ISSN-1307-0428

Journal of International Environmental Application & Science

Publishing Office: Nişantaşı Mah. Dr. Hulusi Baybal Cad. Zemheri Sok, No: 5/A Selcuklu-Konya, Turkey; Tel: +90 332 2363679; Fax: +90 332 2363679.

Frequency: Journal of International Environmental Application & Science (ISSN 1307-0428) is published 4 times per year.

Aims and Scope: Journal of International Environmental Application & Science is dedicated to detailed and comprehensive investigations, analyses and appropriate reviews of the interdisciplinary aspects of renewable sources, municipal and industrial solid wastes, waste disposal, environmental pollution, environmental science and education, biomass, agricultural residues, energy sources, hazardous emissions, incineration, environmental protection topics included experimental, analytical, industrial studies, hydrological recycling, water pollution, water treatment, air pollution, gas removal and disposal, environmental pollution modelling, noise pollution and control. Suitable topics are also included regarding the efficient environmental management and use of air, water and land resources.

Publication information: Please address all your requests regarding orders and subscription queries to: Dr. S. Dursun, Selcuk University, Engineering Faculty, Environmental Engineering Department, 42003-Konya, Turkey. Tel: +90 332-223 2057, Fax: +90 332-241 0635. E-mail: jieas@jieas.com

Guide for Authors

Submission of Papers: Manuscripts for publication may be sent to the Editor-in-Chief, a member of the Editorial Board. Submission address is: Editor-in-Chief, Dr. S Dursun, Selcuk University, Engineering Faculty, Environmental Engineering Department, 42003-Konya, Turkey. Manuscripts can also be sent to any member of the Editorial Board (see inside front cover for addresses). Although this journal is international in scope, all articles must be in the English language. Potential contributors whose first language is not English are urged to have their manuscript competently edited prior to submission. Papers should be written in the third person in an objective, formal and impersonal style.

Manuscript Preparation:

General: Manuscripts must be typewritten, double-spaced with wide margins on one side of white paper. Good quality printouts with a font size of 12 pt are required. The corresponding author should be identified (include E-mail address, Telephone and Fax number). Full postal addresses must be given for all co-authors. Two hard copies of the manuscript should be submitted by regular mail. Papers will be published after evaluation of referees comments.

Abstracts: Each manuscript must be including a brief abstract and a short list of keywords.

Text: Follow this order when typing manuscripts: Title, Authors, Affiliations, Abstract, Keywords, Introduction, Main text, Conclusion, Acknowledgements, Appendix, References, Vitae and Figure Captions followed by the Figures and Tables. Pages should be numbered consecutively. The corresponding author should be identified with an asterisk and footnote.

Symbols and Units: All Greek letters and unusual symbols should be identified by name in the margin, the first time they are used. SI units should be used wherever possible, as recommended in ISO 1000 and BS 5555.

References: All publications cited in the text should be presented in a list of references following the text of the manuscript. In the text refer to the author's name (without initials) and year of publication (e.g. "since Dursun (1993) has shown that..." or "This is in agreement with results obtained later (Boddy, 1984)"). For three or more authors use the first author followed by "et al.", in the text. The list of references should be arranged
alphabetically by authors' names. The manuscript should be carefully checked to ensure that the spelling of authors' names and dates are exactly the same in the text as in the reference list.

References should be given in the following form:


Illustrations: All illustrations should be provided in camera-ready form, suitable for reproduction (which may include reduction) without retouching. Photographs, charts and diagrams are all to be referred to as “Fig(s)” and should be numbered consecutively in the order to which they are referred. They should be accompanying the manuscript, but should not be included within the text.

Tables: Tables should be numbered consecutively and given a suitable caption and each table typed on a separate sheet. Footnotes to tables should be typed below the table and should be referred to by superscript lowercase letters.

Electronic Submission: Authors may submit electronic copy of their manuscript by e-mail or online submission on WEB site of the JIEAS. The final version of the manuscript should be submitted on floppy disk or CD. The electronic copy should match the hardcopy exactly. MS Word is recommended for software for article submission.

Proofs: Proofs will send to the author and should be returned 48 hours of receipt. Corrections should be restricted to typesetting errors; any others may be charged to the author. Any queries should be answered in full.

Subscription: Subscription for the author, the issue contains article published in “Journal of International Environmental Application & Science”, is €75.00 which will be sending to the corresponding author. Journal of International Environmental Application & Science (ISSN 1307-0428) is published since 2006. Subscription rates for a year are: for Institutions: € 200.00 (four issues per a year) Individuals: € 75.00 (four issues per a year)

Copyright: Papers are considered for publication on the understanding that they have not been submitted to any other publisher. With the exception of review papers, the work described must be original and, generally speaking, not previously published. Authors who wish to reproduce illustrations that have been published elsewhere must obtain the permission of the copyright holder.

Correspondence: Papers should be sent to: Dr. S. Dursun, Selcuk University, Engineering Faculty, Environmental Engineering Department, 42003-Konya, Turkey. It may also be sent by e-mail to jieas@jieas.com in Microsoft Office Word 2003 format.

“Journal of International Environmental Application and Science” is indexed in “Index Copernicus, CAS Source Index (CASSI), ProQuest, CABI, Ulrich's™ Serials Analysis System, EBSCO, SCIRUS, ArgosBiotech, NAAEE, The University of Queensland's Institutional” Journal List.

WEB SITE: http://www.jieas.com
E-mail: jieas@jieas.com, info@jieas.com
CONTENTS

B. Cena, M. Aliu, T. Musliu, Measurements of Emission of Gases SO₂, NOₓ, CO and CO₂ from the Burning Process in the Furnaces of Power Plant “Kosova B” 172-174

A. Shehu, P. Lazo, Heavy Metal Speciation in Some Albanian Coastal Sediments 175-180


I. Krasniqi, I. Fejza, S. Avdullahi, M. Vasjari, K. V. K. Krasniqi, A. Behrami, Level of Heavy Metals and the Impact of Anthropogenic Pollution on Some Alternative Springs in Drenica and Mitrovica Zone- Kosovo 186-194

B. Durmishaj, S. Hyseni, F. Shala, B. Fetahaj, Lead and Zinc Contents and Distribution in Mineral Deposit of Përrroi i ngjyrosur-Artana Ore Field (Kosovo) 195-204

A. Cokkizgin, Effects of Lead (PbCl₂) Stress on Germination of Lentil (Lens culinaris Medic.) Cultivars 205-211

T. Boutraa, A. Akhkha, Photosynthesis Rates and Growth Responses of the Desert Shrub Calotropis procera to NaCl Salinity 212-222

C. Diop, M.N. Seck, M. Adj, K. Konate, I.O. H’medy, M.D.G. Seye, A. Coly, A. Tine, Study by Modelling the Scenarios of CO₂ Emissions Mitigation Related to Households Energy Demand in Dakar 223-232

A. Paparisto, E. Halimi, E. Hamzaraj, M. Ifti, O. Lagnori, Quantitative Comparison of the Abundance of Insects between Ecological and Conventional Farms in the Region of Tirana, Albania 233-237

F. Isufi, F. Humolli, S. Bulliqi, The Main Recreative Areas in Podujeva Municipality 238-246

A. Behrami, K. Vaso, I. Krasniqi, Antibacterial Activity of Coumarin Derivatives Synthesized from Hydroxy-4-2H-[1]-Benzopyran-2-one. The Comparison with Standard Drug 247-252

