrogels have been used to study the release properties of 2,4-D herbicide. For the study of the absorption capacity and controlled release of the 2,4-D herbicide from these hydrogels the UV-Vis spectroscopy was used. The concentration of this herbicide into water solution was determined using either 228 nm or 283 nm absorption wavelength. This technique was shown very effective in determination of loading capacities of hydrogels and release kinetics of loaded hydrogels.
Key words: controlled release,UV-Vis spectroscopy, hydrogels, absoption, 2,4-D herbicide

PËRMBLEDHJE
Herbicidi 2,4-D është një ndër herbicidet më të përdorur në shumë vende dhe zbatimi i pakontrolluar në bujqësi kontribuon në kontaminimin e tokës dhe ujërave nëntokësor. Kontributi ynë në këtë punim është zhvillimi i hidroxheleve efektive AAm/DMAEMA /DEG dhe të lira për largimin e herbicidit 2,4-D nga ujërat e kontaminuar. Hidroxhelet janë shfrytëzuar për studimin e karakteristikave lëshuese të herbicidit 2,4-D. Për studimin e kapacitetit absorbues dhe lëshimin e kontrolluar të herbicidit 2,4-D nga këto hidroxhele është shfrytëzuar spektroskopia e rrezatimit UV dhe e ajo e pjesës së dukshme të spektrit. Përqendrimi i këtij herbicidi në tretësirën ujore është përcaktuar duke shfrytëzuar gjatësinë valore të absorbimit në 228 nm ose në 283 nm. Kjo teknikë u tregua mjaft efektive për përcaktimin e kapacitetit të mbushjes së hidroxheleve dhe kinetikës së lëshimit të hidroxheleve të mbushura me herbicid.
Fjalët çelës : lëshim i kontrolluar, spektroskopia UV-Vis, hidroxhele, absorbimi, herbicidi 2,4-D

INTRODUCTION

Hydrogels are crosslinked polymer materials that absorb large quantities of water without dissolution of the material. They have widespread applications in biomedical, biotechnological, pharmaceutical, agricultural, and food industry and other related fields. In the last few decades, the study of absorption properties and controlled release of bioactive agents such as drugs, pesticides and herbicides from polymeric devices has attracted great attention [1-3]. One particular property of the controlled release matrix systems is to control the amount of the released agents to the desired level of efficacy for the needed time of application. There are relationships between the ways in which the agrochemical matrix formulations are synthesized and their

absorption and controlled release properties [4, 5]. Gamma irradiation processing is an important technique which induces polymerization and crosslinking without contamination of the agrochemical gel materials with foreign toxic additives [6-8].

The phenoxy acid group of herbicides is probably one of the widest used herbicide chemical classes [9]. The principal use of 2,4-dichloro phenoxy acetic (2,4-D) is for the control of a broad leaf of weeds in crops including wheat, maize, rice, sorghum, grassland and turf areas. It is also widely used in mixtures with other herbicides to provide weed control in the forestry, orchards and non-crop areas, and for the control of aquatic weeds. The herbicide 2,4-D was first identified in 1942 and marked in 1944. Despite its decades of usage, there are still data gaps concerning 2,4-D's effects on human health and environment risk [10].

DMAEMA is an pH sensitive monomer with adsorption and release properties of 2,4-D herbicide. This is used to obtain controlled release of that herbicide. Different compositions of AAm/DMAEMA/DEG polymers show different elastic and swelling properties. Hydrogels prepared without crosslinking agent, resulted in enhanced swelling kinetic [11,12].

In this study the usability of an cationic polymer prepared by acrylamide (AAm) and 2-(dimethylamino) ethyl methacrylate (DMAEMA) for the controlled release of 2,4-D herbicide spectroscopically has been investigated. The controlled release mechanisms of 2,4-D herbicide from AAm/DMAEMA/DEG polymers obtained by gamma radiation were examined.

MATERIALS AND METHODS.

The monomers used in this study, acrylamide (AAm), 2-(dimethylamino) ethyl methacrylate (DMAEMA) and crosslinking agent diethylene glycol DEG were obtained from Fluka and were used as received.

Four components were used in the preparation of acrylamide- 2-(dimethylamino)-ethyl methacrylate- diethylene glycol (AAm/DMAEMA/DEG) hydrogels in water. The mass proportions of the monomers in the initial mixtures are summarized in Table 1.

Table 1. Hydrogel types and mass/volume content of monomers in the feed solutions for gamma irradiation polymerization and crosslinking.

Gel name	AAm (g)	DMAEMA (ml)	DEG (%)	Water (ml)
1: 0.5AAm/1.5 DMAEMA/ 0.5DEG	0.5	1.5	0.5	1
2: 1AAm/1 DMAEMA/ 0.5DEG	1	1	0.5	1
3: 1.5AAm/0.5 DMAEMA/ 0.5DEG	1.5	0.5	0.5	1

These solutions were placed in PVC straws of 3 mm in diameter and irradiated at 6.4 kGy on Gamma cell. Fresh hydrogels obtained in long cylindrical shapes were cut into 3-4 mm in length. They were dried in vacuum oven in 315 K. Uncross-linked monomers were removed by two days washing in distilled water. Washed and dried hydrogels were used for further investigations.

The herbicide 2,4-D to be loaded into hydrogels was initially dissolved in distilled water, and (0.07-0.08)g dry copolymer discs were loaded with 2,4-D by immersion into aqueous solutions with different concentrations of herbicide. The amount of loaded herbicide was determined spectrophotometrically using Varion Cary 100 model UV-Vis Spectrophotometer at 228 nm or at 283nm. The calibration curve was prepared through UV absorption measurements of 2,4-D herbicide at a concentration range of between 0 and 75 ppm, Fig.1.

The controlled release of 2,4-D herbicide from AAm/DMAEMA/DEG hydrogel matrices were measured after 2,4-D was loaded, swollen gel was placed into a vessel containing 100 ml of HCL solution (in different pH). The aliquots of 3 ml

were drawn from the medium to follow the 2,4-D herbicide release and placed again into the same vessel so that the liquid volume was kept constant. 100 ml of HCL solution were used in all release studies. The calibration tests achieved with UV absorption measurements of pure 2,4-D at different pH values showed no changes in the spectra of herbicide.

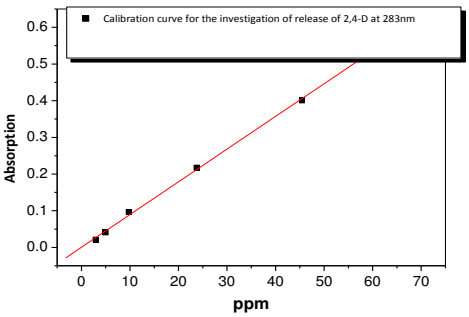
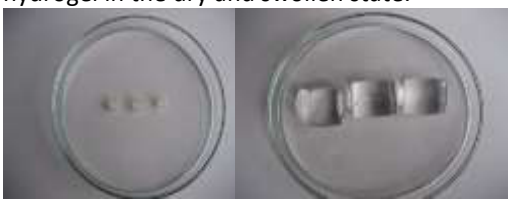


Figure.1. Calibration curve for the investigation of the controlled release of 2,4-D herbicide from hydrogels at 283 nm.

RESULT AND DISCUSSION

Hydrogel-based devices belong to the group of the swelling-controlled drug delivery systems. When the polymer network comes in contact with aqueous solutions, the thermodynamic compatibility of the polymer chains and water causes the polymer to swell. In the picture below is presented 1AAm/1 DMAEMA/ 0.5DEG hydrogel in the dry and swollen state.



The herbicide trapped inside the network dissolves with the imbibed water and begins diffusing out of the gel. In order to examine the transport mechanism from AAm/DMAEMA/DEG polymers, the following Peppas-Sahlin (1) equation is used [13]:

$$\frac{M_t}{M_\infty} = k_1 t^m + k_2 t^{2m} \qquad (1)$$

In this equation M_t / M_∞ is the fraction of the herbicide release, the first term of the right-hand side is the Fickian contribution, the second term being the Case-II relaxational contribution. The coefficient *m* is the purely Fickian release exponent for a device of any geometrical shape which exhibits controlled release.

The parameters such are release exponent *m*, kinetic constants k_1 and k_2 from Peppas-Sahlin equation (1), maximum release rate (max.rel.rate), time needed for maximum release (tnmr), the loading coefficient (lc) (%) and the integration efficacy of controlled release (iecr) are presented in the Table 2. Because the values of the constant k_2 are too small,, it means that the release of the herbicide from the gels is due to the Fickian diffusion processes.

Table 2. The values of seven different characteristic parameters obtained from release experiments of two compositions of AAm/DMAEMA/DEG hydrogels. Temperature 25 0C. pH of the initially swelling 5,3 and pH of the release medium 2 and 5,3.

	0.5 AAm/ 1.5 DMAEMA / 0.5 DEG	0.5 AAm/ 1.5 DMAEMA / 0.5 DEG	1A Am /1 D M AE M A/ 0.5 DE G	1A Am /1 D M AE M A/ 0.5 DE G	0.5 AAm/ 1.5 DMAEMA / 0.5 DEG	0.5 AAm/ 1.5 DMAEMA / 0.5 DEG	1A Am /1 D M AE M A/ 0.5 DE G	1A Am /1 D M AE M A/ 0.5 DE G
	pH =5, 3	pH =2	pH =5, 3	pH =2	pH =5, 3	pH =2	pH =5, 3	pH =2
m	0,62	0,35	0,52	0,64	0,50	0,60	0,48	0,78
k_1,	0,033	0,08	0,18	0,01	0,06	0,15	0,18	0,01

$h^{1/m}$								
k_2, $h^{2/m}$	0,002	0	-0,014	0	-0,004	-0,019	-0,016	-0,0005
mrr %	16	18	53	4	20	32	54	4
Tnmr ,h	32	30	27	28	32	31	32	31
lc %	39	39	22	22	19	19	15	15
iecr	0,12	0,18	0,41	0,11	0,16	0,32	0,43	0,12

The release characteristics of 0.5gAAm/1.5ml DMAEMA/ 0.5% DEG hydrogels initially swelled in pH=2, pH=3.1 and pH=5.3 ares presented in the Figure 2.

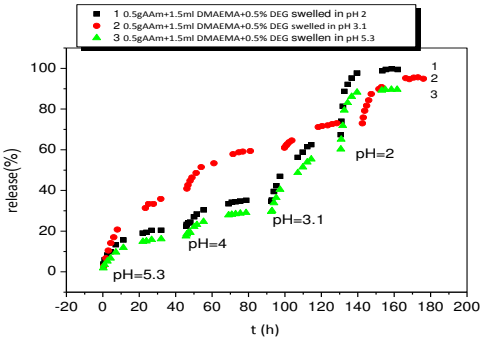


Figure 2. The release curves of 2,4-D herbicide from 0.5gAAm/1.5ml DMAEMA/ 0.5% DEG hydrogels initially swelled in different pH values.

As can be seen from Fig.2, the release curves of 2,4-D of 0.5gAAm/1.5ml DMAEMA/ 0.5% DEG hydrogels depend on the value of initially swelled pH of matrixes. The matrix initially swelled in pH=2 in medium with value of pH=5.3 achievies the equilibrium release of 18% of loaded herbicide, whereas matrix initially swelled in pH=3.1 in the same medium release 38% of the herbicide. The loaded matrix initially swelled in pH=5.3 in the release medium with pH=5.3 achieves the release equilibrium of 16% of the loaded herbicide.

Changing the pH of the release medium from 5.3 to 4; 3.1 and pH = 2, increase the released amount of the 2,4-D herbicide from hydrogels, and in pH = 2 matrixes achieve the maximum release.

The comparation of release curves of 2,4-D herbicide from 0.5gAAm/1.5ml DMAEMA/ 0.5% DEG ang 1gAAm/1ml DMAEMA/ 0.5% DEG hydrogels initially swelled in two different pH values, pH=2 and pH=5.3 where release characteristics are given in mg released herbicide per gram dry gel, is given in Fig.3. The different release curves are obtained depending on pH of release medium.

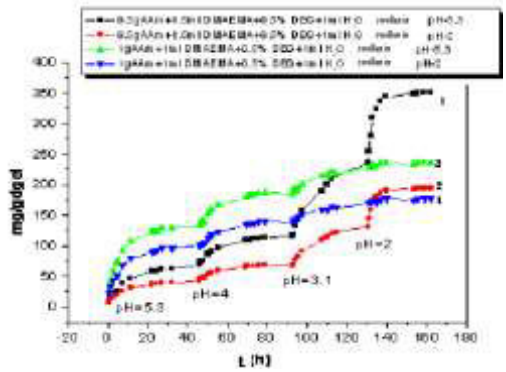


Figure3. Comparation of release curves of 2,4-D herbicide from AAm/DMAEMA/DEG hydrogels initially swelled in two different pH values.

The release differences between different matrixes of 0.5gAAm/1.5ml DMAEMA/ 0.5% DEG hydrogels and 1gAAm/1ml DMAEMA/ 0.5% DEG hydrogels initially swelled in pH=5.3 in the release medium with pH=5.3; 4; 3.1 and pH=2 are given in the Figure 4.

As can be seen from Fig.4, the matrix 0.5gAAm/1.5ml DMAEMA/ 0.5% DEG in the medium with value of pH=5.3 achivies the equilibrium release of 17% of loaded herbicide

whereas the matrix 1gAAm/1ml DMAEMA/ 0.5% DEG in the same medium with value of pH=5.3 achivies equilibrium of 53% of loaded herbicide. The maximum release of loaded herbicide is achivied in the medium with values of pH=2 for both matrixes.

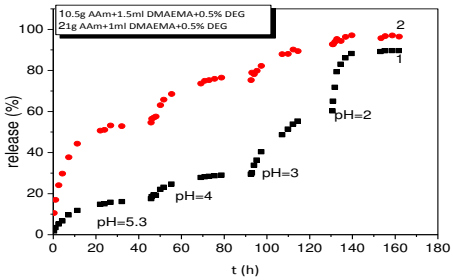


Figure 4. The release curves of 2,4-D herbicide from 0.5gAAm/1.5ml DMAEMA/ 0.5% DEG and 1g AAm/1ml DMAEMA/ 0.5% DEG hydrogels initially swelled in pH=5,3.

CONCLUSIONS

Matrixes from polyacrylamide-2-(dimethylamino) ethyl methacrylate methylene-diethylene glucol (AAm/DMAEMA/DEG) hydrogels were synthesized by gamma irradiation. The concentration of 2,4 D herbicide into water solution placed into UV quartz cuvette was determined using either 228 nm or 283 nm absorption wavelength in room temperature. This technique was shown very effective in determination of loading capacities of hydrogels and release kinetics of loaded hydrogels. Controlled release of 2,4-D herbicide from AAm/DMAEMA/DEG hydrogels is obtained by changing the pH of the release medium, by changing the pH of the initially swollen medium and by different amounts of the monomers AAm and DMAEMA into compositions.

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QUALITY AND ECOLOGICAL CHARACTERISTICS OF MAKROMYCETES (BASIDIOMYCOTA AND ASCOMYCOTA) ON DOBRA VODA MASSIF, REPUBLIC OF MACEDONIA

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SUMMARY
During 2002 -2008 are on Dobra Voda massif, Republic of Macedonia are systematically conduct research makromicetes. In the paper is presented a list of macromicetes (Basidiomycota and Ascomycota), lignicolus and tericolus fungi, registered in the following associations: Quercetum frainetto-cerris, Calamintha grandiflorae Fagetum, azonal vegetation with Populus tremulae, pinus plantings association, meadows and pastures. Of total 335 species of fungi, 203 species belonging tericolus and 132 species are lignicolus From the total number (335), 301species belonging to Basidiomycota, Ascomycota type while only 31 species and two species are miksomicete. A total 301 species, type Basidiomycota is represented by 14 order, 50 families and 120 genus of fungi. Ascomycota type is represented by 7 order, 17 families and 23 genus, a total of 32 species. Order with the largest number of species are: Agaricales, with 163 species, Boletales, 29, Polyporales, 38, Russulales 33 and Pezizales with 19 species.
Key words: Fungi, Ascomycota, Basidiomycota, Dobra Voda, Republic of Macedonia

INTRODUCTION

The Republic of Macedonia is relatively low researched in micologic aspect. But lately the researches are being more frequent in surveys carried out in different territories of our country, such as searches on the mountains: Bistra, Pelister, Jakupica, Galicica Kozhufi, Shar Planina, Osogova and lately in new territories like on Dobra Voda Mountain massive (Ujmiri) etc. The first researches on the territory of the Republic of Macedonia are made by Ranojevic, N., (1909), then Sydow, H., (1921), Lindtner, V., (1950), Litschauer, V., (1939). Major contribution to mycology in Macedonia respectively in makromycetes gives Tortich, M., (1975, 1977, 1988) who explored the mountains of Jakupica and Pelister. In recent years the new territories and different localities of the Republic of Macedonia are being explored very intensively by Karadelev, M., (1989, 1993, 1994, 1995, 1998, 1999, 2000, 2001); Karadelev, M., Nastov, M, Rusevska, K., (2002); Karadelev, M., Rusevska, K.,. (2004); Bauer-Petrovska., Karadelev, M., & Kulevanova, S., (2006), Karadelev, M., & Murati, E., (2008).Karadelev,M .,Sulejmani, S., and Murati, E., (2008).,Murati,E.,Karadelev,M.,(2012).etc.

Based on previous researches in Macedonia there are identified and defined the presence of around 2350 species of macromyceta of whom 250 species are ascomycota and around 2100 species of fungis to basidiomycota.Mountain massive Ujmiri (Dobra Voda, 2062 m), is located in the northern part of Kicevo valley (approximately 15 km north of Kicevo) and together with mountain Bukovik curve , represent a border frame to the valley of Pollog. In the east there are related some peaks and mountains as: Skala (1826), Belezi (1754m), Mountain of Tuhinit (Tuhinit Castle, 1808m) etc., which represent continuous mountain crown. Surveys are carried out in the whole of the

mountain in phytocenosis Ujmiri oak beech, then planted pine, popular vegetation zone with as few phytocenosis meadows, pastures and the river valley vegetation etc. These data are as a result of research conducted in this territory from 2002,2003,2006,2007,until,spring2008

MATERIALS AND METHODS

Surveys are conducted on massive Mountain Dobra Voda (Ujmiri) including several associations (community life) as oak, beech, pine planted, vegetation azonal wild popular and some meadows and pastures from oak forest (*Quercetum frainetto-cerris macedonicum* Oberd. emend. Ht.) and fagus forest (*Calamintho grandiflorae-Fagetum* Em) in the region of Dobra Voda mountain massive in altitude 670-1.650 m.. The material was collected during the years 2002, 2003, 2005, 2006.2007, from spring to autumn and 2008 spring. There is researched the diversity distribution and ecology of fungis, types lignicolus and tericolus macromycetes, their frequency of particular are researched types parasite and mikorize. The material was collected in the mountain range to the highest peaks of mountain Ujmiri (Dobra Voda),with the surrounding villages: Jagoll, Dolenc, Popojan, Tuhin, Prapadisht and Zhubrino etc. A certain specified number of species is identified and determined in the place where they are found in fresh state immediately after is has been collected while in the other part there are made different detailed analysis for identification and determination with the help of the microscope where the fungal spores are identified, cistidies , than its made their measurement chemical reagents (melzer, sulfovanilin, KOH etc) in the mycological laboratory , in the institute of Biology in Faculty of Natural Science and Mathematics in Skopje , under the surveillance of professor dr Mitko Karadelev. For determination of these fungi there were using the newest keys and monographs: BREITENBACH, J., and KRANZLIN,F.,(1981,1986,1991,1995,2000); ERIKSSON, J., RYVARDEN, L., (1975); ERIKSSON, J., HJORTSTAM< K. & RYVARDEN, L., (1978,1981); ALESSIO,C.L (1985); MOSER, M.,(1983); AHTI et al., (2000); BOERTMAN, D., et al., (1992); CORFIXEN, P. et al., (1997); DÄNCKE R, M., (2004) etc. For the determination of some species are used:http://www.Indexfungorum.org/Names/Names.asp:
http://www.mycobank.org/MycoTaxo.aspx
From each type of part is prezerved dried and labeled with key data (location, altitude, date of collection,

RESULTS

LIST OF SPECIES MACROMYCETES REGISTERED IN THE TERITORY ON DOBRA VODA MONTAIN MASSIF (UJMIRI)

MYXOMYCOTA

1.*Lycogala epidendron (L.) Fr.*
2.Arcyria denudata (L.) Wettst., Verh

ASCOMYCOTA

3.Microsphaera alphitoides Griffon & Maubl.
4.Bulgaria inquinans (Pers.) Fr.
5.Ascocoryne sarcoides (Jacq.) J.W. Groves & D.E. Wilson,
6. Bisporella citrina (Batsch) Korf & S.E. Carp.,
7. Sclerotinia pseudotuberosa (Rehm) Rehm
8. Discina parma J. Breitenb. & Maas Geest.
9.. Helvella acetabulum (L.) Quél. *10. Helvella lacunosa Fr.*
11. Mitrophora semilibera (DC.) Lév.
12. Morchella conica Pers.
13.Morchella esculenta (L.) Pers. *14.Verpa bohemica (Krombh.) J. Schröt.* *15. Peziza celtica (Boud.) M.M. Moser*
16.Peziza domiciliana Cooke *17.Peziza vesiculosa Bull.* *18. Anthracobia macrocystis (Cooke) Boud.,*
19..Anthracobia maurilabra (Cooke) Boud.,
20.Humaria hemisphaerica (Hoffm.) Fuckel *21.Otidea concina (Pers.) Sacc.* *22.Otidea onotica (Pers.) Fuckel* *23.Sarcoscypha coccinea*
24.Hymenoscyphus calyculus (Sowerby) W.Phillips
25.Hymenoscyphus separabilis (P. Karst.) Dennis
26.Rhytisma acerinum (Pers.) Fr.

27. Bertia moriformis (Tode) De Not. *28. Diatrype disciformis (Hoffm.) Fr.* *29. Diatrype stigma Sacc.* *30.Hypoxylon fuscum (Pers.) Fr.*
31.Hypoxylon fragiforme (Pers.) J. Kickx f.
32. Xylaria hypoxylon (L) Grev,
33. Hypochrea rufa (Pers.) Fr. *34. Nectria cinnabarina (Tode) Fr.*
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35. Agaricus campestris Scop.
36. Agaricus macrosporus var. macrosporoides (Bohus) Wasser
37. Agaricus romagnesi Wasser (1977),
38. Agaricus silvicola (Vittad.) Peck .
39. Agaricus xanthoderma Genev.
40. Cystoderma granulosum (Batsch) Fayod
41. Cystoderma jasonis (Cooke & Massee) Harmaja
42. Cystolepiota seminuda (Lasch) Bon
43. Lepiota aspera (Pers.) Quél.
44. Lepiota clypeolaria (Bull.) P. Kumm.
45. Lepiota cristata (Bolton) P. Kumm.
46. Lepiota griseovirens Maire
47. Lepiota magnispora Murrill 1912
48. Leucoagaricus leucothites (Vittad.) Wasser
49. Macrolepiota excoriata (Schaeff.) Wasser
50. Macrolepiota mastoidea (Fr.) Singer
51. Macrolepiota procera (Scop.) Singer
52. Hebeloma birrus (Fr.) Gillet
53. Hebeloma sinapizans (Paulet) Gillet
54. Panaeolus papilionaceus (Bull.) Quél.
55. Pholiotina aporos (Kits van Wav.) Clémençon
56. Coprinellus micaceus (Bull.) Vilgalys, Hopple & Jacq. Johnson
57. Coprinus comatus (O.F. Mull.) Pers.
58. Coprinus picaceus (Bull
59. Psathyrella candolleana (Fr.) Maire
60. Psathyrella multipedata (Peck) A.H. Sm.
61. Psathyrella spadicea (Schaeff.) Singer
62. Cortinarius c.f. cinnabarinus Fr.
63. Cortinarius lividoviolaceus Rob. Henry
64. Cortinarius mucosus (Bull.) Cooke
65. Cortinarius trivialis J.E. Lange *66. Crepidotus cesatii (Rabenh.) Sacc*
67. Crepidotus mollis (Schaeff.) Staude
68. Galerina autumnalis (Peck) A.H. Sm. & Singer
69. Galerina marginata (Batsch) Kühner
70. Gymnopus dryophilus (Bull.) Murrill
71. Inocybe asterospora Quél.
72. Inocybe splendens R.Heim
73. Phaeomarasmius erinaceus (Fr.) Kühner
74. Phaeomarasmius rimulincola (Lasch) Scherff.
75. Entoloma conferendum (Britzelm.) Noordel.
76. Entoloma hebes (Romagn.) Trimbach
77. Entoloma pseudoturbidum (Romagn.) M.M. Moser
78. Entoloma sericeum Quél.
79. Entoloma sericeoides (J.E. Lange) Noordel
80. Clitopilus prunulus (Scop.) P. Kumm.
81. Fistulina hepatica (Schaeff.) Si
82. Laccaria amethystina
83. Laccaria laccata (Scop.) Cooke
84. Bovista aestivalis (Bonord.) Demoulin
85. Bovista plumbea Pers.
86. Lycoperdon atropurpureum Vittad.
87. Lycoperdon echinatum Pers.
88. Lycoperdon ericaeum Bonord
89. Lycoperdon molle Pers.
90. Lycoperdon nigrescens Wahlenb.
91. Lycoperdon perlatum Pers.
92. Lycoperdon pyriforme Vent.
93. Calvatia excipuliformis (Scop.) Perdeck
94. Calvatia utriformis (Bull.) Kreisel
95. Vascellum pratense (Pers.) Kreisel
96. Armillaria mellea (Vahl) P. Kumm.
97. Armillaria tabescens (Scop.) Emel
98. Marasmius bulliardii Quél.
99. Marasmius oreades (Bolton) Fr.
100. Marasmius wynnei Berk. & Broome
101. Omphalotus olearius (DC.) Singer
102. Oudemansiella mucida (Schrad.) Höhn.
103. Crucibulum laeve (Huds.) Kambly
104. Cyathus olla (Batsch) Pers.
105. Amanita battarrae (Boud.) Bon
106. Amanita caesarea (Scop.) Pers.
107. Amanita citrina (Pers.) Pers.
108. Amanita excelsa (Fr.) Bertill.
109. Amanita fulva (Schaeff.) Fr.

110. Amanita mairei Foley
111. Amanita pantherina (DC.) Krombh.
112. Amanita phalloides (Vaill. ex Fr.) Link
113 Amanita rubescens Pers.
114. Amanita vaginata (Bull.) Lam.
115. Pluteus cervinus (Schaeff.) P. Kumm.
116. Volvariella gloiocephala (DC.) Boekhout & Enderle
117. Hohenbuehelia atrocaerulea (Fr.) Singer
118. Pleurotus cornucopioides (Klotzsch) Gillet
119. Pleurotus dryinus (Pers.) P. Kumm.
120. Pleurotus eryngii (DC.) Quél.
121. Pleurotus ostreatus (Jacq.) P. Kumm.
122. Pleurotus pulmonarius (Fr.) Quél.
123. Radulomyces molaris (Chaillet ex Fr.) M.P. Christ.
124. Schizophyllum commune Fr.
125. Hypholoma capnoides (Fr.) P. Kumm. *126. Hypholoma fasciculare (Huds.) P. Kumm.*
127. Hypholoma sublateritium (Fr.) Quél.
128. Kuehneromyces mutabilis (Schaeff.) Singer & A.H. Sm.
129. Pholiota oedipus (Cooke) P.D. Orton
130. Pholiota highlandensis (Peck) Singer
131. Stropharia coronilla (Bull.) Quél.
132. Stropharia semiglobata (Batsch) Quél.
133. Stropharia squamosa (Pers.) Quél.
134. Arrhenia lobata (Pers.) Kühner & Lamoure ex Redhead
135. Asterophora parasitica (Bull. ex Pers.) Singer
136. Calocybe gambosa (Fr.) Donk
137. Clitocybe bresadoliana Singer
138. Clitocybe candicans (Pers.) P. Kumm.
139. Clitocybe costata Kühner & Romagn.
140. Clitocybe fragrans (With.) P. Kumm.
141. Clitocybe dealbata (Sowerby) P. Kumm.
142. Clitocybe gibba (Pers.) P. Kumm.
143. Clitocybe lignatilis (Pers.) P. Karst.
144. Clitocybe metachroa (Fr.) P. Kumm.
145. Clitocybe nebularis (Batsch) P. Kumm.
146. Clitocybe odora var. alba
147. Clitocybe subspadicea (J.E. Lange) Bon & Chevassut
148. Clitocybe tubaeformis Beeli
149. Collybia butyracea (Bull.) P. Kumm
150. Collybia dryophila (Bull.) P.
151. Collybia erythropus (Pers.) P. Kumm.
152. Collybia fusipes (Bull.) Quél.
153. Collybia peronata (Bolton) P. Kumm.
154. Collybia tuberosa (Bull.) P. Kumm
155. Hygrocybe conica (Schaeff.) P. Kumm.
156. Hygrocybe pratensis (Schaeff.) Bon
157. Hygrocybe virginea (Wulfen) P.D. Orton & Watling
158. Hygrophorus dichrous Hongo
159. Hygrophorus discoideus (Pers.) Fr. *160. Hygrophorus discoxanthus (Fr.) Rea*
161. Hygrophorus eburneus (Bull.) Fr.
162. Hygrophorus hypothejus (Fr.) Fr.
163. Hygrophorus latitabundus Britzelm.
164. Hygrophorus leucophaeus (Scop.) Fr.
165. Hygrophorus poetarum R. Heim
166. Lepista flaccida (Sowerby) Pat.
167. Lepista inversa (Scop.) Pat.
168. Lepista irina (Fr.) H.E. Bigelow
169. Lepista luscina (Fr.) Singer
170. Lepista nuda (Bull.) Cooke
171. Melanoleuca excissa (Fr.) Singer
172. Melanoleuca graminicola (Velen.) Kühner & Maire
173. Melanoleuca stridula (Fr.) Singer
174. Melanoleuca subalpina (Britzelm.) Bresinsky & Stangl
175. Mycena alba (Bres.) Kühner
176. Mycena arcangeliana Bres.
177. Mycena aurantiomarginata (Fr.) Quél.
178. Mycena epipterygia (Scop.) Gray
179. Mycena erubescens Höhn. 1913
180. Mycena galericulata (Scop.) Gray
181. Mycena meliigena (Berk. & Cooke) Sacc.
182. Mycena pelianthina (Fr.) Quél.
183. Mycena polygramma (Bull.) Gray
184. Mycena pura (Pers.) P. Kumm.
185. Mycena renati Quél.
186. Mycena rosea (Pers.) Sacc.
187. Omphalina pyxidata (Bull.) Quél.
188. Panellus stipticus (Bull.) P. Karst.
189. Pseudoclitocybe cyathiformis (Bull.) Singer
190. Resupinatus applicatus (Batsch) Gray
191. Resupinatus trichotis (Pers.) Singer
192. Tricholoma acerbum (Bull.) Quél.

193. Tricholoma columbetta (Fr.) P. Kumm.
194. Tricholoma equestre (L.) P. Kumm.
195. Tricholoma portentosum (Fr.) Quél.
196. Tricholoma saponaceum (Fr.) P. Kumm.
197. Tricholoma scalpturatum (Fr.) Quél.
198. Tricholoma sejunctum (Sowerby) Quél.
199. Tricholoma ustale (Fr.) P. Kumm.
200. Tricholoma stiparophyllum (N. Lund)
201. Tricholomopsis rutilans (Schaeff.) Singer
202. Auricularia auricula-judae (Bull.) J. Schröt.
203. Auricularia mesenterica (Dicks.) Pers.
204. Boletus aestivalis (Paulet) Fr.
205. Boletus edulis Bull.
206. Boletus betulicola (Vassilkov) Pilát & Dermek
207. Boletus erythropus Pers.
208. Boletus luridus Viv.
209. Boletus queletii Schulzer
210. Boletus regius Krombh.
211. Boletus satanas Lenz
212. Leccinum duriusculum (Schulzer) Singer
213. Leccinum quercinum Pilát
214. Leccinum vulpinum Watling
215. Xerocomus chrysenteron (Bull.) Quél.
216. Xerocomus ferrugineus (Schaeff.) Alessio
217. Xerocomus subtomentosus (L.) Quél.
218. Coniophora puteana (Schumach.) P. Karst.
219. Astraeus hygrometricus (Pers.) Morgan
220. Chroogomphus rutilus (Schaeff.) O.K. Mill.
221. Hygrophoropsis aurantiaca (Wulfen) Maire
222. Paxillus involutus (Batsch) Fr.
223 .Scleroderma areolatum Ehrenb.
224. Scleroderma cepa Pers.
225. Scleroderma citrinum Pers. 1801
226. Scleroderma polyrhizum Pers.
227. Scleroderma verrucosum (Bull.) Pers.
228. Suillus fluryi Huijsman
229. Suillus granulatus (L.) Kuntze
230. Suillus luteus (L.) Roussel
231. Suillus tridentinus (Bres.) Singer
232. Cantharellus cibarius Fr.
233. Cantharellus tubaeformis Fr.
234. Craterellus cornucopioides (L.) Pers.
235. Hydnum repandum L.
236. Hydnum rufescens Pers.
237. Corticium polygonioides P. Karst.
238. Dendrothele acerina (Pers.) P.A. Lemke
239. Vuilleminia comedens (Nees) Maire
240. Calocera cornea (Batsch) Fr.
241. Calocera viscosa (Pers.) Fr.
242. Dacrymyces stillatus Nees
243. Geastrum badiumVittad.
244. Geastrum striatum Quél.
245. Hymenochaete cinnamomea (Pers.) Bres.
246. Hymenochaete rubiginosa (Dicks.) Lév.
247. Inonotus nodulosus (Fr.) P. Karst.
248. Phellinus igniarius (L.) Quél. 1886
249. Phellinus punctatus (P. Karst.) Pilát
250. Phellinus robustus (P. Karst.) Bourdot & Galzin
251. Phellinus torulosus (Pers.) Bourdot & Galzin
252. Phellinus tuberculosus (Baumg.) Niemelä
253. Schizopora paradoxa (Schrad.) Donk
254. Daedalea quercina (L.) Pers.
255. Laetiporus sulphureus (Bull.) Murrill
256. Ganoderma adspersum (Schulzer) Donk
257. Ganoderma applanatum (Pers.) Pat.
258. Ganoderma lucidum (Curtis) P. Karst.
259. Meripilus giganteus (Pers.) P. Karst.
260. Bjerkandera adusta (Willd.) P. Karst.
261. Phlebia rufa (Pers.) M.P. Christ
262. Cerrena unicolor (Bull.) Murrill
263. Datronia mollis (Sommerf.) Donk
264. Dichomitus campestris (Quél.) Domanski & Orlicz
265. Faerberia carbonaria (Alb. & Schwein.) Pouzar
266. Fomes fomentarius (L.) Fr.
267. Hapalopilus nidulans (Fr.) P. Karst
268. Hapalopilus rutilans (P . ers.) Murrill
269. Lentinus strigosus (Schwein.) Fr.
270. Lenzites betulina (L.) Fr.
271. Lopharia spadicea (Pers.) Boidin
272. Polyporus arcularius (Batsch) Fr.
273. Polyporus brumalis (Pers.) Fr.
274. Polyporus squamosus (Huds.) Fr.
275. Polyporus varius (Pers.) Fr.
276. Pycnoporus cinnabarinus (Jacq.) P. Karst.
277. Trametes gibbosa (Pers.) Fr.
278. Trametes hirsuta (Wulfen) Pilát
279. Trametes multicolor (Schaeff.) Jülich 1982
280. Trametes ochracea (Pers.) Gilb. & Ryvarden
281. Trametes pubescens (Schumach.) Pilát
282. Trametes versicolor (L.) Lloyd