L. Kola, P. Lazo, Spectral Separation of Uranine, SRG Extra and Rhodamine WT Fluorescence in Binary Mixtures in Water Samples 253-257

S. Hyseni, B. Durmishaj, M. Rama, M. Zabeli, Trepça Ore Belt and Beloberdo Mineral deposit- Geological Overview and Interpretation, Kosovo 258-263

F. Vinçani, F. Cara, P. Leka, Geochemical-Geophysical Studies for Tecnogen Pollution in Porto Romano, Albania and Their Integration in GIS 264-271

N. Hasi, Geophysical Seismic Investigations for Seismic Station of Prizren (Kosovo) 272-275

I. Ibrahimimi, M. Riazaj, A. Ramadani, Research the Possibility of Transforming the Ferronickel Slag in the Product with the Economical and Environmental Importance 276-281

R.A. Sadykhzadeh, Experimental Ground of Application of Extract from Saffron Inoculun under Heart Ischemia 282-286

F. Cfarku, E. Bylyku, B. Daci, Gross Alpha/Beta Measurements in Drinking Water Samples Using Different Methods 287-290

S.K. Kavitha, P.N. Palanisamy, Optimization of Operational Parameters of the Photocatalytic Degradation of Reactive Red 120 Dye under UV Irradiation 291-305

M.E. Argun, Solar Energy Supported Desalination Processes for Desalting of Sea Water 306-310


Measurements of Emission of Gases SO₂, NOₓ, CO and CO₂ from the Burning Process in the Furnaces of Power Plant “Kosova B”

Besire Cena*, Mehush Aliu, Tahir Musliu
Faculty of Mining and Metallurgy, University of Prishtina, Mitrovica, Kosova

Received February 26, 2010; Accepted June 10, 2010

Abstract The main source of the release of acidifying substances in the environment is the emission of gases that contain dioxide sulphur (SO₂), nitrogen oxides (NOₓ), ammonia (NH₃) and others. These gases are produced during the combustion of combustibles in the sector of the production of electricity, in chemical industry, in metallurgy. The emission, quantity and characteristics of smoke gases emitted after combustion in the furnaces of the Power Plant, depend on the composition of sulphur in lignite itself, whereas the concentration of SO₂ is related to the composition of sulphur in lignite to be burned. Whereas related to nitrogen oxides NOₓ, it greatly depends on the technological process of combustion in furnace. After the combustion process in the furnace of Power Plant “Kosova B” the emitted smoke gases will contain CO₂ as a product of combustion, which is one of the main causes of the global warming of our planet. The purpose of these measurements is to set the emission of these toxic gases SO₂, NOₓ, in gas channels in the Power Plant “Kosova B”, and CO₂.

Key words: gases, pollution, emission, combustion

Introduction

In this study were presented the results of measurements of gases O₂, CO, CO₂, NO, NO₂, SO₂, NOₓ and H₂ after the measures of gas channels in power plant “Kosova B”.

Around 97% of the electric energy generated in Kosovo is obtained from the combustion of lignite in the power plants A and B, whereas only 3% of annual production comes from water flows (Agolli, 1983). Kosovo Energy Corporation is a large polluter of environment, especially in the wide region of Prishtina. The pollution is caused by ash particles and emitted gases such as carbon monoxide (CO), sulfur dioxide (SO₂), nitric gases (NOₓ).

In the narrow meaning of word, air may be considered polluted when it contains substances which are foreign for its natural composition. However, today in this state of global pollution it is almost impossible to discuss about such ideal air (especially in areas populated by humans), therefore air will be considered polluted if it contains substances that are concentrated to the extent of causing damages to the health of humans and their living environment (Rozhaja, Jablanovič, 1984).

The purpose of this study is to determine the level of gas emission in the gas channels of power plant “Kosova B” before they are emitted in the atmosphere, in particular gases that cause acid rain.

Therefore, the main purpose of this study is to determine the concentration of gases such as SO₂ and NOₓ and measures to be taken in accordance with scientific achievements for the prevention of environment pollution by these gases.

Materials and Methods

The measurement of concentration of these gases was done in the operating unit of power plant “Kosova B”. The measurement instrument testo 350-XL Abgas-Anlyesgerät Flye Gas is German made. The methodology for the gas measurement with Testo 350-XL Abgas-Anlyesgerät Flye Gas Analyzer (O₂, CO, CO₂, NO, NO₂, SO₂, NOₓ, H₂, °C) is simple. The German instrument testo 350-XL Abgas consists of sensors and analyzers of respective gases. The gas probe absorbs the gases from the place designed for taking gas samples in channels. The assembled pump absorbs the gases from the gas channel and transmits them to the sensors and analyzers mounted in Testo 350-XL instrument. After the time necessary for the instrument to provide the results, the measurement results will be displayed in the monitor with the possibility of printing them in paper. Testo 350-XL Abgas

*Correspondent: E-mail: blerimbaruti@hotmail.com; Tel: +37744146870 Fax: +37744146870
instrument will signalize (with a red lamp) that the measurement is complete and it will be ready for showing the concentration of gases in channel and the temperature of gases.

The measurements of emitted gases were made in six locations in the two gas channels where probes are placed. The placement of probe for the absorption of gases was done before and after the air heaters and before the absorbing ventilators. There are two parallel lines in power plant “Kosova B” that are symmetrical. The results of measurements made on 11.06.2008 are presented in Table 1 whereas the repeated measurements made on 12.06.2008 are presented in Table 2.

The performances of operating units of B₁ of power plant “Kosova B” during the time of measurements are presented in Table 3.

![Figure 1. Instrument for measurements of emissions of gases](image)

**Table 1. Results of measurements in gas channels 11.06.2008, 11:15**

<table>
<thead>
<tr>
<th>Parameters Gases</th>
<th>Unit</th>
<th>Before air heater 1</th>
<th>Before air heater 2</th>
<th>After air heater 1</th>
<th>After air heater 2</th>
<th>Before absorbing ventilator 1</th>
<th>Before absorbing ventilator 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ %</td>
<td></td>
<td>5.3</td>
<td>5.47</td>
<td>6.55</td>
<td>6.27</td>
<td>8.47</td>
<td>8.2</td>
</tr>
<tr>
<td>CO ppm</td>
<td></td>
<td>73</td>
<td>70</td>
<td>69</td>
<td>75</td>
<td>58</td>
<td>66</td>
</tr>
<tr>
<td>CO₂ %Vol</td>
<td>ppm</td>
<td>13.7</td>
<td>13.7</td>
<td>12.68</td>
<td>12.2</td>
<td>11.12</td>
<td>13.35</td>
</tr>
<tr>
<td>NO ppm</td>
<td></td>
<td>393</td>
<td>487</td>
<td>353</td>
<td>350</td>
<td>321</td>
<td>321</td>
</tr>
<tr>
<td>NO₂ ppm</td>
<td></td>
<td>0.1</td>
<td>1.2</td>
<td>12.3</td>
<td>14</td>
<td>8.6</td>
<td>7.3</td>
</tr>
<tr>
<td>SO₂ ppm</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>2</td>
<td>11</td>
<td>0.00</td>
<td>1</td>
</tr>
<tr>
<td>NOₓ ppm</td>
<td></td>
<td>471</td>
<td>363</td>
<td>374</td>
<td>362</td>
<td>329</td>
<td>326</td>
</tr>
<tr>
<td>H₂ ppm</td>
<td></td>
<td>32</td>
<td>31</td>
<td>28</td>
<td>27</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>Temp. °C</td>
<td></td>
<td>327</td>
<td>327</td>
<td>199</td>
<td>201</td>
<td>166</td>
<td>174</td>
</tr>
</tbody>
</table>