283. Trametes suaveolens (L.) Fr
284. Trichaptum biforme (Fr.) Ryvarden
285. Irpex lacteus (Fr.) Fr.
286. Meruliopsis corium (Pers.) Ginns
287. Phanerochaete tuberculata (P. Karst.) Parmasto
288. Phanerochaete velutina (DC.) P. Karst.
289. Steccherinum fimbriatum (Pers.) J. Erikss.
290. Steccherinum ochraceum (Pers. ex J.F. Gmel.) Gray
291. Terana caerulea (Schrad. ex Lam.) Kuntze
292. Xenasmatella vaga (Fr.) Stalpers
293. Gloeocystidiellum luridum (Bres.) Boidin
294. Hericium erinaceus (Bull.) Pers.
295. Peniophora incarnata (Pers.) P. Karst.
296. Peniophora quercina (Pers.) Cooke
297. Lactarius camphoratus (Bull.) Fr.
298. Lactarius chrysorrheus Fr.
299. Lactarius decipiens Quél.
300. Lactarius deliciosus (L.) Gray
301. Lactarius glaucescens Crossl.
302. Lactarius piperatus (L.) Pers.
303. Lactarius sanguifluus (Paulet) Fr.
304. Lactarius serifluus (DC.) Fr.
305. Lactarius vellereus (Fr.) Fr
306. Lactarius volemus (Fr.) Fr.
307. Lactarius zonarius (Bull.) Fr.
308. Lactarius zonarioides Kühner & Romagn.
309. Russula clariana R. Heim
310. Russula chloroides (Krombh.) Bres.
311. Russula cyanoxantha (Schaeff.) Fr.
312. Russula cyanoxantha var. cutefracta (Cooke) Sarnari
313. Russula elaeodes (Bres.) Bon
314. Russula foetens Pers.
315. Russula fragilis (Pers.) Fr.
316. Russula gigasperma Romagn.
317. Russula nigricans Fr.
318. Russula risigallina (Batsch) Sacc
319. Russula virescens (Schaeff.) Fr.
320. Russula xerampelina (Schaeff.) Fr.
321. Stereum gausapatum (Fr.) Fr.
322. Stereum hirsutum (Willd.) Pers.
323. Stereum rugosum Pers.
324. Stereum subtomentosum Pouzar
325. Hydnellum spongiosipes (Peck) Pouzar
326. Sarcodon cyrneus Maas Geest.
327. Sarcodon imbricatus (L.) P. Karst.
328. Exidia glandulosa (Bull.) Fr.
329. Exidia truncata Fr.
330. Tremella foliacea Pers.
331. Tremella mesenterica Retz.
332. Clavariadelphus pistillaris (L.) Donck
333. Ramaria decurrens (Pers.) R.H. Petersen
334. Ramaria flava (Schaeff.) Quél.
335. Kavinia himantia (Schwein.) J. Erikss.

DISCUSSIONS

The initial incomplete research of macromycetes in the Mountain massive Dobra Voda (Ujmiri), which were mainly processed only fungi community of oak (Quercetum frainetto-cerris) and some meadow communities, a total of 106 species were recorded fungi, of which 61 species are terikolus while 45 lignicolus. From recorded species, 96 species of fungi belonging to the type Basidiomycota while only 8 species of Ascomycota. (Karadelev, Sulejmani and Murati, 2009). In further researches there are involved and some other communities as beech, azonal vegetation, pine groves, meadows and pastures so the number of recorded species in May 2008 reached 280 species, of which 255 belong of Basidiomycota while 25 Ascomycota. Tericolous are 160 species while the 120 species are lignicolous (Karadelev and Murati, 2008). Further comprehensive research is still done in some other communities listed in the higher altitudes like 1.300-1.650 m above sea level, such as beech community (Calamintha grandiflorae - Fagetum Em), but of course not with such intensity compared to the researches on oak community. Apart from these two major communities, researches were made in communities with pine plantations, azonal vegetation with Populus spp, river vegetation with Salix spp and Alnus spp, mixed forest, and some communities of meadows and pastures that are quite common in the area and the mountain of Dobra Voda. In previous studies of these Mountain is Dobra Voda there also were registered macromycetes (Ascomycota and Basidiomycota). From 2002 to 2008 in a database of MAC-fungi to Dobra Voda mountain massive is imported over 700 data and

registered 335 fungi. As most fertile, when registered most fungi are considered in 2007, then in 2006 and 2008, while 2002 and 2003 are considered like less explored. In 2004 and 2005 there is no information or were not researched. Studies have been conducted throughout the year, but as **explored** months certainly autumn months: September, October and November, then spring: April, May and June, while summer and winter due to adverse conditions, such as drought in the summer and bitter cold in winter are less researched. Of the total number of registered macromycetes (333), to the type of Ascomycota belong only 32 species, or about 10%, while the majority belong to the type Basidiomycota, 301 species or about 90%). Listed are two (2) types such as Myxomycota enrolled at the beginning of the list. Treated as tericolus and lignicolus types macromycetes. In lignicolus includes 128 species macromycetes while tericolus 205 species of fungi.

Type Ascomycota is represented in 7 orders, 17 families and 23 genera, with 32 species. As the most abundant order separates Pezizales with 19 species, which of course is about 2/3 (or 60%) of the total number of Ascomycetes.

Type Basidiomycota is represented in 14 orders, covering 50 families and 120 genera, with a total of 301 species,

Orders that are most numerous by species The most regularly: As the most common types are the orders:

1. Agaricales, even with 163 species, followed, 2. Boletales, with 29 species,3. Polyporales, with 38 species

4. Pezizales, with 19 species, 5. Russulales, with 33 species, etc.

According to these results, there is being shown that most of fungi are of the order Agaricales, which also represents more than half of the recorded species, with over 50% of the total number of prominent species. Polyporales followed by about 11%, Russulales 10%, Boletales with 9% and 6% Pezizales while other rows are less represented. In the order of Agaricales, mostly recorded species are from the family Tricholomataceae with 66 species of fungi.

These five lines also make up the majority of fungi with over 86% of the total number of macromycetes registered in the area of massive Mountain Dobra Voda , and even more than 90% of the total number of basidiomycetes explored in the same area as above mentioned.

Generic with most types following: Amanita 10, Agaricus 5, Boletus 7, Clitocybe 12, Hygrophorus 8, Lactarius 12, Mycena 10, Russula 12, Trametes 7, Tricholoma 10, Collybia 6, Entoloma 5, Phellinus 5, Lepista 5 etc.

It is worth mentioning type *Sarcodon cyrneus* registered only once in the locality Gorica near village Popovjani. Many rare species in Europe, known only in Corsica, where is collected under Quercus ilex (Julich, 1984).

CONCLUSSIONS

-From 2002 to 2008 in a database of MAC-fungi to Dobra Voda mountain massive is imported over 700 data and registered 335 fungi

-Of the total number of registered macromycetes (333), type Ascomycota belong only 32 species, or about 10%, while the majority belong to the type Basidiomycota, 301 species or about 90%)

-Treated as tericolus and lignicolus types macromycetes. In lignicolus includes 128 species macromycetes while tericolus 205 species of fungi.

-The most regularly: As the most common types are the orders: Agaricales, even with 163 species, followed by ,Boletales with 29 species , Polyporales with 38 species , Pezizales, with 19 species , Russulales, with 33 species, etc.

-Generic with most types following: Amanita 10, Agaricus 5, Boletus 7, Clitocybe 12, Hygrophorus 8, Lactarius 12, Mycena 10, Russula 12, Trametes 7, Tricholoma 10, Collybia 6, Entoloma 5, Phellinus 5, Lepista 5 etc

SUMMARY

From 2002 until 2008, a large systematic research was conducted in the Mountain of Dobra Voda, from which it is proved that: of the total of 335 species of fungi, 301 are of the phyllum *Basidiomycota* while only 32 are *Ascomycota* and 2 species are Myxomycota. Of the total number,

203 species are part of the terricolus while 132 are lignicolous. Orders with the greatest number of species are the following: *Agaricales (*163*), Boletales (29), Pezizales (20), Polyporales (38), Russulales (30)* etc.

The most frequent tericolous species are: *Agaricus campestris, Amanita rubescens, Boletus edulis, Bovista plumbea, Cantharellus cibarius, Collybia driophyla, Macrolepiota procera, Marasmius oreades, Russula cyanoxantha* etc.The most rare the terricolous species are: *Agaricus romagnesi, Amanita battarea, Amanita mairei, Boletus regius, Clavariadelphus pistilaris, Geastrum badium, Inocybe asterospora, Morchela esculenta, Helvella lacunosa. Fungis with more frequency of the lignicolous are: Armillaria mellea, Irpex lacteus, Trametes hirsuta, Vuilleminia comedens, Polyporus arcularius, Stereum hirsutum, Tremella mesenterica* etc. The most rare species of the lignicolous fungis can be mentioned: *Discina parma, Hericium erinaceus, Hohenbuehelia atrocerulea, Kavinia himantia, Pleurotus dryinus, Phaeomarasmius erinaceus, Resupinatus trichotis etc.* Economycaly important fungis can be *m*entioned in these species: *Agaricus campestris, Boletus edulis, Boletus aestivalis, Cantharellus cibarius, Craterellus cornucopioides, Morchela esculenta, Pleurotus ostreatus* etc.Toxic fungis potentially dangerous for life are: *Amanita pantherina, Amanita phalloides, Agaricus xanthoderma etc*. During this research, 51 new species were recorded for the mycology of Republic of Macedonia .

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PHOTOSYNTHETIC PIGMENTS CONTENT IN SOME IMPORTANT ASSOCIATIONS OF THE VEGETATION IN SKADAR LAKE

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Natural Sciences University of TiranaSUMMARY

SUMMARY
Skadar lake is the biggest lake in the Balkan Peninsula. The total area is 5500 m². Both the sides of lake is a big development of acquatic vegetation. The most important associations are Potameto-Najadetum, Potameto-Vallisnerietum, Potametum natantis, Trapetum natantis, Myriophyllo-Nupharetum, Nymphoideum peltata. These associations include lake shore macrophytes Najas, Vallisneria, Potamogeton, floating macrophytes Nuphar luteum, Trapa natans, Numphaea alba. Plant samples were collected on the both sides of the lake where is determined the content of photosynthetic pigments. Photosynthetic pigments were extracted with 80% acetone and their concentrations are expressed in mg/g dry absolutely leaf .Their measurement is made in the bands f 663, 645.470, of spectrophotometer. The higher values of chlorophyll in the species Vallisneria spiralis was found in September (0.544mg / g). For the species Najas marina the higher values of chlorophyll was found in October (0.440mg / g).
Key words: Skadar lake, photosynthetic pigments, macrophyte.

PËRMBLEDHJE
Liqeni Shkodrës është liqeni më i madh në Gadishullin Ballkanik me një sipërfaqe ujore rreth 5.500 m2. Në liqenin e Shkodrës ka një bimësi ujore që zhvillohet në të dy krahët e tij Shoqërimet më të rëndësishme bimore janë Potameto-Najadetum, Potameto-Vallisnerietum, Potametum lucentis, Potametum natantis, Trapetum natantis, Myriophyllo-Nupharetum, Nymphoideum peltata. Në këto shoqërime përfshihen makrofitet bregliqenore Najas, Vallisneria, Potamogeton, makrofitet notuese si Nuphar luteum, Trapa natans, Numphaea alba. Janë marrë kampionë me bimë në dy krahët e liqenit ku janë përcakuar përmbajtja e pigmenteve fotosintetikë. Pigmentet fotosintetikë u ekstraktuan me aceton 80% dhe përqëndrimet e tyre janë shprehur në mg/g gjethe absolutisht të thatë. Matja e tyre është bërë në fotospektrometër në gjatësitë e valëve 663, 645,470, Për specien Vallisneria spiralis vlera më e lartë e klorofilës a u gjet në shtator (0.544mg/g) .Për specien Najas marina vlera më e lartë e klorofilës u gjet në tetor (0.440mg/g).
Fjalët kyçe: Liqeni i Shkodrës., pigmente fotosintetike makrofite

INTRODUCTION

Skadar lake is the largest lake on Balkan Peninsula. The drainage area of the lake is about 5500 km² 4.470 km² in Montenegro and 1030 km² in Albania. The lake area is 368 km². The lake volume varies between 1.8 km² in dry periods to 4.1 km³ during wet periods. The lake depth is about 7-10m and the maximum lake depth reaches 44 m (1, 2).

Skadar lake is known as a hight biodiversity ecosystem. The variety of the species per 100 m² is S/A=0.8752. We can mention important habitats like: the Eye of Shegan, the Eye of Viri, the underwater meadows in Shegan, the reeds-xunkth in Shkoder, Vrake and Buze Uje, the forests of the shores in the areas of Shegan - Kamice, Shkoder-Vrake, Zogaj-Shiroke(8).

Aquatic and wetland flora is very rich. About 242 species of macrophytes are known from which 10

are algae(Characeae), 1 musk, 1 fir , 7 species are members of Equisetaceae family, 115 are Monocotyledons and 107 Dicoyiledons(3).

The most important associations of the vegetations types according to Pulevic et al(2001) are : Najadetum marinae ,Potameo-Najadetum, Potameo- Vallisnerietum, Potameo-natantis, Trapeum-natantis. Myriophyllo-Nupharetum lutei, Nymphoidetum peltata, Phragmitetum australis, Tyhpaetum latifolia, Ludwigetum palustris, Leucojo-Fraxinetum angustifolia(8).

Summary of the most important asociations of the vegetation types

Najadetum marinae (Fukarek 1961) assemblage overgrow the Lake bottom in depths zones more than 3m. This community is the most resistant on light deficiency. Dominant species is Najas marina but there are also species like Potamogeton perfoliatus, Myriophyllum spicatum, and Vallisneria spiralis. The afore mentioned species are typical hydrophyte.(4).

Potametum perfoliati association is common in the depth zones between 1 and 3 meters and is characterized by higher species diversity then others associations in the Lake. This association inhabits areas with colder water. Dominant species is Potamogeton perfoliatus and all other constituents are in hydrophyte type of plants. Constituents include: Myriophyllum spicatum, Myriophyllum verticillatum, Potamogeton crispus, Potamogeton pectinatus, Ceratophyllum demersum.(4)

Potametum lucentis is a community that develops in inshore part of the lake .Dominant species of this community are Potamogeton lucens and Ceratophyllum demersum while others are far less abundant(4).

Myriophyllo –Nupharetum lutei include species from Potamion association: Najas marina, Najas minor, Potamogeton perfoliatus, Potamogeton. crispus. It is characterized by presence of species Nuphar luteum,. This association inhabits colder water masses in littoral and are in contrast to association *Nymphoidetum peltatae* that inhabits wormer water masses of littoral (4)

Floating vegetation is also represented by the communities Nymphaeto-Nupharetum lutei Lakušić 1965 and Trapetum natantis T h. Mull. Et Gors. 60. Trapetum natantisi is largely widespread community in the Shkodra/SkadarLake. Water-nut developsits wide population and communities in the inner and deeper part of the floating macrophyta zones as a continuous belt connecting this zone with that of the submerged vegetation (4).

Between a large number of plant species it is necessary to make a selection of species that are considered «target species». Target species are defined the species which meet the one of the criteria of the Berne Convention. In the area of Skadar lake are 3 globally threatened species Trapa natans, Marsilea quadrifolia dhe Caldensia parnassifolia (3)

Matherial and Methods

Macrophytes integrate diverse ecosystem quality: temporal, spatial, chemical, physical, and biological qualities (6). The presence, distribution and abundance of macrophytes in a lake basin depends on many environmental parameters intrinsic to the basin(5)

We collected plant samples in 6 stations and we have determined in situ the pH, temperature, electrical conductivity with a Test Combo meter (Hanna Instrument). In the laboratory we have made the identification of collected samples using floras and keys of vascular plants . The samples collected are submited to the treatement for the determination of photosynthetic pigments.

For extraction we have taken the midsection of the leafs. Samples are placed in a PES filters to calculate the content of the pigments referred to the dry matter weight. As a solvent is used the acetone considered the most suitable for extraction in the case of tissue with high water content. Based on properties that have chlorophyll as volatile substances, all operations for the extractions are performed as soon as possible. During the work we have avoided the direct sun light. For each sample we determined the humidity to calculate the content of

pigments referred in mg / ml and in mg / g dry matter . Determination of pigment is made on the basis of non-destructive spectrophotometric method. Absorption spectra of chlorophyll a, chlorophyll b and carotenoids allow to determine the content of the pigments in the extract without preliminary separation at 663, 645.470 wavelengths. To determine the content of pigments are used Rebelen equations.(7)

Results and Discussion

In the collected samples we found:

Station Shkodra 1 Ceratophyllum demersum and Potamogeton perfoliatum. We found in Shiroke(Station 2) the species Vallisneria spiralis. We found Najas marina species in western and eastern shore Zogaj(Station 3), Vrake, Koplik(Station 4). We found Trapa natans in Shegan (Station 6) and Shiroke(Station 2).

It is a threatened species including the Convention Bernes.The content of photosynthetic pigments were higher in September than during October for the two shores of the lake.