**Table 2. Results of measurements in gas channels 12.06.2008, 11:30**

<table>
<thead>
<tr>
<th>Parameters Gases</th>
<th>Unit</th>
<th>Before air heater 1</th>
<th>Before air heater 2</th>
<th>After air heater 1</th>
<th>After air heater 2</th>
<th>Before absorbing ventilator 1</th>
<th>Before absorbing ventilator 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ %</td>
<td></td>
<td>5.91</td>
<td>6.18</td>
<td>6.23</td>
<td>6.71</td>
<td>8.55</td>
<td>8.92</td>
</tr>
<tr>
<td>CO ppm</td>
<td></td>
<td>78</td>
<td>69</td>
<td>72</td>
<td>76</td>
<td>57</td>
<td>71</td>
</tr>
<tr>
<td>CO₂ %Vol</td>
<td>ppm</td>
<td>14.6</td>
<td>14.3</td>
<td>13.15</td>
<td>13.51</td>
<td>12.70</td>
<td>14.15</td>
</tr>
<tr>
<td>NO ppm</td>
<td></td>
<td>421</td>
<td>497</td>
<td>531</td>
<td>541</td>
<td>421</td>
<td>423</td>
</tr>
<tr>
<td>NO₂ ppm</td>
<td></td>
<td>0.4</td>
<td>1.5</td>
<td>11.7</td>
<td>16</td>
<td>8.5</td>
<td>7.7</td>
</tr>
<tr>
<td>SO₂ ppm</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>3.25</td>
<td>11</td>
<td>0.00</td>
<td>2</td>
</tr>
<tr>
<td>NOₓ ppm</td>
<td></td>
<td>375</td>
<td>355</td>
<td>379</td>
<td>362</td>
<td>337</td>
<td>333</td>
</tr>
<tr>
<td>H₂ ppm</td>
<td></td>
<td>33</td>
<td>32</td>
<td>28</td>
<td>27</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>Temp. °C</td>
<td></td>
<td>327</td>
<td>327</td>
<td>199</td>
<td>201</td>
<td>166</td>
<td>174</td>
</tr>
</tbody>
</table>
Table 3. Main parameters of Unit B1 during the measurements

<table>
<thead>
<tr>
<th>Date</th>
<th>11-06-08</th>
<th>12-06-08</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time h</td>
<td>11:30</td>
<td>11:15</td>
<td></td>
</tr>
<tr>
<td>Power MW</td>
<td>289</td>
<td>285</td>
<td>287.2</td>
</tr>
<tr>
<td>Ash %</td>
<td>14.7</td>
<td>15.2</td>
<td>15.62</td>
</tr>
<tr>
<td>Cal. Value J/kg</td>
<td>7943</td>
<td>8321</td>
<td>8002.6</td>
</tr>
<tr>
<td>$Q_{coal}$ t/h</td>
<td>366</td>
<td>368</td>
<td>365</td>
</tr>
<tr>
<td>$Q_{ash}$ t/h</td>
<td>53.8</td>
<td>55.93</td>
<td>56.98</td>
</tr>
<tr>
<td>$Q_{gas}$ Nm$^3$/h</td>
<td>1380 10$^3$</td>
<td>1368 10$^3$</td>
<td>1381 10$^3$</td>
</tr>
</tbody>
</table>

Discussion and Conclusion

Based on the obtained results presented in tabular form we can conclude that SO$_2$ has a lower concentration than expected in channel 2 after the air heater 2. SO$_2$ is 11 ppm and after heater 1 we found the value 2 ppm, whereas in other measured channels the instrument recorded the value 0.00.

Whereas in the repeated measurement the values did not change significantly as it can be seen in table 2. After the measurements and analysis of measurement results and after obtaining these values of SO$_2$, we consulted the literature and came to the conclusion that in the fireplace of the furnace occurred the phenomenon of natural removal of sulphur. The natural desulfurization because the lignite used as combustible in the furnace contains high composition of CaCO$_3$ and MgCO$_3$. In the fireplace there will be a quick reaction between CaO, SO$_2$ and O$_2$ thus producing CaSO$_4$. This reaction occurs at the temperature above 750°C. Under this temperature the reaction practically ceases and as a result the natural desulfurization does not take place (Gill, 1984).

This fact that is very favourable for power plant “Kosova B” is explained with the high presence of CaO in fly ash (-35%), which is a crucial factor in the so-called desulfurization process. The values obtained after the measurements in the gas channels for NO, NO$_2$ and NO$_X$ are presented in table 1, whereas the repeated measurements in table 2. The obtained value of 487 ppm is the highest value obtained in the gas channel before the air heater 1, whereas the lowest value is 321 ppm obtained in both sides of the channels before the absorbing ventilator.

These values do not exceed the maximal concentration permitted (MCP) which is NO$_X$ mg/Nm$^3$ dry 6% O$_2$ of 500 mg/Nm$^3$. For NO$_2$ the instrument recorded a value from 1.2 to 12.3 ppm. whereas for the value of NO$_X$ the instrument testo 350-XL Abgas does not record the values that exceed the MCP of 500 mg/Nm$^3$, since this values varies from 471 to 326 ppm. For CO the testo 350-XL Abgas instrument used for the measurement, recorded the value from 75 to 68 ppm. whereas for O$_2$ 5.47% before the air heater, which is lower than it should be (6%), whereas after the air heaters reaches the value of 8.2% which shows the passage of fresh air in the fitting of air heater and this amount reaches up to approximately 100.000 Nm$^3$/h. Testo 350-XL Abgas-Analysegerat Flye Gas instrument also measures H$_2$ where the obtained value of H$_2$ was 32 ppm before the air heater which gradually decreased to 24 ppm before the absorbing ventilator. In the repeated measurements the values were approximately the same.

In line 2 before the heater the instrument showed a value from 11 ppm for SO$_2$ whereas before the heater shows the value 0.00. This phenomenon occurred because of the presence of a gas channel connected to the absorbing ventilator which serves to form the sub pressure in the ash system where the concentration of SO$_2$ is supposed to originate from the ash process.

The main measures for the minimization of the emission of NO$_X$ are the reduction of combustion temperature and reduction of the percentage of excessive air in the furnace (Gjurgjeala, 2007).

The emission of NO$_X$ is caused by the projection of air combustion system and by optimizing the operation parameters.