Coordinates of Sampling Stations

Shkodra 1	42º 05',39"	N	19◦ 48' 13" E
Shiroke	42º 06' 03"	N	19◦ 44' 94" E
Zogaj	42 º 4' 19''	N	19◦ 26' 58'' E
Vrake	42 º 12' 07''	N	19◦ 47' 65" E
Koplik	42 º 18' 73"	N	19◦ 41' 50" E
Shegan	42º 27' 23"	N	19◦ 39' 35" E

For species Vallisneria spiralis the value of chlorophyll **a** (0.554mg / g) and carotenoids (0.201mg / g) resulted higher in September. Whereas the value of chlorophyll **b** resulted higher in October (0.174mg / g)(Fig 1,3). In the Najas marina species the highest value of chlorophyll **a** is determined in October (0.440mg / g), whereas the highest value of chlorophyll **b** is in September (0.141mg / g). In terms of sampling stations Najas marina founded in the eastern side of the lake (Vrake) has the value of chlorophyll **a** (0.440mg / g) highter compared to the west side of the lake. (Fig .1,2,3,4)

The values of pH are included in the interval (**7.86-8.56**) and the conductivity values are (0.14-0.19mS / cm).

West Coast(September 2013)

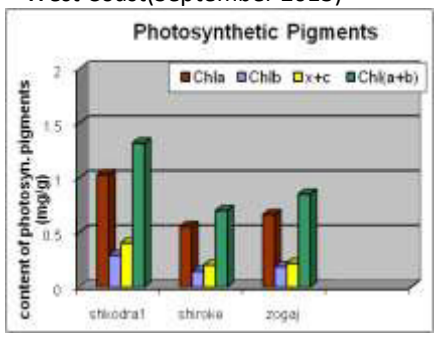


Fig .1

East Coast (September 2013)

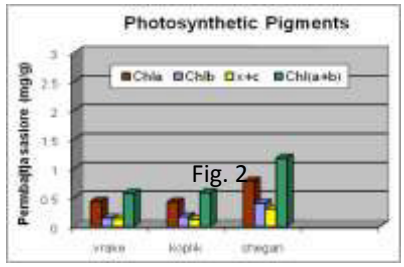


Fig. 2

West Coast (October 2013)

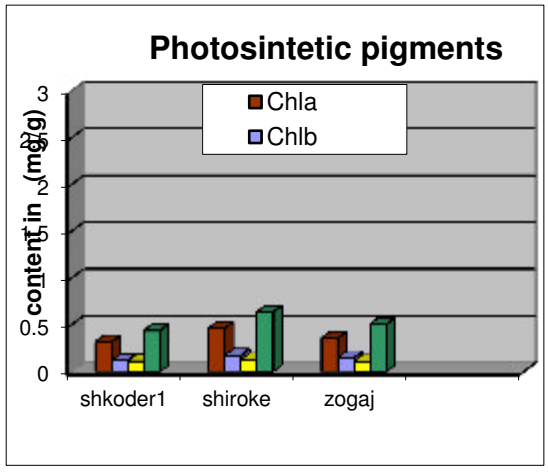
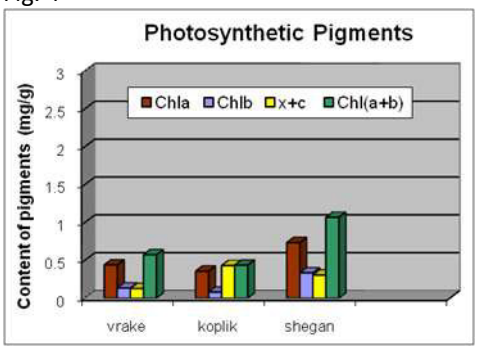


Fig .3

East Coast(October 2013)

Fig. 4



Conclusions

Species foundet in the sampling stations are part of the lake shore macrophyte associations and represent a significant part of the littoral system of lakes .

There is a diversity of species both in the western and eastern sides of the Skadar lake.

Trapa natans is an endangered species foundet on both coasts .

Two sides of the lake present different content of the photosynthetic pigments.

Najas marina species has the hightes values of the chlorophyll **a** in October whereas the hightest value of chlorophyll **b** is in September.The photosynthetic pigment values attributed to this species are higher on the **eastern side** (Vrake) than on **the western side** (Zogaj).

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THE IMPACT OF THE LOCAL MULTIPLE OF MEDIANS ON DETECTION AND FALSE POSITIV RATE OF FIRST-TRIMESTER PREGNANCY SCREENING FOR ANEUPLOIDIES

NDIKIMI I SHUMËFISHIT TË MEDIANES LOKALE NË SHKALLËN E DETEKTIMIT DHE FALS POZITIV NË TESTIN E TREMUJORIT TË PARË TË SHTATZËNISË PËR ANOMALI KROMOZOMIKE

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PËRMBLEDHJE
Testi i tremujorit I të shtatzënisë për rrezik trizomie 13, 18, 21 është jo-invaziv. Vlerësimi i saktë i rrezikut në tremujorin I kërkon një saktësi të Shumëfishit të Medianes(MoM) të korrigjuar me peshën e nënës për shënuesit gausian; Transparencën Nukale, Gonadotropina Korionike lirë-β, Proteina-A Plazmatike Shoqëruese e Shtatzënisë. Përdorimi i SHM lokale në kalkulatorin e rrezikut për trizomi në vend të vlerave përkatese të parazgjedhura nga programi i aparatit mundëson rillogaritjen e shkallës së detektimit dhe fals pozitiv bazuar në vlerat e korrigjuara me peshën të SHM. U krye rillogaritja e SHM për grupmoshe në kampionin prej 326 nëna shtatzëne me një fetus. Referencë sherbeu përfundimi i shtatzënisë dhe kariotipi. Nga përdorimi i SHM lokale 3 raste kaluan në zonën e rrezikut të lartë (cutoff 1:250) në atë të ulët. Përdorimi i SHM lokale përmirëson lehtësisht DR dhe FPR. Numër më i madh rastesh nevojiten për të konfirmuar rezultatet.
Fjalë çelës: MoM, T21, T18, PAPP-A, hCGβ.

SUMMARY
First trimester screening is a non-invasive risk calculation test for trisomy 13, 18, 21. Reliable risk calculation depends on good estimates of weight corrected multiple of medians (MoM) for markers as nuchal-translucency thickness, freeβ-human chorionic gonadotropin, Pregnancy-Associated Plasma Protein-A in maternal plasma. Using local MoM values in risk calculator instead of default values allowed us to recalculate the detection (DR) and false positive rate (FPR) and to compare it with the DR and FPR calculated by means of MoM default values of commercial program. Recalculation of local MoM for 326 women, singleton pregnancies, was carried out each age-group. Confirmation reference served birth outcome and karyotype data. At 1:250 risk cut off value, 3 cases moved from high to low risk zone using the local MoM. A slight improvement in DR and FPR was observed compared with the commercial program. Larger number of patients is needed to confirm the results.
KEY WORDS: MoM, T21, T18, PAPP-A, fhCGβ

INTRODUCTION

The screening for chromosomal aneuploidies during the first trimester of pregnancy has become a routine procedure in Albania by now. The risk calculation for chromosomal abnormalities during the first trimester screening is important for the overall population and pregnant women, firstly to avoid the invasive tests like chorionic villus sampling or amniocentesis, both carrying a risk for premature pregnancy termination, and secondly to help parents to take the right decision on the proper time. Freeβ-human Chorionic Gonadotropin (fhCGβ) and Pregnancy-Associated Plasma

Protein-A (PAPP-A) are two maternal plasmatic proteins and both serve as biochemical markers for the combined test. In combination with the third marker, nuchal-translucency thickness (NT), is possible by means of the risk calculator to assess the risk for aneuploidies (T21, T18 and T13).

We have been following in cooperation with several obstetric clinics all pregnant women sent by them to Intermedica bio-clinical laboratory since 2009. We have been reporting the results on our study periodically on both, the first and the second trimester screening. Based on the results of our prior studies[1,2] the Detection Rate (DR) of the first trimester screening, calculated with by default Multiple of Medians (MoM) of the commercial program for the first trimester screening were slightly different compared with the international experience[3,5,6,7,8] which can reach a DR=90% at FPR=5%. One of the reasons for these differences could have been the low number of cases in our first study, and the use of the default weight adjusted MoM values in the risk calculator instead of the local weight adjusted MoM. MoM weight corrected (MoMcor) values are a mandatory data item for the screening methods (Spencer *et al.,* 2003/a) [4]. A greater number of pregnant women with singleton pregnancy and the risk calculation based on the MoM weight adjusted Albanian values could lead to a better DR. The objective of this study is firstly to verify the capacity of the combined test in avoiding the invasive tests. This can be done through comparing the test risk assessment with the birth outcome or karyotyping results. Secondly, to verify the impact on DR and FPR of the risk assessments results calculated with the default MoM weight corrected values and Albanian ones.

METHODS AND MATERIALS

The inclusion criteria used to select the pregnant women are based on: age (18 years or older at enrollment), clinically confirmed cases with singleton pregnancy, gestational age>10weeks+0 days, planned or completed prenatal serum blood screening (blood drawn during first trimester within 24h from NT measurement), accessible pregnancy records and available for data collection, (ultrasound examinations, invasive prenatal procedures if performed, patient age and weight etc., through the compilation of an application-form prepared by the respective laboratory), no anamnesis for T21,T18 and T13, no smoker patients and Albanian women by origin. All pregnancy cases have decided by themselves to undergo the combined test for several reasons like age, prior miscarriages experiences without any specific reasons, and following their doctors advice. All blood samples are analyzed for maternal serum concentrations of two biochemical markers, fhCGβ and PAPP-A. The concentrations values of both biochemical markers are performed with COBAS6000 modular analyzer. All laboratory kits for both fhCGβ and PAPP-A are provided from ROCHE company. All calculation are done by means of EXCEL, MedCalc12 statistical software programs and the risk assessment for T21, T18 and T13 has been performed with risk assessment calculator of ssdlab5 statistical program. The reference standard confirmation for each case was birth outcome, karyotype data and in three cases the NIPT (non-invasive pregnancy test). All collected data are classified in excel spreadsheet with all detailed information per each case including age, weight, gestational age (expressed in days) biochemical markers concentrations (mIU/L), risk assessments for T21 and T18-13, CRL(mm) (crown-rump length) and MoM values for each marker. In order to respect confidentiality of the patient each patient has a code which corresponds with the number in the list and to first letters of name and surname. The log-linear method is used to calculate the national maternal weight adjusted MoM values[5]. Crude detection rates and false-positive rates were calculated based on the results of both (default and Albanian) risk assessments by means of null hypothesis and likelihood ratios.

RESULTS AND DISCUSSION

We have screened 514 pregnant women in Intermedica laboratory in Tirana, Albania from

November 2009. In our database are identified 326 singleton pregnancies that matches with our inclusive criteria and their actual status has been confirmed through pregnancy outcome or karyotype procedure.

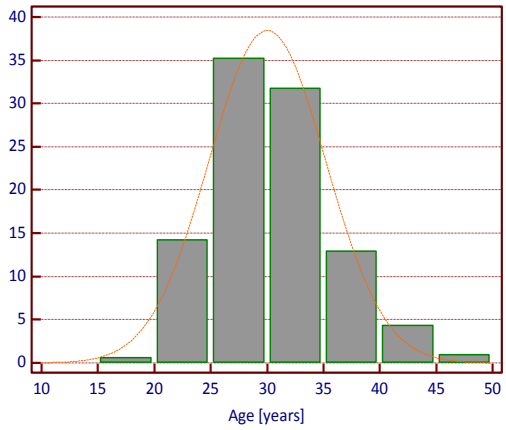

Figure 1 Distribution of maternal age

The overall age median is 29.5 years old (with CI 95% for the median from 29 to 30 years) with a range of age from 17 to 47 years old.

The figure 1 shows the maternal age distribution of 324 normal pregnancies. The dot line curve represents the normal distribution and the corresponding relative frequency of corresponding histogram class if the distribution was normal (Kolmogorov-Smirnov p=0.0024). The overall maternal weight median of 324 normal is 62kg (with CI 95% for the median 60 to 63kg) with a range from 42 to 106kg. The weight arithmetic mean is equal 62.61kg (with CI 95% 61.54 to 63.67kg).

All karyotype procedure are performed by analyzing the amniotic liquid. 188 pregnancies are not yet confirmed and are not considered in this study. Risk calculation were performed by means of default MoM values based on the gestational age (GA). The Albanian MoMcorr values for both fhCGβ and PAPP-A are calculated with log-linear method[9]. The weight adjustment reduces the population variability of the markers[10].

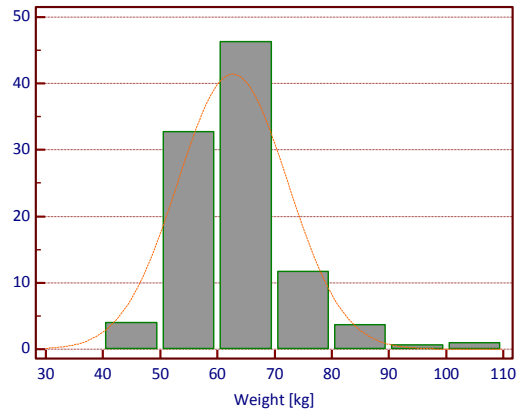

Figure 2 ***The maternal weight distribution***

The figure 2 shows the maternal weight distribution of 324 normal pregnancies. The dot line curve represents the normal distribution and the corresponding relative frequency of the corresponding histogram class of weight if the distribution was normal (Kolmogorov-Smirnov p=0.0025).

In the table 1 are presented the default median values of MoMcorr (MoMcorr-d) and the Albanian MoMcorr (MoMcorr-a) with 95% interval of confidence (CI) according to GA. Following the procedure proposed from Neveux at al[11] the median of MoMcorr values should be more or less 1.00. Both median fit nearly well with this procedure (the Albanian median of MoMcor is closer to 1.00 than that of default MoMcor for both biomarkers: median MoMcorPAPP-A-a=0.93 whether the median MoMcorPAPP-A-d=1.38, and median MoMcorfhCG-a=0.92 whether median MoMcorfhCGf-d=1.12 (95% CI). In 92% of the paired median values of the MoMcorrPAPP-A-a are lower than MoMcorrPAPP-A-d, and in 77% of the paired median values of MoMcorfhCG-a are lower than that of MoMcorfhCGf-d. The differences between the two medians are significant, two tailed probability for MoMcorfhCGβ is p=0.0295 and for MoMcorPAPP-A is p=0.002 (the Wilcoxon test for paired samples).

Table 1 The median MoM values with 95% of CI (default and Albanian)

GA [days]	MoMcor fhCGf-a	MoMcor fhCGf-d	MoMcor PAPPA-a	MoMcor PAPPA-d
77	0.90	1.12	0.86	1.32
78	0.88	1.12	0.87	1.36
84	0.95	1.17	0.90	1.40
85	1.32	0.96	0.90	1.18
86	1.03	1.46	0.90	1.19
87	0.67	0.90	1.09	1.02
89	0.89	0.87	0.96	1.53
90	0.96	1.08	1.00	1.52
91	0.84	1.24	0.93	1.41
92	0.92	1.26	0.91	1.38
93	0.87	0.76	0.87	1.11
94	0.98	1.05	1.00	1.34
95	0.96	1.38	0.96	1.40

The screening test results evidenced out of 326 cases 25 of them were positive for T21, T18 and T13 and 301 were true negative. The further procedures confirmed 2 true positive out of 25 positive cases T21 (23 cases were false positive. Both two T21 cases are detected from the combined test and were within the cutoff (1:250) high risk zone (1:69 and 1:5).

The variation of the median values of the table 1 has an impact on the final risk assessment when instead of default weight adjusted MoM values we use the Albanian ones. In the table 2 are presented the 25 positive risk assessment for T21, T18 and T13 calculated both with default (d) MoM and Albanian (a). The highlighted rows represents two confirmed cases with Down syndrome (T21) and the bolded rows represents the three false positive cases that moved from high risk zone, when calculated with default weight adjusted MoM, to low risk zone when calculated with Albanian weight adjusted MoM (from 1:200 to 1:880; 1:69 to 1:341 and 1:78 to 1:275). No similar changes of risk assessment were observed regarding the T18 and T13 FP cases.

The calculation of likelihood ratios when using default MoMcor gives the following results: sensitivity=100% (95% CI: 19.29% to 100%); specificity=92.9% (95% CI: 89.54 % to 95.45 %); disease prevalence=0.61% (95% CI: 0.09 % to 2.20 %); positive likelihood ratio=14.09 (95% CI: 9.50 to 20.89); positive predicted value=8% (95% CI: 1.22 % to 26.07 %); negative predicted value=100% (95% CI: 98.77 % to 100.00 %).

Table 2 Risk calculation (T21, T18, T13)

GA	T21-d	T21-a	T18-13-d	T18-13-a
77	1:14	1:40	1:8577	1:88180
78	1:69	1:10	1:105	1:102
78	1:97	1;138	1:3605	1:4653
84	1:49	1:53	1:2424	1:1613
85	1:200	1:880	1:100000	1:100000
86	1:71	1:258	1:23503	1:55594
87	1:68	1:82	1:28045	1:33296
88	1:109	1:99	1:88354	1:98065
88	1:76	1:196	1:100000	1:100000
89	1:79	1:98	1:100000	1:100000
89	1:234	1:203	1:89076	1:87054
89	1:128	1:97	1:5273	1:6023
90	1:111	1:10	1:58471	1:821
90	1:150	1:189	1:98700	1:78650
90	1:5	1:10	1:25	1:52
91	1:36	1:55	1:16681	1:100000
91	1:13	1:21	1:10040	1:14697
92	1:69	1:341	1:4134	1:28149
92	1:78	1:275	1:81825	1:100000
94	1:145	1:125	1:99804	1:98760
94	1:44	1:103	1:8065	1:5064
94	1:22	1:21	1:100000	1:11719
95	1:74	1:108	1:100000	1:100000
95	1:201	1:188	1:78043	1:100000

When using the local(Albanian) MoM's the sensitivity=100% (95% CI: 19.29% to 100%); specificity=93.83% (95% CI: 90.63 % to 96.19 %); positive likelihood ratio=16.20 (95% CI: 10.60 to

24.77); disease prevalence=0.61% (95% CI: 0.09 % to 2.20 %); positive predicted value=9.09% (95% CI: 1.38 % to 29.20 %); negative predicted value=100% (95% CI: 98.77 % to 100.00). The crude detection rate for the default MoM values is DR=93.52%, at the respective FPR=7.1%; for the local MoM values is DR=94.15%, at FPR=6.17%.

CONCLUSIONS

The results shows that there are differences between the likelihood ratios and FPR values between methods (default MoMcor and local MoMcor), meanwhile the differences between DR values are statistically negligible. The use of the local MoMcor improves the risk assessment by lowering the number of false positive cases (from 23 to 21; from 7.1% to 6.17%) but it didn't change the DR. Lowering the FPR value is very helpful for each individual risk assessment, because for each pregnant women that will screen for aneuploidies in the first trimester is important to have the best estimate of the risk for her. However, a larger number of patients may be is needed to confirm the results.

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COMPARATIVE STYDY OF SOME NEW LINES OE DRY BEANS

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SUMMARY
Bean planting's structure consists of varieties and land races, which are characterized by a long plant cycle. Consequently they are subject to high temperatures and water deficit stress, mainly during the reproductive stage producing low and unstable yields. In these conditions it is indispensable to renew bean's structure with new varieties with shorter plant cycle, which are less subject to the above mentioned stress. For this purpose, in ATTC Fushe Kruja, during 2008-2009, there were studied five new lines created by artificial hybridization in our country. The obtained data showed that three lines like: L3221, L232 and L545 achieved higher yield compared to the variety Shijak. This result is a consequence of their earlier flowering, which is mainly reflected in higher values of production per plant elements. To have them spread in the production it is necessary to first compare them in terms of demonstrative evidence in larger areas.
Key words: hybridization, population, plant's architecture, variety, linë

Introduction

In the climatic conditions of the last decades, bean plant's production has been dependent mainly on intensive flowering period of the varieties, where the production is determined by the first 20 days of flowering. Within this sub-period, the varieties with an intensive flowering in the first 12 days have the potential to provide 80% of the production, (3,5). This means that besides other aspects of improving the technology, it is necessary the replacement of old varieties with earlier ones, which even if they could have less capacity in production, they still guarantee a real higher sustainable yield.

Materials and methods

The experiment was established at the experimental field of ATTC Fushe-Kruja during 2008-2009. In the study included were 5 new lines created through artificial hybridization and the traditional variety Shijak one of the most cultivated in Albania. The experimental design was a randomized block design with three replicates. Each plot consisted of five rows, 5 m long at a distance of 0.5 m from each other. The distance between plants, within the rows, was 10 cm. The three central rows from each plot were harvested to determine seed yield, which was adjusted to 14% seed moisture content. Yield components were measured on a random sample of 10 plants per plot just previous to the final harvest. All traits were registered at maturity

Results and Discussion

According to the length of plant cycle our data showed that the lines and the variety in the study are divided into two groups. The first group includes lines with a cycle of 80-83 days and the second group includes the lines with a plant cycle of 86-89 days, such as Shijak and line 934. The longest cycle in this group result by the longest reproductive period. This fact has not affected the final production (table 1).

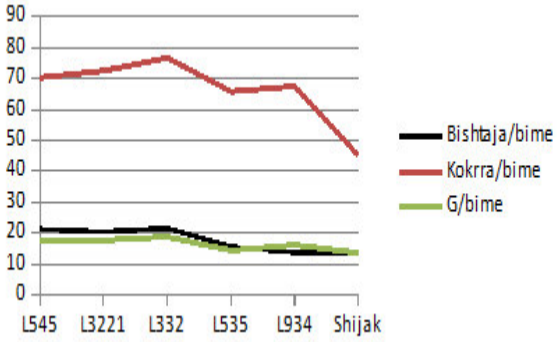
The results about production components showed the existence of differences between the genotypes studied. So, lines 545, 3221 and 232 in general have higher values of production elements per plant. Especially the number of grains per plant was almost double in the line L332 compared with the variety Shijak (Figure 1).

These differences were reflected also in the final production. The higher yields were obtained in above mentioned three lines. This result is mainly due to the higher number of pods per plant and grains per plant (Figure 1, and table 2).

Table 1. Plant cycle per day in beans' lines and populations (2 years average)

Lines and populations	Periods		Entire Plant Cycle, Germination-maturation
	Vegetative	Reproductive	
Shijak	37	52	89
L 535	37	46	83
L 545	35	45	80
L 3221	35	47	82
L 232	35	48	83
L 934	37	49	86

Figure 1. Productions element of lines involved in the study



Such phenomena can be explained by the rapid growth of these lines and by the short period of their massive flowering, which allows them to form more productive pods in the first flowering period, (3, 5). The period, 10-12 days of duration of this phase, is decisive for yield, because earlier pods, formed large number of grains pod-1. Comparing the average yields of lines in the two years of study we can observe significant differences between the years. The first experimental year (2008) was a typical stressed year for the dry bean plant. High temperature has accompanied entire plant cycle, especially during the reproductive phase of the plant growth. The temperatures over 38°C significantly affected the efficiency of the assimilates transport to the grains of the studied lines. Among the lines in the study, L- 232 has given about 0.36 tons ha-1 more than the traditional variety Shijak, while L- 3221 has given about 0.35 tons ha-1 more than Shijak. All lines, excluding L- 934, realized a significantly higher yield compared to the variety Shijak.

Table 2. Yield of the different lines and Shijak variety in the two years of the experiment.

Lines	Yield (ton ha^{-1})		Averagen yield in two years (ton ha^{-1})
	2008	2009	
Shijak	1.9	2.52	2.21
L 535	2.21	2.54	2.375
L 545	2.38	2.66	2.52
L 3221	2.33	2.78	2.555
L 232	2.47	2.87	2.575
L 934	2.14	2.55	2.345
D0.05	0.272	0.212	
D0.01	0.376	0.324	

Indeed, to assess production capacity should not consider only the level of production components expression and the length of the plant cycle The architectural construction of the plant is an important element that explain growth characteristics and physiological bases of production, (1, 4). From this viewpoint, lines 545, 3221 and 232 have a planofile placement of the leaves, compared to the other lines. This leaf structure limits their plant cycle duration and

theoretically it is decisive for inferior growth indicators in the reproductive phase, and at the same time, it limits their productive ability. On the other hand, the other lines have an erectofil construction of leaf structure, which gives them the opportunity to have a longer plant cycle, a prolonged assimilation of dry matter and a potential possibility for higher production. But in Mediterranean climatic conditions with high temperature and lack of rainfall during summer these lines and populations fail to create a surplus of assimilations and transport it to the reserve organs (2, 6). It is enough only for a prolonged and not efficient vegetation, which is manifested by issuing new leaves. This is the reason why in our climatic conditions, with the impact of the stress of high temperature during reproductive cycle, varieties and lines with longer plant cycle have smaller redistribution coefficient of dry matter than those with shorter plant cycle. Only thus we can explain that although the lines 545, 3221 and 232 have shorter active assimilation than other lines, they have a faster translocation and a higher coefficient of assimilations redistribution in favor of reserve organs.

Conclusions

1. The renewal of the variety structure of dry bean is a constant necessity, by introducing new varieties and lines with shorter plant cycle and intensive flowering in the first 12 days of this phase.
2. It should not just start from the elements of production to evaluate variety productive ability, but also from the structural construction of the plant closely related to the terrestrial climatic conditions of an area.
3. Lines 545, 3221 and 232 have given higher yield than other lines and the Shijak variety. Their introduction in the variety structure requires further experimental tests in demonstrative fields with larger surface.

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TEST WEIGHT, GRAIN YIELD AND PROTEIN HERITABILITY AND GENOTYPE X ENVIROMENT INTERAKTION OF DURUM WHEAT

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SUMMARY
The aim of this study was to investigate the genotype x environment interaction and heritability of grain yield, and to estimate the correlation among the yield and quality traits of durum wheat. Twelve durum wheat (Triticum durum) genotypes were grown in three consecutive planting seasons from 2008 to2010 according to a randomized complete block design four times replicated. The combined analyze of variance indicated that years and genotypes were significantly different for grain yield, protein content and test weight, while genotype x year interaction was insignificant only for test weight. Broad sense heritability of grain yield, protein content and test weight were 0.64, 0.68 and 0.32 respectively. Grain yield had a positive significant correlation (r = 0.38**) with thousand kernel weight, which had a significant correlation (r = 0.32**) with test weight. Protein content had negative significant correlation (r = - 23**) with grain yield and r == - 20* with thousand kernel weight.
Key words: heritability, correlation, test weight, protein, variance

Introduction

Test weight is used for classification of wheat. Expressed as weight per unit volume of grain, it is influenced more by the environment. (Ghaderi, A, and Everson E.H, 1971, George HL Heyne EG, and Walter TL., 1966, Budak, 2000). Environment and heritability are two factors that affect test weight, grain size and protein content. The influence of environmental impact can be different in different genotype (Ghaderi A, Everson E.H and Yamazaki W. and t. 1971 Heyn, EG and Walter, T. L, 1966). Lodging and delay in ripening grain weight reduce the test weight, the grains are numb and low rate of flour, too. (Weibel, R.O and Pendleton, J.W.,1964, Johnson, V.A., Biever, K.J ., 1966, Yamazaki, W. T, and Briggle, L.W., 1969). Therefore, in this point of view, it is important to study the genotype x environment interaction, based on test weight.

On the other hand, the wheat breeders, also, need to recognize the inheritance and correlations between test weight, grain production, yield traits and quality when the objective of breeding program is improvement of these features, etc. (Hyso, M., Kashta, F., 2000, Xhomo, A., Guga, E., 1984, Johnson, V. A, Biever, K.J, Haunold, A and Schmidt, J. W, 1966). The objective of our study was assessment of genotype x environment interaction, inheritance and correlations between test weight, grain production and protein content in some new wheat genotype.

Material and methods

In our study there were included 12 new durum wheat genotypes, created in recent years in our country. The study was conducted in 2007-2009 in the experimental field of the ATTC-Lushnje. The experiment was designed according a randomized block with three replications. Each treatment comprised 10 m^2 (2 x 5 m) for each replication. Inter row distances were kept 20 cm. In the three years of study days to flowering, 1000 grain weight, grain yield, expressed in g/plot, and test weight (kg/hl) were recorded. Protein content was determined with the Kjeldal

method (Nx5.7). The data obtained were processed according to known methods and statistical correlation analysis and coefficient of variation, was performed (Steel, R.G.D., and J.H.Torrie, 1980, Tartari T, 1988). Inheritance of traits studied, as test weight, grain production and protein content was assessed as the proportion of genotypic variance with phenotypic one. For the statistical elaboration of the data the analyses of variance was used for all the characters.

Tab 1 Analysis of variance for grain yield, protein content and test weight

Source of variance	DF	Grain yield	Protein content	Test weight
The general	107			
Repetition	2	9432**	0.52	8.12
Year	2	3417264**	3.14**	51.16**
Genotype	11	2268432**	4.12**	12.26*
Genotype x year	22	698458*	1.32**	9.31
Error	70	33219	0.43	6.14
Cv		8.38	4.98	2.76
Averages				
$D_{0.05}$		214.64	0.64	2.14
$D_{0.01}$		297.30	0.78	2.65

Results and Discussion

The combined analysis of variance shows that there are significant differences between the years of study and genotypes, for all the parameters studied, while the interaction genotype x year was significant only for production of grain and protein content (Table 2). This fact shows that there is variation in all traits between year and genotype. The fact that interaction genotype x year is significant for the yield and content of protein, indicate that the genotypes under our study behaves in different way during the three years of study. However, the relative magnitude of year, genotype and interaction genotype x year for all of the features was immense. This data show that the variation of study of yield and test weight are affected more by year than by genotype, while the variation of content protein, due to genotype was the height of it because of the year.

Coefficient of variation (CV) for grain production (8.38) was much higher than for the content of protein (4.98) and for test weight (2.76). This means that random environmental fluctuations cause a variation about three times larger for grain production and about 2 times larger for the production of protein, compared with that of test weight.

Tab 2. Grain yield, protein content and test weight in new genotypes of durum wheat

Lines in study	Grain yield (g $plot^{-1}$)				Protein content (%)				Test weight (kg hl^{-1})			
	2007	2008	2009	Average	2007	2008	2009	Average	2007	2008	2009	Average
Creso	4430	3650	5270	4420	13.99	13.43	12.57	13.33	79.6	79.5	84.2	81.1
Duro 46/Bp x Mesappia	3060	4160	4930	4050	14.48	13.28	13.76	13.84	78.8	80.0	84.3	81.0
Latino x QFN	4270	4090	5830	4730	12.96	12.73	13.42	13.03	79.6	79.1	85.0	81.2
Latino x Dyarbakir	32.10	39.10	49.70	4030	14.08	13.57	13.54	13.73	79.8	79.5	83.3	80.8
Gato299 x Latino	4220	4690	5260	4720	14.55	11.50	13.36	13.10	79.4	79.2	83.5	80.7
4022 x Agimi	39.20	3920	5620	4490	12.59	12.27	13.91	12.92	81.2	80.4	85.1	82.2
Lnbar x	3720	3380	4910	3850	15.49	13.64	13.86	14.33	78.5	80.7	84.3	81.2

Lara												
5/11-1 x Mus CD	4490	4580	5240	4770	15.29	14.96	13.35	14.53	80.8	79.7	85.3	81.9
Adamello x 5/11-1	4200	4720	5130	4680	14.20	12.81	15.25	13.18	81.2	80.6	84.5	82.1
Valforte x Dyarbakir	4110	4300	5230	4550	12.67	13.43	13.11	13.07	81.4	81.2	83.5	81.9
QFN x Creso	4220	4620	5460	4770	14.28	13.60	13.45	13.77	80.6	79.7	83.5	81.2
Ç178 x Salapia	3490	3590	5990	4360	15.20	12.27	13.49	13.65	79.8	81.2	85.1	82.0
Average	3900	4130	5320	4450	1413	13.10	13.36	13.53	80.1	80.1	84.3	81.5

Tab 3: Genotype components and phenotypic variance and heritage

Variances	Component of variance		
	Grain yield (g plot^{-1})	Protein content	Test weight (kg hl^{-1})
Genotype	154586	0.38	0.48
Genotype x Year	312104	0.51	1.43
Phenotypic	242613	0.56	1.51
Heritage	0.64	0.68	0.32

Tab 4. Coefficients of correlation between studied traits

Trait	Grain yield (g plot^{-1})	1000 Grain weight (g)	Protein content (%)	Vitreous grain	Test weight (kg hl^{-1})
Heading days	0.27*	0.12	0.26**	0.24**	0.26**
Grain yield (g/plot)		o.38**	-0.23**	-0.08	0.53**
1000 grain weight			-o.20*	-0.04	0.32**
Test weight				0.58**	-0.23**
Vitreous grain					0.11

From the data analysis of variance (Table 2), we can notice that lines 5/11-1 x Mus CD and QFN x Creso have higher grain yield per treatment (4770 g), while the line Inbar x Lara had the lower value (3850 **g**) for all of three years of study. In 2009 year, the yield is the highest (5320 g), while other two years had an average yield almost the same. The interspecific line, 4022 x Agimi had the lowest content of protein (12.92 %), while the line 5/11-1 x Mus CD had the highest one (14.53 %). Regarding the protein content, the values for the years 2008 and 2009, for all of the genotypes, present very small differences, but they are higher in 2009 for almost all of the genotypes studied. The test weight is above 80 kg hl^{-1} in most of the genotypes. This fact is explained by the negative impact of the conditions of the year, especially in the grain filling period. On the other hand, the highest yield achieved this year has been associated with higher test weight, due to the positive correlation between these two traits. Analyzing the component of genetic variation due to genotype, we can see that they are ½ and 1/3 of all of the variation, respectively, because of the interaction genotype x environment, for grain production and test weight. Heritage in broad terms, for grain production, protein content and test weight, were 0.64, 0.68 and 0.32 respectively. The heritage of the test weight was significantly lower than that cited by some other

authors. The above results indicate that the grain production and protein content are less affected by environmental factors, especially when the action of stress during grain filling phase is within the limits of elasticity. As mentioned above, grain production and protein content are more controlled by environment as compared to the test weight.

Analysis of correlation between the studied traits (Table 4), shows that there is significant correlation (r = 0:53 **) between grain production and test weight, which means that there are the same genes that control the above features. Grain production has also positive significant correlation with 1000 grain weight (r = 0.38 **), which in turn has a positive correlation with test weight (r = 0.32 **). This is an expected result, since the 1000 grain weight is the component of grain production. However, the weight of the grain is not direct component of test weight, while grain density, which is the direct component of its overall weight, is associated with the best grain weight (Yamazaki.W.T and Briggle,L.W., 1969). On the other hand, the protein content has significant negative correlation with the production of grain (r = -0.23 **) and 1000 grain weight (r = -0.20 *), but positively correlated with vitreous grain (r = 0:58 **). Based on all of the mentioned above, we can say that the selection for the 1000 grain weight and test weight, increases the yield, but reduces the protein content in grain. It must be emphasized that the time of heading is positive correlation with grain production (r = 0:27 *), protein content (r = 0:26 *), vitreous grain (r = 0:24 **) and testy weight (r = 0:26 **). So, as long as the period of germination-heading, are so high the value of the traits mentioned above.

Conclusions

* This data taken from our study, shows that the years and genotype have significant differences for all of the studied traits, and the variation due to the year condition, is higher than that between genotypes.

* The highest values of the coefficient of variation, compared to that of protein content and test weight, show that environmental changes affect more on grain production compared with the other two features.

* Components of variation due to genotype were larger than those of the interaction genotype x year, as well as for grain yield, and for test weight, too.

* Data taken tell us that there is a positive correlation between grain yield and test weight and simultaneously between these two features with the weight of 1000 grains. So we can conclude that selection based upon 1000 grain weight, and it test weight are associated with increased yield.