Reference


Heavy Metal Speciation in Some Albanian Coastal Sediments

Alma Shehu*, Pranvera Lazo

Department of Chemistry, Faculty of Natural Sciences, Blv. “Zog I”, Tirana, Albania

Received February 15, 2010; Accepted April 23, 2010

Abstract: The evaluation of concentration levels and distribution of heavy metals in different fractions of coastal sediments in order to assess possible anthropogenic inputs in this area is presented. The speciation of heavy metals (Fe, Mn, Cr, Ni, Cu, Pb, Cd, Zn) as well as their total concentration has been determined in six coastal sediment samples collected in Albania. A good correlation has been found for Cr, Fe, Zn, Cu, Mn and Pb in the entire area, indicating the same origin for these metals in the analyzed sediments. The extraction procedure of heavy metals was conducted via three step extraction procedure. During the step A considerable levels of total Mn (about 30-40%) were found in exchangeable form and adsorbed to carbonates. Metals bounded to such fractions are presumed to be more bio available presenting a potential risk for biota and aquatic system. During the step B considerable part of other metals were extracted which reveal the domination of reductive nature of the sediment studied. So, about 10% of Ni, 19% of Mn, 30% of Fe and about 25% of Pb were extracted during the second step of extraction. About 22% of Fe, 22% of Cu, 8% of Cr, 10% of Ni were found to be bound to organic matter and present as sulphides, extracted mainly during the third step of extraction (step C). The most part of all heavy metals resulted to be associated to the most refractory fraction of the sediment, which constitute up to 50% of the total concentration. Distribution of heavy metals in different fractions of sediments showed that there were differences between the mineralogical structure of the Adriatic and Ionian Sea sediments. Levels of total heavy metals present in the sediments of the coastal area showed the same variations as has been reported by other studies of the area confirming the natural origin of the heavy metals.

Keywords: metal speciation, BCR method, sequential extraction, marine sediments;

Introduction
The basic goals of most chemically oriented water-quality studies have been used to evaluate environmental conditions and to identify different sources of constituents and pollutants. Analyses of heavy metals content and distribution in sediments is found to be a common way in assessing the extent of anthropogenic input impact on a certain area (Ure et al. 1992) because they can act as reservoirs for many trace elements. Determination of the total concentration alone can lead to an overestimation of the anthropogenic contribution of a particular heavy metal as the mobility, transport and partitioning of trace elements in a natural aquatic and terrestrial system is a function of the chemical forms of the element, controlled by the physico-chemical and biological characteristics of the system (Campanella et al. 1995). The tendency of an element to be accumulated by organisms depends in particular upon the capacity of a sediment water system to release in solution trace elements via sorption-desorption and dissolution-precipitation reactions. Therefore, it is necessary to take into account the distribution of elements among different fraction of the origin sediments (Tessier et al. 1979). In this context, trace metal species identification tends to be more appropriate than total metal concentration. So many methods are proposed in evaluating speciation of heavy metals, but the sequential extraction is found to be one of the most appropriate ones (UNEP, 1995). In the present study the BCR sequential extraction procedure, proposed by the Bureau of the European Community, is used to isolate different species of heavy metals. The “BCR” Sequential extraction procedure was applied in order to assess the distribution of heavy metals in different fractions of coastal sediments (Campanella, 1995). Three samples were chosen for this reason, two of them belonging to Adriatic Sea, (samples 1 and 2) and one to Ionian Sea (sample 6). About 2 g of pre-treated sediment sample

* Corresponding: E-Mail: a.shehu@albnet.net; Tel: +355684081078
(<63µm) was treated regarding the respective procedure (Table 2) in 50 ml polyethylene tubes with exactly 20 ml of appropriate extracting reagent. The liquid phase was separated from the solid phase by centrifugation at 3500 rpm for 20 min. The remaining was washed with 10 ml distilled and the washing solution was gathered with the first extraction solution. The final solution was diluted to 50 ml and was ready to be used for analyses. “BCR 701” reference material was used for quality control of the speciation analyses as well as blank determinations was carried out for each fraction of metals determined. The Adriatic Sea is an oblong land locked basin, bordered on the western side by the Apennines and on the eastern side by the Dyrrhachian chain. For many years it has been regarded as a heavily polluted sea because of its morphology and dynamics (Pigorini, 1968). Albania lies on the south-east shores of the Adriatic Sea some 100 km at the closest point from Italy, its largest external trading partner. Like its neighbours in the Balkans, Albania has a rich and diverse geology including globally significant reserves of nickel and chrome, and regionally significant resources of copper, bauxite, and iron ore. From the late 1970s through 1990, Albania was the principal European chromite producer, with yearly production in the range of 750 - 800 thousand tons, ranking it second in the world in exports and third in production (Shallari, 1998).

The Albanian coastline is 476 km long, and the Adriatic and Ionian Seas have a great impact on the climate, flora, and fauna in the country. Adriatic shore is mainly sandy, whereas Ionian is almost total rocky alternated with pebble or hard sandy shores. Most of the Albanian rivers flow into the Adriatic Sea and their courses have an important effect on the country's coastal biodiversity. It has been estimated that on the Albanian coast, large quantities of waters with more than 50x10^6 t of suspended solids per year enter the south-eastern Adriatic (UNEP-MAP, 1992).

**Materials and Methods**

**Data set and site description**

Sediment samples were collected during spring 2008 whereas geographical position and depth of each station is reported in Table 1.

**Table 1.** Co-ordinates and depth of sediment sampling stations.

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Depth (approx. m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40°24'00,069&quot;N</td>
<td>19°28'33,830&quot;E</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>40°21'24,390&quot;N</td>
<td>19°24'26,334&quot;E</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>40°23'57,773&quot;N</td>
<td>19°26'27,149&quot;E</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>40°27'09,153&quot;N</td>
<td>19°25'23,782&quot;E</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>40°27'05,743&quot;N</td>
<td>19°14'23,762&quot;E</td>
<td>115</td>
</tr>
<tr>
<td>6</td>
<td>40°05'23,758&quot;N</td>
<td>19°33'24,860&quot;E</td>
<td>120</td>
</tr>
</tbody>
</table>

Six sediment samples, of which five belong to Adriatic Sea sediments (1-5) and one to Ionian Sea (6). Specific samples were chosen in points where the discharges from different rivers which flow directly to the sea could influence the levels of heavy metals in Sea sediments. Consequently, sample 1 was taken in a point where three of the main rivers of Albania flow, such as Drini, Mati and Ishmi River. Samples were collected using a stainless steel grab and sampled from the centre of the grab to avoid contamination by the metallic parts.

After draining off the excess water, they were placed in polyethylene containers and stored at -20°C until analysis. A small amount of each sample was air dried and sieved through a 2.0 mm screen. The fraction of sediment smaller than 2.0 mm was well homogenized by grinding in an agate mortar until the material passed through a 0.063 mm nylon sieve and subsamples for the determination of heavy metals were dried at 105°C. After drying, samples for chemical analyses were stored in airtight plastic vials until required. In figure 1 positions of sampling stations are shown.

**Analytical procedure.**

The total metal content was determined after treatment of samples with 4ml of aqua regia (HCl/HNO₃, 3 : 1) and heated in a microwave oven (CEM MDS 2000) with the following program: 5 min at 250W power, 5 min at 320W power and 10 min at 380 W. The digests were filtered and made
up to 20mL with deionised water, transferred in polyethylene containers and stored at 4°C until analysis. All the reagents employed were of Suprapure grade (Merck). The determination of Zn, Cu, Fe, Mn, Cr, Pb was carried out using Flame AAS System for Fe, Cr, Ni, Mn and Cu determination as well as ETA-AAS System for Pb and Cd determination. All measurements were conducted using a Varian SPECTRA 10-Plus atomic absorption spectrophotometer equipped with GTA-96 graphite furnace. Chemical modifier such as NH₄H₂PO₄ was used for Cd and Pb determination with ETA-AAS. SDM-2/TM and IAEA reference material were used for quality control of total determination analyses of sediments. Blank analyses were carried out, showing negligible contamination. Table 3 shows the results of the total metal concentration (mg.kg⁻¹) in six samples studied also illustrated in Figure 2.