* Negative correlation between the protein content and grain yield and 1000 grain weight reduce the possibility of selection for increasing simultaneous of both two traits. Positive correlation between vitreous grain and protein content increases the protein contend, while work to select for high vitreous grain.

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THEORITICAL (DFT, B3LYP) AND EXPERIMENTAL STUDY OF SOME PYRIDINE DERIVATIVES FOR THE USE AS POTENTIAL INHIBITORS IN THE PROTECTION OF IRON AGAINST THE CORROSION

STUDIMI TEORIK (DFT, B3LYP) DHE EKSPERIMENTAL I DISA DERIVATEVE TË PIRIDINAVE PËR PËRDORIMIN E TYRE SI INHIBITORË POTENCIAL NË MBROJTJEN E HEKURIT NGA KORROZIONI

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PËRMBLEDHJE
Në studimin tonë si inhibitorë janë përdorur komponime heterociklike të klasës së piridinave - molekula organike që si heteroatom në strukturën e tyre përmbajnë atomin e azotit dhe të cilat posedojnë edhe substituente të tjera (atome halogjene, grupe amine apo metile). Pasi që metodat kompjuterike mundësojn kalkulimin e shpërndarjes së densitetit elektronik të molekulës, këto metoda japin të dhëna shumë të rëndësishme [HOMO - Highest Occupied Molecular Orbital dhe LUMO - Lowest Unoccupied Molecular Orbital, diferencën e energjisë HOMO-LUMO, momentin dipolar, etj] të cilat mund të shfrytëzohen në korrelimin e vetive të llogaritura në mënyrë teorike (Density Functional Theory - DFT, metoda me funksionalin Becke, 3 parametrik, Lee-Yang-Parr - B3LYP) me vlerat e llogaritura eksperimentale për molekulat e inhibitorëve. Eksperimentalisht studimi është kryer përmes matjeve potenciodinamike të cilat kanë mundësuar llogaritjen e përqindjës së inhibimit të korrozionit nga molekulat e tilla. Këto molekula shprehin efikasitet të lartë të inhibimit në mbrojtjen e hekurit nga korrozioni dhe se kalkulimet teorike mundësojn që të para-llogaritet sjellja e tyre në rritjen e këtij efikasiteti.
Fjalët çelës: llogaritje DFT, inhibitorë, piridinë, mbrojtje nga korrozioni.

SUMMARY
In our study as inhibitors were used various heterocyclic derivatives compounds of the pyridine class – organic molecules containing nitrogen atom and which possess other substituents (halogen atoms, amine or methyl groups). Because the computational methods allow the calculations of the electronic density distribution of the molecule, these methods provide important data [HOMO LUMO, the energy difference HOMO-LUMO, dipolar moment, volume of the molecule, etc.] which can be used in the correlation of the properties calculated theoretically (DFT, B3LYP) with those experimentally obtained values calculated for molecules as inhibitors. Experimental study was conducted through potentiodynamic measurements and classics weight loss tests which enabled the calculation of the corrosion inhibition percentage of the molecules. These molecules express high efficacy of the inhibition in the protection of iron against the corrosion and the theoretical calculations enabled the pre-calculation of their behavior in order to increase their efficiency.
Key words: DFT calculations, inhibitors, pyridine, protection against corrosion

INTRODUCTION

Iron and its alloys represent a most widely used materials in the construction (pipelines in the oil and gas industry, etc.). Even though they possess very desirable mechanical properties, the problem with such materials is their susceptibility to the corrosion [1]. In acidic aqueous media the iron is prone to react with acids and this

enhances greatly its corrosion rate. The poor resistance of this material in the aggressive media can be overcome by the use of different protection strategies such as: surface modification (through covalently bonded organic films from reduction of the diazonium salts [2] [3], phosphonic acids [4], silanes[5], carboxylic acids[6], etc.), the use of the corrosion inhibitors[7], etc. The protection of metals by the mean of the inhibitors is industrialized, so there is a huge number of organic molecules that are commercially available for this purpose and they include: carboxylic acids, quaternary ammonium salts, amines, alcohols, etc[7]. In general the common feature of these molecules is that they contain nitrogen, oxygen or sulfur atoms. Corrosion inhibition by different derivatives of pyridazinic[8],benzotriazole[9],
benzimidazoles[10] or other organic inhibitors[7] in most cases exhibits more than 90 % corrosion protection, this is comparable with the barrier effect of the grafted films created by reduction of the diazonium salts[2] [3]. The inhibition exhibited by those molecules is affected by their size, the electron density at donor atoms and the orbital distribution of the donating electrons[8][10].The usefulness of the quantum chemical methods have been proven as a tool that enables the possibility to determine molecular structures and furthermore to elucidate the electronic structure and the reactivity of molecules, giving a practical mean to design novel more efficient inhibitors[9-13].

EXPERIMENTAL

For electrochemical tests, the electrode was prepared by embedment of iron wire (d=2mm) inside a Teflon® tube by epoxy resin. The electrode surface before each measurement was polished with SiC paper wetted by aluminum oxide (particle size 0.6 micron) polishing suspension, then washed and cleaned ultrasonically in water.
Electrochemical test

The electrochemical studies were carried out with PalmSens potentiostat in a traditional three-electrode cell at 298K. A graphite tip and a saturated calomel electrode (SCE) were used as auxiliary and reference electrode, respectively. The potentiodynamic polarization curves were obtained ate least from −400 mV to + 400 mV versus Open Circuit Potential (EOCP) with a sweep rate of 1mVs−1. All experiments were performed under atmospheric conditions. Each experiment was repeated at least three times to check the reproducibility.

Computational details

The DFT calculations for the pyridine derivative molecules were accomplished by means of the Spartan®[14] software to analyze the structural and electronic parameters; the structures were fully optimized. The Becke's three-parameter hybrid functional (B3LYP)[15][16] method in combination with the B3LYP/6-31G(d,p) basis set has been chosen for calculations. Molecular parameters like the electronegativity, global hardness and softness, electron affinity and ionization potential may well be defined in relationships of the energy of the HOMO and the LUMO can be calculated, in reproducible manner by this DFT/B3LYP method[14][16].The electronegativity (X) is the amount of the power of an electron or group of atoms to attract electrons towards itself[17] (Equation 1).

$$X \approx -1/2(E_{HOMO}+E_{LUMO}) \quad \text{(Equation 1)}$$

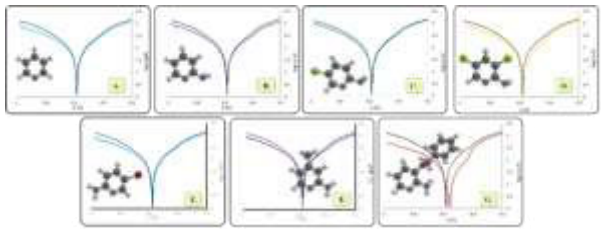

Figure. 1. Polarization curve and corrospondin inhibition efficiencies (IE in %) for mild steel in 0. 1 M H3PO4 in the presence (line) and absence of: A. Pyridine (IE=6.65 %) , B.pyridin-2-amine

(IE=8.80 %), C. 4-methyl-pyridin-2-amine (IE=22.46 %), D. 5-bromopyridin-2-amine (IE=10.71%), E. 5-chloropyridin-2-amine (IE=12.91%), F. 3,5-dichloropyridin-2-amine (IE=24.14%), G. 3-(benzyloxy)-pyridin-2-amine (IE=54.29%) (dashed line) at scan rate of 1 mV/s (measured at 25°C).

Chemical hardness (η) is the amount of the resistance of an atom to a charge transfer (Equation 2).

$$\eta \approx -1/2(E_{HOMO}-E_{LUMO}) \quad \text{(Equation 2)}$$

Chemical softness (σ) is the measure of the capacity of an atom or group of atoms to receive electrons[18] (Equation 3).

$$\sigma \approx 1/\eta = 1/2(E_{HOMO}-E_{LUMO}) \quad \text{(Equation 3)}$$

Ionization potential (I) is defined as the amount of energy required to remove an electron from a molecule (Equation 4)[19], while the electron affinity (A) is defined as the energy released when a proton is added to a system[20].

$$I \approx -E_{HOMO} \text{ and } A \approx -E_{LUMO} \quad \text{(Equation 4)}$$

The testing of the correlation between the calculated quantum parameters and practically found inhibition efficiencies was done through the use of Statistica software[21].

RESULTS AND DISCUSSION

In the Figure 1. are presented the anodic and cathodic polarization curves of mild steel electrode in aqueous 0.1 M H_3PO_4 in the absence and presence of various pyridine derivatives electrochemical parameters, such as corrosion potential (Ecorr) and corrosion current density difference between the EHOMO and the ELUMO values.

The IE (%) was calculated using the following equation:

$$IE(\%) = [I_{corr(abs.in)} - I_{corr(pres.in)}]/[I_{corr(abs.in)}] * 100$$

In all of pyridine derivatives (Figure. 2) the HOMO orbital has the highest distribution on the N, which implies that this is the regions of the molecule with the highest tendency to donate electrons. (Icorr) were calculated from the intersection of anodic and cathodic Tafel slopes and are shown in the Table 1. together quantum parameter We have calculated also the molecular volume (MV) of three studied compounds.

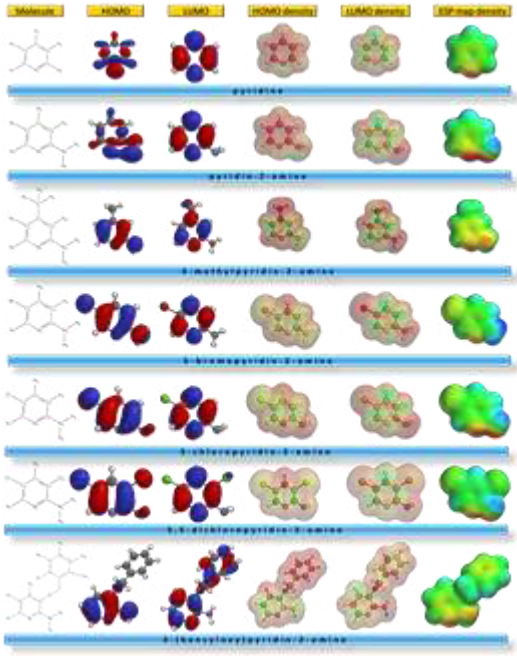

Figure. 2. Optimized structures, HOMO, HOMO density, LUMO and LUMO density's for the studied pyridine derivatives. (B3LYP/6-31G (d,p) results in vacuo).

Molecular volume governs the surface coverage of the inhibitor on the metal surface. The compound that would have the highest surface coverage of the metal typically corresponds to that with greatest inhibition efficiency. This is evident when we analyze the correlation coefficient in the Table 1. Furthermore, because all the pyridine derivatives have their highest electronic distribution at the region of heterocyclic nitrogen atom (see the ESP map in Figure 2.), this means that the mechanism of the adsorption of all the studied pyridine derivatives remain the same. This gives importance directly to the molecular volume, CPK surface and ovality

of in the inhibition process (Table 1.).The energy difference between the EHOMO and the ELUMO, ΔE, tells about the reactivity of the molecule towards other chemical species. The molecule with the lowest ΔE value has the highest tendency towards reactivity and would favorably interact with the metal surface. This is in very good agreement with the experimentaly found values. According to hard-soft-acid-base (HSAB) theory, soft acids interact preferentially with soft bases and hard ones with hard bases. Metals are generally considered to be soft acid, therefore they would preferentially interact with inhibitors that have high σ values and low η values, this is again what we found (correlation coefficient +0.8431 σ and -0.7921 η) when analyzing values in the Table. 1

Table. 1. The correlation between the calculated quantum paramters with the practically found inhibition efficiencies.

CONCLUSIONS

The inhibition efficiency of the 2-amino-pyridine derivatives has been investigated by experimental techniques and quantum chemical approaches. Potentiodynamic measurements put in evidence the inhibitor properties of these pyridine derivatives toward ion corrosion in aqueous acid medium. The quantum chemical calculations revealed information about the active centers (of the compounds) which would likely interact with the metal surface. Experimental and theoretical results show that the inhibition efficiencies are highest for pyridine systems that contain extra rings and halogen atoms.

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EVALUATION OF ENTRANCE SURFACE DOSE ON PATIENTS IN RADIOLOGY

VLERËSIMI I DOZËS HYRËSE SIPËRFAQËSORE TE PACIENTËT NË RADIOLOGJI

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PËRMBLEDHJE
Për të bërë llogaritjen e dozës hyrëse në sipërfaqen e trupit të pacientit përdoren disa modele, te cilët bazohen në parametrat dhe madhësitë karakteristike që vlerësojnë procesin e ekspozimeve të pacientëve me anë të pajisjeve radiologjike, siç janë: tensioni në kV, që zbatohet në gypin e rrezeve X, largësia prej vatrës së burimit deri tek sipërfaqja e trupit të pacientit, largësia nga vatra gjer tek filmi, ekspozimi që zbatohet në mAs, faktori i shpërhapjes, e të tjera. Ky studim ka për qëllim të vlerësojë dozën hyrëse sipërfaqësore të pacientëve në radiologji përmes përdorimit të dy modeleve. Nga përfundimet e përftuara vërejtëm se këto modele dhanë rezultate që justifikojnë matjet e drejtpërdrejta që janë kryer me anë të detektorëve termolumineshentë (TLD). Sipas modelit Faulkner, vlera e llogaritur e dozës hyrëse sipërfaqësore (DHS) për një lloj ekzaminimi është 0,61 mGy, ndërsa për të njëjtin ekzaminim, vlera e saj e matur drejtpërdrejtë me TLD është 0.69 mGy. Sipas modelit Tong dhe Tsai, vlera e llogaritur e dozës hyrëse sipërfaqësore për një lloj ekzaminimi është 0,35 mGy, ndërsa për të njëjtin ekzaminim, vlera e saj e matur drejtpërdrejtë me TLD është 0.36 mGy.
Fjalët çelës: ekspozimi i pacientit, doza e hyrjes sipërfaqësore, TLD

SUMMARY
To evaluate the entrance dose in the patient's body surface several models are used, which are based on the characteristic parameters that describe the process of exposure to patients by radiological equipment, such as: voltage in kV that is applied to the X-ray tube, the distance from the focus of the source to the surface of the patient's body, the distance from focus to the film, exposure expressed in mAs, backscatter factor, etc. This study aims to evaluate the entrance surface dose on patients in radiology, through the use of two models. From the results obtained, we noted that these models gave results that justify direct measurements that were performed by thermoluminescent detectors (TLD). According to Faulkner model, the calculated values of entrance surface dose (ESD) for a kind of examination is 0.61 mGy, while for the same examination, its value measured directly with TLD is 0.69 mGy. According to Tong and Tsai model, the estimated value of entrance surface dose for a kind of examination is 0.35 mGy, while for the same examination, its value measured directly with TLD is 0.36 mGy.
Key words: patient exposure, entrance surface dose, TLD

INTRODUCTION

X-ray examinations in health care become the largest source of exposure for the population. Measurements of patient entrance surface dose provide valuable data for radiation protection of patients on radiographic X-ray equipment. The entrance skin dose (ESD) for patients undergoing diagnostic X-ray examinations is a measure of the

radiation dose absorbed by the skin where the X-ray beam enters in the patient. In radiological exposure a periodic dose assessment should be done to enhance the optimization of the radiation protection of the patients and to deliver minimum dose during the examinations. The need for standardization of medical exposure has been supported through different recommendations on the guidance levels for various radiographic examinations, by international organizations. Usually the patient doses have been evaluated by calculations based on radiographic conditions, or using model based on several assumptions. Direct measurement of patient dose or entrance surface dose is difficult to perform in many patients due to its time requirement; however, such direct measurement is essential since it incorporates all aspects of radiography from the radiographic equipment used, to the conditions of each patient. In this paper we evaluated the entrance surface dose of X-ray on patients exposed to radiological examinations. This assessment is performed by the two models. In accordance with the requirements arising from these two models, we have done dosimetric measurements by thermo-luminescent detectors (TLD) evaluated backscatter and incident doses. We carry out two series of measurements, performed at two medical centers: Regional Hospital of Prizren and Radiological Specialist Ordinance "Imazheria" in Rahovec. For readings the TLD detectors we used the Thermo Scientific system HARSHAW 4500, at the Institute of Applied Nuclear Physics in Tirana.

METHODS AND MATERIALS

For the assessment of entrance surface dose, TLD measurements procedure requires to consider all technical characteristics of radiation device: volt-ampere curve, exposure from X-rays tube, and filtering of the radiation sources. Each thermoluminescent dosimeter (TLD) contains two crystals. Two TLD are located within radiation beam in front of and behind the patient, but without interfering the appearance of the body, whose image is required in radiography. Another TLD is located at the side, out of the beam in 1.0 meter distance from the center of the beam, in order to measure and evaluate backscattered dose. To carry out measurement for the two models, for each type of examination, dosimeters were exposed even without the presence of the patient, at a distance one meter in the center of the X-ray beam. The exposure of dosimeters is done at the same parameters (mAs, kV, etc.) as they were used in corresponding examination with the presence of the patient. In the situation of exposure without the presence of the patient, we executed two exposures. In the situation that the dosimeters are exposure with the presence of the patient, for efficiently reading, dosimeters were held in those positions to 10 exposures on different patients for the same examination. The following figure shows the ways of placing the dosimeters and characteristic distances used during measurement process for evaluating entrance surface dose at radiological examinations.

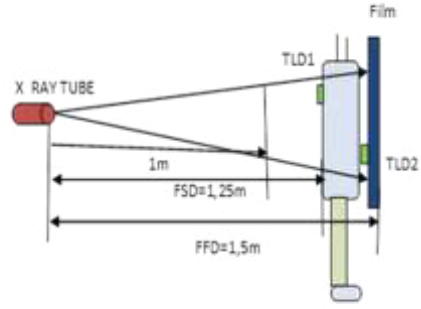

Figure 1. Measurement in presence of patient

RESULTS AND DISCUSSION

For the evaluation of entrance radiation dose on the patient's body surface, we used two models [1]. These are models based on physical characteristic parameters and geometric sizes of which depend on the process of patient exposures from radiological equipment. These are: voltage (kV) applied to the X-ray tube, the focal distance of the source to the patient's body

surface (Focus-Skin Distance), distance from the focus to the film (Focus-Film Distance), applicable exposure (expressed in mAs), Backscatter factor, and others. After calculations, we noted that these models justify direct measurements that were carried out by the thermoluminescent detectors.

Faulkner Model: According to this model the entrance surface dose (ESD) can be estimated by knowing the exposure that gives X-rays tube at 1 meter distance from the source (Tube Output) expressed in unit (mGy/mAs), in the center of the beam. This exposure should be done by using the exposure value 10 mAs and voltage 80kV [2]. Also, in this model, is the value of exposure that is used to the respective exposure of the patient (mAs), which represents the production of current (mA) and the time of exposure (sec), focal distance from the beam up to the patient's body surface (FSD) and the backscatter factor (BSF). The formula of this method is:

$$ESD = TubeOutput\left(\frac{mGy}{mAs}\right)_{1m} \times \left(\frac{kV}{80}\right)^2 \times \left(\frac{100}{FSD}\right)^2 \times \frac{mAs}{BSF}$$

The value of exposure that X-rays tube gave at 1 meter distance, in the center of the beam, in the case of relevant exposure is: Tube Output = 0.88 mGy/10mAs. The average voltage that was used by 10 exposures to different patients, has the value U = 72.5 kV. The average value of exposure of patients from 10 different exposures is 16 mAs. Backscatter factor should be taken BSF = 1.2. Distance from focus of beam to the patient's body surface is FSD = 125 cm. These values are used to calculate ESD:

$$ESD = 0{,}88\frac{mGy}{10mAs} \times \left(\frac{72{,}5kV}{80kV}\right)^2 \times \left(\frac{100}{125}\right)^2 \times \frac{16mAs}{1{,}2}$$

After calculating, the value of the entrance surface dose estimated according to Faulkner model is: ESD = 0.61mGy. Direct measurements with TLD crystals, for this exposure, after reading in the HARSHAW 4500 system, showed the value of entrance dose **ESD** = 0.69 mGy, which is close to the value calculated by the model.

Tong and Tsai Model: This model suggests that the entrance surface doses to be proportional to the production of free air exposure (FAE) with the ratio between the absorption coefficients of biological tissue and air and backscatter factor [3]. The formula proposed by Tong and Tsai is:

$$\text{ESD} = \text{FAE} \times 0.00877\left(\frac{\text{mGy}}{\text{mR}}\right) \text{x} \left(\frac{\frac{\mu}{\rho}tissue}{\frac{\mu}{\rho}air}\right) \text{x BSF}$$

The value of exposure of air from the tube, without the presence of the patient at 1.5 m distance is FAE = 0.28 mGy. The ratio between the absorption coefficients of biological tissue and air is 1.06 for all energies that are used in radiography [4]. The value $0.00877\left(\frac{mGy}{mR}\right)$ is the coefficient used to convert the dose from the unit mR into mGy, because 1mR = 0.00877 mGy. Backscatter factor should be taken BSF = 1.2. These values are placed on the formula above:

$$ESD = 0{,}28mGy \times 0{,}00877 \times \frac{mGy}{0{,}00877mGy} \times 1{,}06 \times 1{,}2$$

After calculating, the value of entrance surface dose is: ESD = 0.35 mGy. Direct measurements with TLD for this kind of exposure showed the entrance dose value ESD = 0.36 mGy, which is nearly equal to the value calculated by the Tong and Tsai model.

Even in the second series of measurements, after we read the values of TLD's, through the same procedure, we did entrance surface dose assessment. The second set of measurements was performed with TLD for the same type of examination (CHEST-PA) but with other radiological equipment. We did again the Entrance Surface Dose assessment according to two selected models. Following tables present the results of all measurements and readings.

Table 1 Results of measurements and readings in the Regional Hospital of Prizren

TLD	Position	Electric charge (nC)	Dose (mGy/1 exposure)	ESD level by IAEA [6]
TLD-1	At the entrance of patient`s body	12.24 nC	0.33 mGy	0,4 mGy
TLD-2	At the exit of the patient`s body	1.68 nC	0.05 mGy	
TLD-3	Lateral (1.0 m from the center of the beam)	0.56 nC	0.015 mGy	

TLD	Position	Electric charge (nC)	Dose (mGy/1 exposure)	ESD level by IAEA
TLD-1	At the entrance of patient`s body	13,39 nC	0,36 mGy	0,4 mGy
TLD-2	At dhe exit of the patient`s body	1,46 nC	0,04 mGy	
TLD-3	Lateral (1.0 m from the center of the beam)	0,75 nC	0,02 mGy	

Table 2 Results of measurements and readings in SRO " IMAZHERIA", Rahovec

Series of measurements	ESD by TLD readings	ESD calculated by Faulkner model	ESD calculated by Tong and Tsai model
First	0,69 mGy	0,61mGy	////////// ////////// /
Second	0,36 mGy	////////////// //////	0,35 mGy
Second	0,20 mGy	0,25 mGy	0,18 mGy

Table 3 Summary of Results by TLD readings and assessments by models

CONCLUSIONS

In diagnostic radiology measurement of the delivered dose is very important to minimize unnecessary exposure. Evaluation of entrance spin dose (ESD) in patients during diagnostic examination in radiography from direct measurements with TLD and according to two models, shows that the values calculated by the models are within the limit levels recommended by many international organizations [7]. According to the first model, the calculated value of entrance surface dose was 0.61 mGy, while direct measurements value with TLD was 0.69 mGy. Namely, the value calculated by the Faulkner model, is not off limits of deviation comparing practically measured value with TLD. According to the second model, the calculated value of the entrance surface dose turned out 0.35 mGy, which is also very close to the value direct measured value with TLD, which was 0,36 mGy. Even in the second series of measurements, the results of using these two models, the results of direct measurements with TLD were very close to each other.

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GRAPHITE DECORATED WITH COPPER/COPPER OXIDE NANOPARTICLES AS AN AMPEROMETRIC SENSOR FOR PHENOLS

GRAFITI I DEKORUAR ME NANOGRIMCA BAKËR/OKSID BAKRI SI SENSOR AMPEROMETRIK PËR FENOLE

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PËRMBLEDHJE

Nanogrimcat Bakër/Okside bakri (CuNPs) i kemi përdorur si modifikues të elektrodës me pastë karboni (CPE) për përcaktim të komponimeve fenolike. Për shkak të rëndësisë që ka, objektiv i kësaj pune ka qenë hulumtimi në përcaktimin e komponimeve të ndryshme fenolike duke përdorur elektrodën me pastë karboni. Grafiti i dekoruar me nanogrimca bakër/okside bakri është përgatitur duke e nxehur në atmosferë inerte përzierjen e thate tëgrafitit dhe acetatit të bakrit. Mekanizmi i reaksionit të fenolit në electrode është studiuar duke aplikuar voltametrinë ciklike dhe amperometrinë hidrodinamike në tretësirë të buferit fosfat 0.1 M (pH 7.5). Me anë të amperometrisë hidrodinamike është krahasuar përgjigjja ndaj fenolit e elektrodës me pastë karboni të dekoruar dhe elektrodës së pa modifikuar si dhe të modifikuar në brendi me bakër dhe okside të tij.Mënyra e thjeshtë e modifikimit të grafitit jep shpresë në përcaktimin e komponimeve fenolike në potencial të aplikuar më të vogël. Raporti i nanogrimcave të bakrit ndaj grafitit dhe potenciali i aplikuar në sensor janë optimizuar për një përgjigjje më të mirë të sensorit.
Fjalët çelës: sensor, pastë karboni, fenol, oksid bakri, nanogrimca.

SUMMARY

Copper/copper oxides nanoparticles (CuNPs) were used as modifier of the carbon paste electrode (CPE) for the detection of phenol compounds. Due to its importance, the objective of this work was investigation on detection of different phenolic compounds with carbon paste electrode. Graphite decorated with copper oxides nanoparticles was prepared by heating in inert atmosphere of dry mixture containing graphite and copper acetate. The reaction mechanism of phenol on electrode was studied using cyclic voltammetry and hydrodynamic amperometry in phosphate buffer solution 0.1 M (pH 7.5). Decorated carbon paste electrode response to phenol is compared with unmodified carbon paste electrode and bulk modified CPE with copper and copper (II) oxide in hydrodynamic amperometry. The easy way of graphite modification is promising for the determination of phenolic compounds in lower operating potential. Ratio of copper nanoparticles to graphite and working potential of sensor was optimized for better response to phenolic compounds.
Key-words: sensor, carbon paste, phenol, copper oxide, nanoparticles

1. Introduction

Phenol compounds such as chlorinated phenols and related aromatic compounds are known as widespread components of industrial waste. Phenols are one of the major and persistent pollutants of the environment. They are considered as primarily pollutant components in wastewater due to their high toxicity, high oxygen demand and low biodegradability [3,6-8]. There have been lots of methods reported on the determination of phenols, namely colorimetry, gas chromatography, high-pressure liquid chromatography (HPLC), spectrophotometry, biosensor-based method, capillary electrophoretic method and electrochemical methods. Among them, conventional colorimetry and spectrophotometry are easily disturbed by the colors of detected components. Gas chromatography usually takes a long time to make previous separation, while HPLC needs the preparation of flow phase, which will consume lots of organic solvent and may cause new environmental pollutants. Capillary electrophoretic method has the high detection limits. Compared to methods mentioned above, electrochemical technique has attracted considerable interest due to its suppleness, convenience and low cost [4]. In terms of phenols and related compounds, waste treatment and detection are two major research directions. In both fields electrochemical methods are of prime importance [1-3,5,7,8,11,12]. These methods are based on the direct oxidation or reduction of substrate onto an electrode surface. Carbon paste electrodes (CPE) are widely used as the working electrode because it shows high stability and precise in detection. But the demerit of low sensitivity gives the CPE limitation in practice. In order to enhance the electrochemical response, great efforts have been made on CPE. One of the effective steps was the treatment of modification. The CPE was bulk and surface modified with some kinds of materials that were more sensitive to phenols, by which the reaction currents were enhanced and the detection sensitivity was improved [9,10,13]. However, the modified electrode also has some disadvantages: first, the preparation of modified electrode is not convenient and sometimes might be complicated; second, the dressing agent might flake off and the modified electrode can easily fouled, which would lower the reproducibility in detection. This paper suggested a simple and convenient method to improve the detection sensitivity of the CPE without reducing its stability. By using Copper/copper oxides nanoparticles (Cu/CuONPs) as modifier of the carbon paste electrode (CPE) [9] we investigate enhance in responses and behavior of hydroquinone, phenol, toluhydroquinone and 2,5-dihydroxybenzoic acid with electro-analytical techniques. Results obtained with this sensor were compared with unmodified carbon paste electrode and bulk modified CPE with copper (II) oxide in hydrodynamic amperometry measurements.

2. Experimntal

2.1. Reagents

All chemicals used were p.a. grade, hydroquinone, phenol, 2,5-dihydroxybenzoic acid and graphite powder (<20 μm, synthetic) were obtained from Sigma Aldrich. Toluhydroquinone, copper (II) oxide and copper (II) acetate were supplied by Fluka and paraffin oil by Merck. Phosphate buffer solution 0.1M (pH = 7.5) was prepared from sodium dihydrogen phosphate dihydrate and di-sodium hydrogen phosphate dodecahydrate, obtained from Lachner. Phenolic compounds solutions were prepared in Phosphate buffer solution (pH = 7.5). Redistilled water was used for preparing solutions.

2.2. Apparatus

Voltammetric experiments and amperometric measurements were performed with PalmSens controlled by a computer PSTrace Software,. A three electrode system was used, where an Ag/AgCl (Metrohm 6.0733.100) electrode served as the reference electrode, a platinum wire electrode served as the auxiliary electrode and a CPE, a CPE-CuO or a CPE-Cu/CuONPs served as

the working electrode. All potentials reported were versus the Ag/AgCl 3M KCl electrode. Nitrogen was used for degassing the solutions. A magnetic stirrer provided convection of the solution.

2.3. Electrode preparation

The carbon paste electrode (CPE) was prepared by hand-mixing graphite powder and paraffin oil with a ratio around 70/30 (w/w). The CPE-CuO 5% (containing 5% CuO in mass of graphite) was prepared by mixing and homogenized copper (II) oxide 0.629 mmol and graphite powder 0.950 g and then mixing with paraffin oil in a ratio 70/30 (w/w). Also CPE-Cu/CuONPs 5% (containing 5% Cu/CuONPs in mass of graphite) was prepared by mixing and homogenized copper (II) acetat 0.629 mmol and graphite powder 0.950 g and heating at 250^{o}C for 4h and then mixing with paraffin oil in a ratio of 70/30 (w/w). The prepared pastes were packed into the cavity of a Teflon tube (4 mm diameter). A new surface was obtained by smoothing the electrode onto a Teflon plate. An electrical contact was established to interconnect electrode surface and potentiostat via a copper wire.

3. Results and discussion

Voltametric methods were used to characterize the electrochemical behavior of modifier on carbon paste electrodes for phenolic compounds detection. The investigation was focused on response of unmodified (CPE) and modified carbon paste electrodes in phenolic compounds, such as: Hydroquinone (HQ), phenol, toluhydroquinone (THQ) and 2,5-dihydroxybenzoic acid (DHBA).

3.1. Cyclic voltammetry

Cyclic voltammogras in figure 3.1. shows the voltamograms of unmodified carbon paste electrode. The electrode response to hydroquinone (30 mg/L) is evidently with oxidation and reduction potential around 0.25 V respectively 0.05 V. Modified electrode with copper/copper oxide nanoparticles Cu/CuONPs (figure 3.2) shows a bit different picture because background currents are higher and oxidation and reduction peaks are not well shown. The oxidation of metallic copper around 0 volt is happened and its back reduction near -0.30 V. After addition of 30 mg/L hydroquinone the peaks are overlapped because except electrochemical reduction the chemical reaction is happened between hydroquinone and Cu/CuONPs. The oxidation and reduction peaks of copper and hydroquinone appear very close to each other and peaks are not well defined

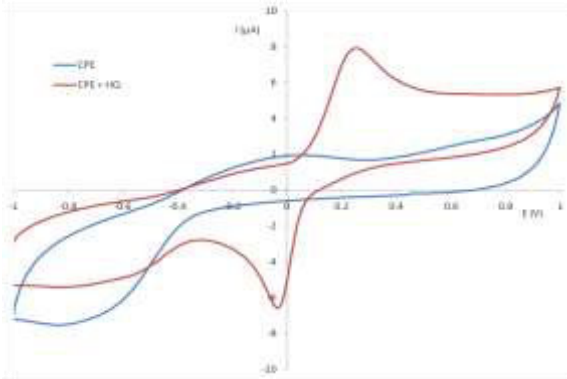

Figure 3.1. Cyclic voltammogram with CPE as working electrode in (–) phosphate buffer solution 0.1 M pH 7.5 and in (–) hydroquinone solution with concetration of 30 mg/L. Potential -1 V – 1 V vs. Ag/AgCl., scan rate 50 mV/s.

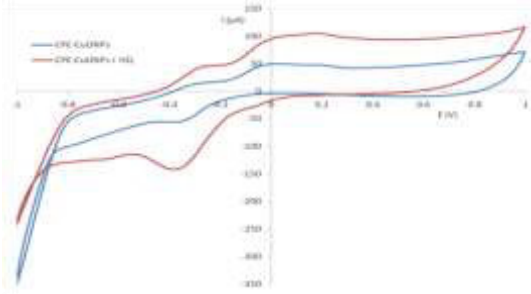

Figure 3. 2. Cyclic voltammogram with CPE-CuONP as working electrode in (–) phosphate buffer solution 0.1 M pH 7.5 and in (–) hydroquinone solution with concetration of 30 mg/L. Potential -1 V – 1 V vs. Ag/AgCl., scan rate 50 mV/s.

3.2. Hydrodynamic amperometry

For quantification of aforementioned phenols we performed measurements in hydrodynamic amperometry using CPE, CPE-CuO 5% and CPE-Cu/CuONPs 5% as working electrodes. Modified electrodes were tested in different operating potential from -400 mV to +400 mV, for response to hydroquinone (not shown here) and chosen potential was 200 mV. In this operating potential electrode shows a good repeatability during measurements and the signal was higher compared to other operating potential. In more positive potential exist the risk of copper dissolution and the electrode response will change during every measurement. In figure 3.3 are shown results with three electrodes in different concentration of hydroquinone in phosphate buffer solution 0.1 M (pH 7.5). From these results it is obvious that better signals were obtained in case of copper/copper oxides modified carbon paste electrode (CPE-Cu/CuONPs 5%) when it is used as working electrode. Also, amperometric measurements have been performed with modified CPE with different amount of Cu/CuONPs in mass of graphite. In continuo, with this working electrode have been performed amperometric measurements in quantification of phenol, toluhydroquinone and 2,5-dihydroxybenzoic acid. Better results were obtained for hyhroquinone and toluhydroquinone, also registered signals were approximately and significantly higher than signals of phenol and 2,5-dihydroxybenzoic acid (figure 3.4). A quasi-linear relation between concentration and signal could be obtained for hydroquinone concentrations up to 80 mg/L with a sensitivity 0.131 μA $L \cdot mg^{-1}$ and a correlation factor R^2 = 0.994 with operating potential 200mV mV(Figure 3.5). Sensor shows good stability after 10 cyces in cyclic voltammetry.

$$I(\mu A)=0.131\ C(mg/L)+0.239 \quad (1)$$

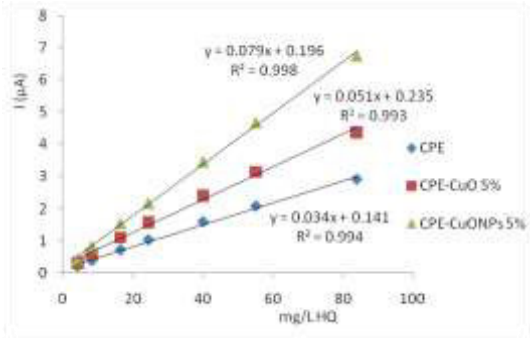

Figure 3.3. Hydrodynamic amperometric calibration curves for hydroquinone of CPE, CPE-CuO 5% and CPE-Cu/CuONPs 5% at potential 200 mV vs. Ag/AgCl.