Figure 1. Map of sampling stations

Table 2. Reagents used and operational conditions of the “BCR” sequential extraction method.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Fraction isolated</th>
<th>Extracting Reagent</th>
<th>Shaking time and temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Acid-soluble (bound to carbonates and exchangeable)</td>
<td>20 ml 0.11 mol/l CH₃COOH</td>
<td>16 hours at room temperature</td>
</tr>
<tr>
<td>B</td>
<td>Reducible (bound to Fe/Mn oxides)</td>
<td>20 ml NH₂OH.HCl 0.5 mol/l (pH =2)</td>
<td>16 hours at room temperature</td>
</tr>
<tr>
<td>C</td>
<td>Oxidizable (bound to organic matter and in sulphide form)</td>
<td>5 ml 8.8 M H₂O₂ (Evaporation) + 25 ml CH₃COONH₄ 1 mol/l</td>
<td>16 hours at room temperature</td>
</tr>
</tbody>
</table>

Table 3. Heavy metals total content (μg/g, except Fe in mg/g) in sediments. Data represent the mean ± standard deviation of three replicates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>Cd</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>173.0±3.4</td>
<td>69.0±1.8</td>
<td>507.9±8.9</td>
<td>12.7±1.0</td>
<td>83.6±2.4</td>
<td>0.12±0.01</td>
<td>1235.3±18.2</td>
<td>459.9±8.5</td>
</tr>
<tr>
<td>2</td>
<td>155.2±2.3</td>
<td>35.1±1.0</td>
<td>499.4±9.0</td>
<td>14.1±1.1</td>
<td>79.2±2.3</td>
<td>0.09±0.01</td>
<td>642.7±12.4</td>
<td>416.1±8.4</td>
</tr>
<tr>
<td>3</td>
<td>309.1±6.7</td>
<td>44.4±1.1</td>
<td>335.3±4.3</td>
<td>19.5±1.2</td>
<td>123.0±5.4</td>
<td>0.10±0.01</td>
<td>847.7±12.9</td>
<td>495.5±9.2</td>
</tr>
<tr>
<td>4</td>
<td>314.7±6.1</td>
<td>46.0±1.1</td>
<td>333.4±3.5</td>
<td>13.2±1.3</td>
<td>105.7±3.2</td>
<td>0.13±0.01</td>
<td>784.7±11.0</td>
<td>472.4±9.6</td>
</tr>
<tr>
<td>5</td>
<td>311.2±5.4</td>
<td>45.0±1.2</td>
<td>333.9±3.4</td>
<td>17.3±1.3</td>
<td>114.5±3.1</td>
<td>0.12±0.01</td>
<td>813.6±10.0</td>
<td>481.5±8.0</td>
</tr>
<tr>
<td>6</td>
<td>90.5±1.2</td>
<td>29.8±1.0</td>
<td>269.9±3.4</td>
<td>9.6±1.0</td>
<td>80.4±2.0</td>
<td>0.12±0.01</td>
<td>623.2±11.4</td>
<td>302.0±8.3</td>
</tr>
</tbody>
</table>
Results and Discussion

In Table 3 (and Figure 2) results of total concentration of heavy metals in six samples of Albanian marine sediments are implied. To assess the reproducibility of the method, three sub-samples are analyzed simultaneously along with a blank. As it can be seen Cr, Zn, Mn, Fe and Pb showed the highest concentrations in sediments sampled in stations 3, 4 and 5 near Otranto channel, Shkumbini and Vjosa Rivers mouth, while lowest values were found in stations 6 sampled in Ionian Sea. Sample 1 show highest concentration of Ni, Cu and Mn as well as Fe.

![Figure 2. Total heavy metal concentration in sediments.](image)

All the values were in good agreement with the permitted levels of heavy metals and do not show any impact of the anthropogenic pollution. Samples of Adriatic Sea sediments are characterized by higher levels of heavy metals compared to Ionian Sea sediment samples. Data related to geologic composition of hydrographic basins of Albania show that sediments of Adriatic Sea are mainly of ultra basic origin, generating higher levels of metals such as Ni, Cr, etc, whereas sediments of Ionian Sea are characterized by carbonates structure, where metal content is low (Lazo, 2008, Herut et al. 2006). From the other hand, Albanian rivers, which almost all flow to Adriatic Sea, are characterized by high levels of suspended solids, exceeding several folds the value of 25 mgL⁻¹ EC Directive 78/659 (Miho et al. 2005) as well as high levels of specific metals, depending of the area where they flow. High levels of Cu are found in sediments of Mati River which flow in the area where the mining industry of cooper melting has been developed (Miho et al. 2005). High levels of Cr and Ni have been found in previous studies in Drini River (Neziri et al. 2006).

The correlation coefficient matrix (p=1%) between heavy metals contents is reported in table 4. As it can be seen, Fe, Cr, Zn, Cd and Pb are positively and highly correlated in the entire area, indicating a common origin of these metals whereas Ni, Mn, and Cu showed low correlation with the other elements, indicating a different source of their presence.

Table 4. Correlation matrix between metal concentrations in sediments

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>Cd</th>
<th>Mn</th>
<th>Fe*100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1.00</td>
<td>-0.22</td>
<td>-0.99</td>
<td>0.58</td>
<td>0.94</td>
<td>0.45</td>
<td>-0.23</td>
<td>0.85</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>1.00</td>
<td>0.33</td>
<td>-0.38</td>
<td>-0.22</td>
<td>0.53</td>
<td>0.99</td>
<td>0.23</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td>1.00</td>
<td>-0.62</td>
<td>-0.94</td>
<td>-0.37</td>
<td>0.34</td>
<td>-0.80</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
<td>0.81</td>
<td>-0.34</td>
<td>0.21</td>
<td>0.62</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
<td>0.21</td>
<td>0.43</td>
<td>0.90</td>
</tr>
<tr>
<td>Cd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
<td></td>
<td>0.47</td>
</tr>
<tr>
<td>Mn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3. Distribution of heavy metals in different fractions of sediments

Histograms in figure 3 represent results on heavy metal content found in different fractions (named A, B, C and residue) of sediment samples after sequential extraction analyses. The percentage value of extractable part of heavy metals in each fraction against the total concentration as well as total extractable part was used to study the distribution of heavy metals in marine sediments. If we consider the total extractable part of heavy metals, it resulted relatively low comparing with the total content and does not exceed 50% of the total for all metals except for Mn. Consequently, heavy metals of the marine sediments are characterized by a low mobility and the most part of them are not easily mobilized in solution. Mn is the metal extracted in higher percentages, about 60% of the total.

Considerable levels of Mn, varying from 31% to 40% and about 20% of Cu in sample 2 as well as about 20% of Cd in sample were found to be in exchangeable form and bound to carbonates, extracted mainly during the first step of extraction (phase A). The most part of all other metals was found to be extracted during the phase 2 (phase B) which is a fact of the reductive dominating medium of the sediment studied. So, about 10% of Ni, 19% of Mn, 30% of Fe and about 25% of Pb were extracted during the second step of extraction. About 22% of Fe, 22% of Cu, 8% of Cr, 10% of Ni were found to be bound to organic matter and present as sulphides, extracted mainly during the third step of extraction (phase C). In this case they can be released in solution only after strong acidic treatment. The distribution of heavy metals in different fraction of sediments can be used as indicator of the sediment mineral composition. Consequently, is we analyze the distribution of heavy metals in different fractions of the sediments we see that there are differences between Adriatic and Ionian Sea sediments.

The percentage of the total metal found in residual fraction resulted to be higher in sediment which belongs to Ionian Sea for metals Cu, Zn, Cr and Ni compared to sediment samples of Adriatic Sea. Metals resulted to be mostly extracted during the third phase, whereas in the first two phases the amount extracted was undetectable. Also, the percentage of Mn bounded to carbonates resulted higher for this sample (about 40%) compared to Adriatic sediment samples which confirms the fact that the mineral composition of sediments of Adriatic and Ionian Sea is different. The reason of different ways
of metal distribution in sediments of the Adriatic and Ionian Seas comes in many ways. First we should mentioned that all the rivers which flow in Albania go directly to Adriatic Sea being so the main source of higher levels of heavy metals. Secondly, many other factors such as mineral composition as well as physico-chemical properties of the sediment have direct effect on the distribution of heavy metals in different fractions of the sediments.

**Conclusions**

Sequential extraction procedures permit the evaluation of heavy metals distribution among the various chemical forms in which they are present in sediments. This allows the evaluation of environmental risk due to mobility and bioavailability of the different forms of heavy metals. Total extractable part of heavy metals resulted to be low comparing with the total concentration and does not exceed 50% of the total except for Mn for which the value resulted about 60%. Considerable levels of Mn and about 24% of Cu in sample 2 were found in to be in exchangeable form and bound to carbonates, extracted mainly during the first step of extraction (phase A). Metals bound to this fraction are presumed to be more bio-available and thus may represent a potential risk for biota and living organisms. Based on the results given for metal distribution in different fractions of sediment, we can conclude that there are differences in mineral composition of sediments of Adriatic and Ionian Sea.

**References**


The Contribution of Organic Sector in the Albanian Agriculture

Elvira Leksinaj¹*, Gianni Cicia², Luigi Cembalo², Teresa Del Giudice², Maksim Meço¹, Taulant Nelaj¹

¹Faculty of Economy and Agribusiness, Tirana, Albania; ²University of Naples “Federico II”, Naples, Italy

Received December 28, 2009; Accepted June 1, 2010

Abstract: What is nowadays known as organic farming in Albania is at an initial phase. It is mainly located in the so-called “marginal areas” by small farms. Organic market in Albania can be considered as at a very starting stage with small niches marketing point but with a growing interest of consumers for fresh productions with limited processing activities. The condition for a better partaking in the country’s markets is, however, desirable since commercial and trade between Albania and other countries, mainly EU’s, is readily growing. The aim of the present research work is to present a descriptive analysis of the structural and productive indicators of the organic and, at large, the whole agriculture sector in Albania. The first part of the paper analyses the economical and social framework of today’s Albanian farming, which is still far from the European Union standards. Although organic farming in Albania is not as regulated as it is in the EU, we tried to outline to what extent organic farming can reach a productive and economical perspectives for local development. In the second part of the paper we analysed the situation of the potential of organic farms by means of a SWOT analysis. The strength and weakness points for the farms, together with the possibilities and threats of the organic market pointed out by environmental analysis, are selected with the intention of addressing the main issues and attempting to delineate some peculiar policies and market intervention for overcoming the actual nodal points.

Keywords: Albanian agriculture, organic potential farms, SWOT analysis, premium price.

Introduction

Over the past few years organic products have witnessed a massive development in terms of crop adaptability practices and in the applied norms as well as in the assessment on consumer side. The latter has been well placed to gain a well-defined identity in the possible scenarios of development and integration of the agricultural sector into the regional economy and beyond.

In several instances, the increase in production might attest to the successful implementation of a certification program of the areas of land long organic by nature rather than the reversal of the agricultural system. It is the case of Albania that might be able to adopt the certification procedures for the recognition of the organic products in order to attain or better boost the economic worthiness of production.

One of the critical points that present themselves in the Albanian organic agriculture has been depicted from the inadequacy of the evaluation of the products. The operating lack of the commercialization chain, the missing integration of supply chain and the weak links among manufacturers, processors/exporters and consumers make the Albanian producers face an ever decreasing profit once they return to organic products. On the other hand this is going to favour traders and exporters who stand to gain more in terms of the margin of profit.

The existing organic agricultural systems are characterized by small-sized and fragmented structures, far from being organized in groups and not integrated into supply chain. Thus, the establishment of the ever-increasing fully-operating forms capable of permitting concentration of supply is taking on notes of urgency along with the provision of farmers with a contractual power.

The framework of Albanian agriculture

The transition in the agricultural sector in Albania began in the wake of the elections (31 March 1991) with a process of de-collectivization of state-owned manufacturing units, which had functioned

*Corresponding: E-Mail: leksinaj@libero.it; Tel: 00355692770075; Fax: 00355472200874
during the socialist planned economy. The outcome was de-collectivization of state cooperatives in favour of a "rapid, spontaneous and conflict-filled transition".

This paper attempts to describe the Albanian transition process taking into account the socio-economic structure of a post-communist country, which in late 1991 did not follow the free market rules. In particular, specific attention is being focused on a general economic analysis. It has been noted as to how the transformations have completely changed the dimensions and structures of the country's economy by conditioning the biggest part of the productive agricultural activities.

The problem of Albanian agriculture can be fully understood if it is engaged not only in an economic system but also in a socio-political one. The solution was the expression of radical changes and of a structural economic evolution. This will be the approach adopted by the paper in order for us to better understand structured change at the farm-level in the agricultural sector in Albania.

The key factor of transition from a cooperative system to the private one was the low level of incomes of workers in cooperatives. Therefore it was decided for a small plot of land to be distributed in order to produce positive and fast effects in the incomes and in the food needs of the population. The Albanian government in contrast to other countries of Eastern Europe was not conditioned in its choice of the reform from the legal protection of private property rights. This was so, because all of agricultural land was nationalized during the collectivization period.

The speed of the Albanian de-collectivization process may be linked to the set desire of Albanian farmers to abandon the cooperatives. However, this liberal phenomenon with the full opening of the markets, the termination of assistance and other forms of state support constitute a single and unique case at the international level.

Albania has been and continues to be a typically “agrarian” country, in which over 50% of population lives and works in rural areas, and which has as its major activity the agricultural sector, in which roughly 75-80% of work days are spent on farms. On the other hand, we figure as a country which exports 450-500 million Euros worth of agricultural and food products. This amount with 2008 in mind turns out to be approximately in the region of 500 million Euros (MAFCP, 2008). Every year, roughly 25-30% of the food needs are imported from overseas markets, which has brought a negative trade balance in this field. With reference to the same source the imports in agricultural and food products have been 10 times as high as the exports. So, Albania is classified under the group of “structurally importing” countries or, in other words, a group of countries which are considered to be the most vulnerable and the most exposed to the current situation and the perspective of price increases and the various turbulences of the international agrarian markets.

Although Albania is an agrarian country where agriculture accounts for roughly 22-23% of the GDP, yet the return it gets from the state budget and other public financing is 15:20 times smaller. During the transition period the budgets targeting agriculture were anywhere between 0.5-1.5 of the GDP, at a time when the biggest part of them was geared towards the operational expenses for salary and additions on salaries rather than for direct investments.