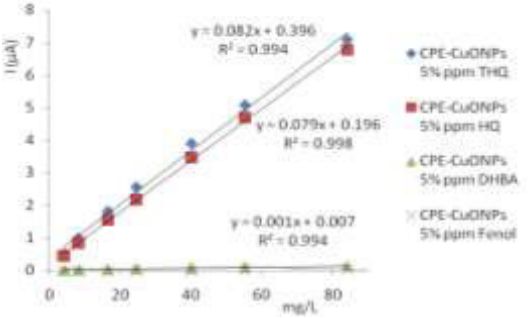

Figure 3.4. Hydrodynamic amperometric calibration curves for toluhydroquinone, hydroquinone 2.5-dihydroxybenzoic acid and phenol of CPE, CPE-CuO 5% and CPE-Cu/CuONPs 5% at potential 200 mV vs. Ag/AgCl.

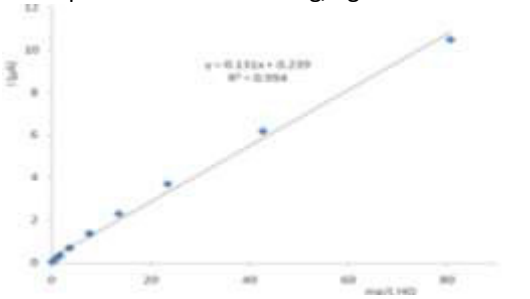

Figure 3.5. Hydrodynamic amperometric calibration curves for hydroquinone of CPE-Cu/CuONPs 5% at potential 200 mV vs. Ag/AgCl.

In table 3.1. are summarized results for sensitivity of modified and unmodified electrodes for different phenolic compounds, and it is seen that electrode modified with Cu/CuONPs shows a lower sensitivity to toluohydroquinone compared

to unmodified and modified with copper (II) oxide. Amount of 5% Cu/CuONPs to graphite gives the better results for hydroquinone and for toluhydroquinone is going to decrease in higher content of Cu/CuONPs.

4. Conclusions

The work presented here has clearly demonstrated that heterogeneous carbon sensors (carbon paste electrodes) with copper/copper oxide nanoparticles as a mediator exhibit improve the performance for the determination of hydroquinone compared to unmodified electrodes because the modifier lowers the over-potential for the electrochemical oxidation of the analyte. The suggested reaction mechanism assumes the chemical reduction of copper (II)/(I) to copper (I)/(0) by the hydroquinone which in turn is copper electrochemicaly oxidized. The modified electrodes have a long life time, good stability and high sensitivity which can be exploited for the determination of hydroquinone up to 100 mg/L.

Table 3.1. The sensitivity of modified electrodes and unmodified electrode to various analytes

	Sensitivity ($\mu A \cdot L \cdot mg^{-1}$)			
	HQ	THQ	DHBA	Phenol
CPE	0.034	0.329	0.004	2.00E-05
CPE CuO 5%	0.051	0.251	0.002	1.00E-05
CPE CuONP 5%	0.079	0.082	0.001	1.00E-05
CPE CuONP 3%	0.038	0.37	\	\
CPE CuONP 5%	0.079	0.082	\	\
CPE CuONP 7%	0.03	0.067	\	\

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DETERMINATION OF PHYSICAL AND CHEMICAL PARAMETERS OF WATER ON THE SITNICA RIVER FLOW
PËRCAKTIMI I PARAMETRAVE FIZIK DHE KIMIK TË UJIT NË RRJEDHJEN E LUMIT SITNICA

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PËRMBLEDHJE

Sipas të dhënave të deritanishme Sitnica është lumi më i gjatë dhe njëherësh më i ndoturi në Kosovë. Ky lum është i ekspozuar nga nje sërë ndotjesh të ndryshmet, si: ujërave të zeza urbane , rurale, industriale dhe atyre bujqësore. Ky studim është kryer për të pasur një pasqyrë më të saktë mbi gjendjen aktuale të cilësisë së ujit në lumin Sitnica. Mostrat e ujit për studim dhe analizë janë marr në dhjetë vende. Analizimi i parametrave fiziko – kimik si : temperatura, turbullira, përçueshmëria, pH, Oksigjeni i tretur, SHKO, SHBO, nitratet, fosfori total, fosfatet, detergjentët, amoniaku, sulfatet, kalciumi, magneziumi , metale e rënda,etj, është realizuar në Laboratorin e Institutit Hidrometeorologjik të Kosovës. Sipas rezultateve eksperimentale vlerat e shumicës së parametrave të studiuar kanë treguar varirueshmëri nga vendmostrimi në vendmostrim të një trendi të rritjes me rritjen e distancës nga burimi duke treguar përkeqësim të cilësisë së ujit të lumit Sitnicë.

Fjalë kyçe: Parametrat, ndotja e ujit, lumi Sitnica

SUMMARY

According to preliminary data, Sitnica is the longest river and at the same time the most polluted one in Kosovo. This river is exposed to a variety of different pollutions, such as urban, rural and industrial sewage, as well as those agricultural. This study was conducted to have a more accurate picture of the current water quality circumstances in the river Sitnica. Water samples for the study and analysis were taken in ten sample places. Analysis of physic - chemical parameters such as temperature, turbidity, conductivity, pH, dissolved O2, SHKO, SHBO, nitrates, total phosphorus, phosphates, detergents, heavy metals, etc., are performed in the laboratory of the Hydrometeorology Institute of Kosovo. According to experimental results the values of the most studied parameters showed variability from one to another sample place to an increasing trend with distance increasing from the source indicating the deterioration of water quality of Sitnica River.

Key words: Parameters, Water Pollution, Sitnica River.

INTRODUCTION

Although water is a renewable resource, the misuse and mismanagement of the water system can cause a problem in the quality and providing the potable water. Water can be polluted in many chemical and biological ways, and it can become unclean for drinking and cannot be used for other services [7].

Water quality, resulting as bad, is a threat to the ecosystem itself and for human health. This is a particularly serious problem and indicates a great interest for solutions to developing countries,

where environmental management practices cannot ensure a compliance to economic development [1] [3] [4].

Emphasizing that the water quality is related to a fact that the earlier civilizations were always located along or near water sources. Developments around water resources were often used as a measure of health and socioeconomic status of many nations worldwide [2]. Rivers and their stream flows are heterogeneous, as in spatial as well as in terrestrial aspect, so many scientist, have documented this heterogeneity by focusing on physico chemical dynamics of rivers [5].

This study is an attempt to characterize trends of physico chemical attributes of the water quality at 10 monitored sample places, in the stream flows of Sitnica River in two periods of time, March and July 2014.

Historically, the river Sitnica has been surrounded by many living quarters and it has been one of the most important factors for the development of these villages. Until recently, water that has flown along the river has been important for living quarters, as it was used as a source for a supply with drinking water, irrigation, fishing and recreation [6].

Currently, the quality of Sitnica River water is under the influence of a number of factors, but the main sources of water pollution in this river are from urban, industrial and agricultural waste discharges. The objective of this study was to determine the physical and chemical parameters, comparison of results between monitored periods in the water of Sitnica River and analysis of the water pollution level of this river by anthropogenic factor.

MATERIAL AND METHODS

Sitnica River throughout its stream flowing from the source to outfall into the river Ibër takes large amounts of pollutants from all water flowing of urban, rural, industrial and those from agricultural land rinse, therefore the research which was realized in the period 2013 – 2014 was the aim of this work.

This work was realized with the determination of physical and chemical parameters in water samples of Sitnicia River by making their comparison between monitored periods to have more accurate picture on the current state of water quality in the river. Sampling is performed by using equipment and container based on the ISO 5667-6 standard, the samples were taken in two periods of time (March and July 2014), at 10 monitoring stations throughout the Sitnica River flow, from its source to influx in the river Ibër.

Sample bottles were labelled with the date and source of sampling; they were kept in refrigerators at 4 ° C and transported under the appropriate procedure.

Analysis of water samples taken in the river Sitnica is performed in the laboratory of the Kosovo hydro meteorological Institute. Water quality parameters are determined by using the following measuring equipment: WTW 350i for temperature and electrical conductivity, AQUALITIC / PC COMPACT for turbidity, pH measurement values are made with pH- meter HI 98130, dissolved oxygen was determined with HI 9146 , SHBO5, SHKO, total suspended matter, nitrates, detergents with spectrophotometers SECOMAN type model Pastel UV, total phosphorus with SECOMAN PRIM LIGHT while determining the amount of heavy metals that were determined by atomic absorption Spectrophotometer of American label Perkin Elmer, type Analyst 400. Applied methods to these devices are in conformity with standard methods such as: DIN, ISO and EN.

RESULTS AND DISCUSSIONS

A summary of the results of this study, the physical and chemical analysis are shown in table below No. 1, 2 and 3. In the table are reflected the sampling places (A1-Devetak, A2-Vojnovc, A3-Gracka, A4-Lipjan, A5-Vragoli, A6-Kuzmin, A7-Plemetin, A8-Pestova, A9-Mitrovica and A10— before joining the Iber River), measurement units of physic - chemical parameters monitored, recorded values for each analyzed parameter and their comparison between two monitoring periods (March -July

Figure 1. Geographical location of the river and monitoring stations

RESULTS AND DISCUSSIONS

A summary of the results of this study, the physical and chemical analysis are shown in table below No. 1, 2 and 3. In the table are reflected the sampling places (A1-Devetak, A2-Vojnovc, A3-Gracka, A4-Lipjan, A5-Vragoli, A6-Kuzmin, A7-Plemetin, A8-Pestova, A9-Mitrovica and A10— before joining the Iber River), measurement units of physic - chemical parameters monitored, recorded values for each analyzed parameter and their comparison between two monitoring periods (March -July)

Physical parameters	Time (00:00)		Weather		Temperature (^{0}C)		Flavor (smelling)		Turbidity (NTU)		Electro conductivity µScm-1		TSS (mg/L)	
	March	July	March	July	March	July	March	July	March	July	March	July	March	July
A1	11:00	10:06	Sunny	Sunny	6.4	14.9	Odorless	odorless	9.5	61	262	280	<0.1	<0.1
A2	11:41	11:40	Sunny	Sunny	10.1	20.1	Average	odorless	5.7	31	532	530	24	19.8
A3	12:11	12:06	Sunny	Sunny	12.7	21.2	Weak	odorless	3.3	14.4	645	560	30	23
A4	12:27	12:38	Sunny	Sunny	13	21.9	Heavy	odorless	5.9	10.9	708	540	22	23.6
A5	12:50	13:12	Sunny	Sunny	12.5	23.5	Weak	heavy	9.8	7.5	720	670	19.6	**30.2**
A6	13:11	13:34	Sunny	Sunny	14.0	22.2	Heavy	odorless	64	31	884	770	25.8	57.5
A7	14:00	14:26	Sunny	Sunny	13.2	19.9	Average	odorless	7.7	17.2	831	660	18.6	25
A8	14:42	15:14	Sunny	Sunny	12.4	21.6	Weak	odorless	3.5	5.2	612	680	19.6	44.5
A9	16:45	15:52	Sunny	Sunny	12.6	22.2	Weak	odorless	4.0	5.4	616	640	32.5	71.5
A10	17:00	16:45	Sunny	Sunny	12.7	22.6	Odorless	odorless	2.9	85	618	640	28.4	109

Table 1: Presentation of the results of the physical parameters monitored

Chemical parameters	pH (0-14)		O2 %		BOD (mg/L)		COD (mg/L)		TOC (mg/L)		NO_3^- (mg/L)		DET. (mg/L)		P total (mg/L)		Phenol (mg/L)	
	M	J	M	J	M	J	M	J	M	J	M	J	M	J	M	J	M	J
A1	7.99	7.85	93.3	95	8.5	1.9	18	4.2	5.6	1.3	<0.01	<0.01	<0.1	<0.1	<0.002	0.053	<0.025	<0.025
A2	7.76	7.30	55.6	26	2	9.2	3.8	28.8	1.6	6.9	<0.01	<0.01	1.1	0.7	0.31	0.0338	<0.025	<0.025
A3	7.75	7.25	55.2	22	17	34.5	30	57	9.4	27.6	4.3	<0.01	0.4	<0.1	0.58	0.799	<0.025	<0.025
A4	7.69	7.31	40.7	23	11.3	25.2	24.4	48	7.6	20	1.8	<0.01	0.2	0.5	0.71	0.708	<0.025	<0.025
A5	7.71	7.32	63.8	39	12.5	8.4	27.2	20.6	8.4	4.2	8	5.6	<0.1	<0.1	0.70	0.932	<0.025	0.445
A6	7.69	7.48	30.7	27	29.2	26.2	60.5	83	19.8	20	<0.01	<0.01	2	2.4	1.68	1.238	0.216	0.869
A7	7.80	8.27	5.5	34	13.9	31	26.4	56	9.8	24.8	<0.01	2.4	1.4	1.6	0.77	0.504	0.089	0.125
A8	7.78	7.78	50.5	24	5.4	29.4	11.3	72.5	3.3	22.8	6.5	5.9	<0.1	<0.1	0.33	0.657	<0.025	<0.025
A9	7.76	7.48	69.1	49	5.5	43.6	12.8	93	3.8	28.2	6.7	9.9	<0.1	<0.1	0.41	0.441	<0.025	0.054
A10	7.71	7.47	68	53	20.6	59.8	44	134	13.7	41.4	6.2	10	<0.1	<0.1	0.54	0.458	<0.025	<0.025

Table 2: Presentation of the results of chemical parameters monitored

Heavy metals	Fe		Mn		Zn		Ni	
Sampling points	March	July	March	July	March	July	March	July
A1	0.106	0.347	0.031	0.204	0.012	0.021	0.027	0.015
A2	0.342	0.735	0.193	0.585	<0.01	0.062	0.043	<0.01
A3	0.322	0.373	0.223	0.550	0.004	<0.01	0.040	0.013
A4	0.276	0.289	0.277	0.850	<0.01	<0.01	0.045	0.014
A5	0.447	0.116	0.469	0.445	0.011	<0.01	0.038	0.016
A6	0.525	0.333	0.472	0.705	0.030	0.242	0.044	0.028
A7	0.290	0.161	0.282	0.495	<0.01	0.028	0.055	0.021
A8	0.279	0.172	0.228	0.455	<0.01	0.051	0.038	0.025
A9	0.369	0.110	0.321	0.450	0.421	3.115	0.055	0.026
A10	0.376	0..332	0.329	0.600	0.415	3.780	0.056	0.039

Table 3: Results of the concentration of heavy metals

Analyzed water samples of Sitnica River had different temperature during two monitoring periods. Water temperature in March varies from (A1) 6.4-14 (A6) and in July (A1) 14.9-23.5 C (A5), Aromes – whose intensity increases due to urban discharges from the average level in to extreme odorous (A5,A6), and continued in other stations were it gets weakened due to other rivers which are less polluted , like river Llap. Turbulence was always present due to rainfall, especially in sampling places A10 (85 NTU) in July that caused by heavy rain meanwhile the erosion of the river Trepca. Electro conductive values were different from station to station. Lower values of 262(March) and 280 (July) µS/cm are measured in A1 (Devetak), while the highest values are registered 884(March) and 770 (July) µS/cm in the monitoring station A6 (Kuzmin). TSS values from one to another sample place have increased as the cause of the matters content in the suspension of all polluted or discharged water during the stream flows.

Analysed samples regarding chemical parameters have shown values with minor changes. Lower values of pH were 7.69 (March) and 7.25 (July), while higher values of pH were 7.99 and 8.27. Regarding the oxygen saturation in two monitoring periods the highest values were found in sample place A1 resulting in the purity of the water. For Biochemical oxygen consumption analysed in water samples the values vary from 1.4 - 29.2 mg / L during March and from 1.9 - 34.5 mg / L in July. SHKO values during March vary from 1.7 - 60.5 mg / L, while in July vary from 4.2 - 134 mg / L. so the lowest values of SHKO are found in sample place A1 while the highest values in sample place A10. This makes us understand that SHBO5 and SHKO in the first period had the increasing of organic pollution but that is actually lower than in the second period where the amount of water has been lower due to the summer season.

For detergents and total phosphorus in two monitoring periods, the highest values were recorded in A6 as a result of the collector influence of Pristina and Fushë Kosova. Also the phenols have increased in sample places A6 during the two periods as a result of these two collectors.

The results presented in table no. 3 show that the analysis made in 10 sampling places for determining the amount of heavy metals in two monitoring periods, Fe, Mn and Ni were present in all sample places, while Zn in some of the monitored sample places was under the level of detection applied method, SAA flame techniques. Increased values of all metal ions from the sample place A6 in A5 are the result of the Graçanka river impact, the river which contains pumped waters from mines of Zvecan.

CONCLUSIONS AND RECOMMENDATIONS

From the results obtained both in the field as well as in the lab this time were ascertained also the

effects of urban wastewater discharges, industrial and agricultural land rinsing in the river flowing from one to another sample place of Sitnicia. Based on the values presented we can conclude that the maximum contamination of the river is specified in the sample place A6 especially based on parameters such as SHKO, SHBO, detergents, phenols, total phosphorus and heavy metals, as a result of impact of Pristina and Fushe Kosova discharged waters.

Therefore to ensure a normal state of good ecological status it is necessary to prevent further pollution which could be achieved by developing and implementing projects relevant for the protection of water resources from already known pollutions discharged in the rivër.

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