The average farm size is in the region of 1.2 ha per household (MAFCP, 2008). At a time when that one too appears to be fragmented into some 1.8-3 million strips of land. Out of a total of 22-23% of the impoverished population or extremely poor strata, 99% of such population dwells in rural areas. So it’s logical for such poverty to be dubbed “rural poverty”.

The key solution prescribed for the farms has been provided by foreign-funded projects and other major contributions from many donors out there. These contributions have indisputably gone into agriculture. Yet the private investments coming from within the country this sector have been negligent. To prove this, suffice it for us to refer to the credit index percentage for agriculture and other rural areas as compared to others sectors. Only 1-1.2 % of the bank credits in total have been given to the agricultural sector over the past two years, while the service sector (including trade, hotels and other catering services) has had credits up to 38% with construction at 20-21%.

The structural policies have become indispensable for Albania, when this is seen within the context of supply concentration in the internal production process, or the enormous allocation of financing and investment, the rapid modernization of agricultural and of the rural space. In this context, a very meaningful element of these policies is the organic agriculture and its contribution to be given to the Albanian agriculture yet (Leksinaj et al., 2009).
Organic farming in Albania

**Structure of organic farms in Albania**

The Organic agriculture in Albania is closely associated with the establishment of the Organic Agriculture Association (OAA) in 1997 in Tirana with the support of the international donors. From December 1998 onwards OAA proves to be an associated member of IFOAM. Over the 4 first years small projects have been executed, which have contributed to the increase and availability of information on organic farming. In this context a role has been played by international organizations such as Avalon, USAID, GTZ have carried out several projects by running promotion activities. In 2001 the SASA project (sustainable agricultural support in Albania) funded by the Swiss Cooperation for development (SDC) and SECO implemented by FiBL.

Other such organizations as Avalon, USAID and GTZ have also proposed a number of other projects which have allowed for the realization of other promotional activities.

Initially the Organic Agriculture Association was carrying out the functions of the farmers’ association which had adapted the organic method of cultivation, of the assistance and technical counselling, along with the control and certification of the organic farming. Afterwards seeing the existence of many roles for just a single association, with the risk becoming imminent from the emergence of conflict of interests, in 2006 the Organic Agriculture Association assumes the administration of the farmers’ association, BioAdra are established which deals in providing technical counselling as well as Albinspekt that will cover the functioning of certification of organic produce.

Only in January 2009 the Private standard of Bioadria is approved for organic farming with Albinspekt, upon the national accreditation, is recognized even from Ministry of Agriculture, Food and Protection of Consumers, (MAFPC), which is functioning in full conformity with the Albanian law 9199, dated 26.02.2004 on “Production, processing, certification and marketing of products “Bio”. With such recognition being granted Albinspekt as the only domestic certifying body in the country is capable of getting for its operators subsidies given by the state to the organic agricultural sector. The exported products will have to be certified by a foreign organization. In Albania there exist the following certification bodies: BioInspecta, ICEA, SCAL, BSC.

In close reference to the recent years it is worthwhile to underline the subsidies in the organic agricultural sector. In 2009, as was the case in 2008, the Albanian government offered a scheme for subsidies in organic agriculture, a scheme which is defined in Decision of Council of Ministers, no. 18, dated 7.1. 2009 on “Defining basic criteria of sectors that will be supported, along with the measures of benefits from the Agricultural Program Fund and Rural Development” as well as on the respective ordinances of Ministry of Agriculture, Food and Protection of Consumers and Ministry of Economy. In this Decision of Council of Ministers it has been set out there subsidies go to operators for the certification of bio agricultural products from the cultivated plants, including:

- for products targeting internal markets not less than 50 % of costs, but not larger than 20,000 leks/farms.
- for products intended for export, 50% of the costs of certification, but no more than 70,000 leks/farm/year;

The BIO certified operators including those who intend to implement this production method in 2009, should apply to Directorate of Agriculture in districts to get hold of such subsidies. The certification from Albinspekt is recognized for such a subsidy scheme.

**The perspectives of organic production in Albania**

It is reasonable to argue that in Albania, as in other countries, there exist the proper conditions for the distribution and commercialization of organic products. This potential should be exploited to the advantage of the future perspective of development of organic agriculture (Leksinaj, 2007). By acting in such a manner we would most likely observe an increase in the export of agricultural products towards the EU countries, taking into account the current problems and the costly certification.

In Table 1 the situation of the organic potential farms was included by applying the a SWOT analysis. According to the methodology of qualitative analysis the role of the interviews with privileged witnesses is that one which embraces the verification and integration of information that has
come from statistical data. Such an analysis, which join both a structural and dynamic-forecasting feature, is concerned with the economic, social and demographic aspects, not to mention the natural implications arising from the local developments, this seen from the urban and territorial perspectives.

The main requirement for identification of “witnesses” or “experts” has been their ability to recognize the territory and the local reality; they might also be mouthpieces of specific interests (which in fact several of them are), even though they appear to be experts representing much more general interests. The information obtained via the interviews has been formulated in a general fashion. Experts have brought in specific evaluations, which are related to the sector or areas where they have been practicing. Only in the final evaluation stage a coherent and general tableau of results has been set up in the form of the SWOT analysis.

Table 1. SWOT analysis

<table>
<thead>
<tr>
<th>Strong points</th>
<th>Weak points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full integration possibilities into supply chain</td>
<td>Small-sized farms</td>
</tr>
<tr>
<td>Low cost of labour force</td>
<td>Lack of a system of standard quality control</td>
</tr>
<tr>
<td>Favourable environmental conditions</td>
<td>Difficulties in identification of clients</td>
</tr>
<tr>
<td>Organizational powers</td>
<td>Difficulties in identification of suitable trade</td>
</tr>
<tr>
<td>Bigger opportunities from European markets</td>
<td>Difficulties in supply segment</td>
</tr>
<tr>
<td>Potential leadership in the internal markets</td>
<td>Lack of a price policy</td>
</tr>
<tr>
<td>Availability in innovations</td>
<td>Packaging and other non-suitable promotional instruments</td>
</tr>
<tr>
<td>Household traditions</td>
<td>Difficulties in keeping accounting data</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Threats</th>
<th>Possibilities</th>
</tr>
</thead>
<tbody>
<tr>
<td>A poorly defined snapshot of Albania as a producer of organic products</td>
<td>Demand on the rise</td>
</tr>
<tr>
<td>Barriers in exports owing to certification</td>
<td>Likely synergies among farmers</td>
</tr>
<tr>
<td>Competition among reputed farms</td>
<td>Availability in the market spaces</td>
</tr>
<tr>
<td>Technological viability</td>
<td>Benefits in the market</td>
</tr>
<tr>
<td>Lack of well-defined and clear internal reference norms</td>
<td>Differentiation in prices</td>
</tr>
<tr>
<td>Trade agreements</td>
<td>Availability of a technical assistance service</td>
</tr>
</tbody>
</table>

Source: Our direct processing work.

The weak and the strong points for the farms along with the possibilities and threats of the market of “organic” which have come to the fore in the environmental analysis have been selected and presented with the view to having a summary of issues that would help solve the implementation of productive strategies and marketing. The variables under consideration are a fruit of the joint work of authors and experts in the administration of farms. What it seems straightforward to notice is the existence of the general rules in favour of the objective “the attainment of a premium price from the organic products in the market, particularly in the European one” (Leksinaj et. al. 2009).

Conclusions

The perspectives of contribution to organic agriculture, aside from the market aspects, have to be seen in their broader sense. It should be argued that the creation of the organic agriculture might contribute to the conservation of the traditional customs and practices. The possibility of using a higher premium than labour might encourage the population to deal in agriculture for much longer.

Even the environmental aspect constitutes yet another determining factor to the development of organic agriculture. The agricultural activities have a significant impact on the structure, composition and quality of territory by provoking here and there degradation and impoverishment of the natural resources. The control over the utilization of the synthesis substances and other appropriate production techniques usher in benefits in both the territory and society, whose effects should work to keep the soils in good shape, in maintaining biodiversity and the sustainable development of rural areas.
The organic agriculture has proven that it is able to provide efficient possibilities on diversification and penetration into the market, this when reference is being made to both marginal and less developed areas. These possibilities do guarantee a satisfactory return for farmers and retains a satisfactory use of the natural resources. We recommend a series of interventions in the integrated organic system to occur over an efficient action plan at the national level that is primarily intended:
- to satisfy and make the normative framework on the sector much easier to be implemented;
- to promote organic agriculture at all levels;
- to organize with other links of supply chain at the start and at the end of the production cycle, that is by improving the availability of inputs, by promoting processing and the positioning of products in the market;
- to support the formation, research and extension
- to develop the organic product markets through a consolidation of the exports, as well as affair share of attention to the typology of the potential customers in the food market (urban populations with high incomes, tourists that appreciate the rural wealth and the nature of the country).

In this context the organic agriculture enters into a bond with the programs of territorial development and the ecological conservation of the landscapes by justifying any type of oriented support by means of measures and specific interventions in the context of the environment policies. The presence of such policies constitutes one of the development of a connection between policies of territory conservation and agriculture in the strategic activities of the development program of agriculture, programs where the environmental policies, tourism and organic agriculture constitutes the entirety of a sustainable solution and an evaluation of food products, in the rural development and the protection of territory.

References
Level of Heavy Metals and the Impact of Anthropogenic Pollution on Some Alternative Springs in Drenica and Mitrovica Zone – Kosovo

Islam Krasniqi¹, Islam Fejza², Sabri Avdullahi³, Majlinda Vasjari³, Kozeta Vaso¹ Kimete Krasniqi⁴, Aziz Behrami⁴

¹Department of chemistry, Pristine; ²University of Pristine, Faculty of Mining and Metallurgy, Mitrovica; ³University of Tirana, Department of Chemistry, Tirana; ⁴Department of Toxicology, Pristine, Kosova

Received January 19, 2010; Accepted April 21, 2010

Abstract: This paper studies the quality status of drinking water for the five alternative springs in Drenica and Mitrovica zone. There have been determined seven water physical and chemical parameters and the levels of eight heavy metals Fe, Zn, Mn, Cu, Ni, Cd and Pb. In parallel with the determination of physical and chemical values, we have also determined anthropogenic pollution (chemical and technological processes at “FERONIKEL” Smelter in Drenas). The determination of physical and chemical parameters had been carried out immediately after water sampling in springs, while the identification of levels of heavy metals had been made at the National Public Health Institution in Pristine by Spectrophotometer of Atomic Absorption in the flame of low level of the detection expressed in µg/ml or ppm. A calibrating curve on ppm levels of detection had been created for each metal and then the sample absorbance had been made. The research was carried out during the two seasons of summer-winter 2007-2008. The outcomes of physical-chemical parameters obtained for five springs are a result of average values permitted, and as for identified levels of heavy metals, some of them exceed MPV (maximum permitted value) of the WHO’s standards with all springs. Heavy metals result in higher levels than permitted by the World Health Organization (WHO’s) standards are Ni, Pb, Mn and Cr. The excess of permitted levels of the WHO with these springs may be attributed to geomorphologic structure and geochemical phone and anthropogenic pollution (. The fifth up-coming spring examined “Kroi i Fshatit”, located in Zhazhe results in very high levels of Ni, Pb and Mn, and same may not be used for drinking by the Community, even in emergent cases.

Keywords: heavy metals, geochemical phone, anthropogenic pollution, spectrophotometry of atomic absorption –SAA, springs.

Introduction

The study has treated five alternative springs in Drenica and Mitrovica, which can be used in emergent cases without preliminary treatment by the Community. There have been determined the levels of heavy metals and the impact of anthropogenic pollution (chemical and technological processes with "Ferronickel" Smelter in Drenas and "Trepça" Mine, in Mitrovica). The research was made during the summer – spring seasons 2008-2009. The Study includes the following springs:

1) Kroi i Mbretit, location Koretice e Larte, Drenas
2) Kroi i Fshatit location Dritan, Drenas
3) Xhurrama, location Shkabe, Drenas
4) Kroi i Fshatit location Krasaliç, Skenderaj
5) Kroi i Fshatit location Zhazhe, Mitrovica

Collecting basins in this Region are the river Drenica, Sitnica and Iber (Rugova et al, 1989). All the streams in the region examined with a slope from 5% to 17% gravitate in the direction of these basins [Anonym, (2003) Institute for the Development of Water Resources - Master Plan 1983–2003, Beograd]. The Plateau of Drenica, the zone of Çyçavice, as well as zone of Mitrovica have a harsh mounting continental climate. The annual quantity of rainfall on these zones varies from 680 mm – 790 mm.

* Corresponding: islamkrasniqi89@hotmail.com; Tel: +377044182016
From the geological aspect, this region consists of different types and ages of rocks. In the region of Mitrovica, village Zhazhe, dominate mainly volcanogenic rocks of Tertiary age (dacites, andesites, quartzlatites) and serpentinites, limestone’s, marbles, schist’s of older geological ages (Jurassics and Triussics). Along the river flows there are to be found quaternary deposits (Avdullahi et al., 2008). The spring examined in village Zhazhe is in conjunction with schist’s and carbonated rocks, serpentines, series of conglomerates, sediments of Cretaceous, deposits of Pliocene and Quaternary dominate on the region of Drenica (Vaso P (2005) Elaborate of geological characteristics of Baks Mine-Skenderaj, Kosovo). The Drenica spring is located between these contacts. From the administrative and geographical aspect the above-mentioned localities are located among the municipalities of Drenas, Skenderaj and Mitrovica.

**Purpose of Study**

The object of Study has been the research of physical and chemical characteristics of five alternative springs in the Drenica and Mitrovica zone, whose water could be used by the Community in cases of emergency and possible catastrophes as well as environmental disorder, without preliminary treatment (Avdullahi & Fejza, 2002).

**Materials and Methods**

During the research of these springs we have used the methods in used in the field and in laboratories. The work in the field included the determination of springs that are the object of the Study, determination of geographic coordinates, locality, municipality, and basin as well as the status of the spring, if it is usable or non-usable. The sampling relating to laboratory analysis was carried out in plastic dishes of one litter. The following is the determination of the parameters in the field: [Temperature, Electric Conductivity, pH, NTU, $O_2$, $O_3^-$]. The level of heavy metals: Fe, Zn, Mn, Cr, Cu, Ni, Cd dhe Pb was determined after bringing the samples in the Laboratory and the samples examined were analysed during the summer 2008 and spring 2009 seasons. To determine the quality of water there were used "Standard Methods for Examination of Water and Wastewater, “20” Edition“(APHA 1998). Instrumental methods are used for following analysis: Spectrophotometer of Atomic (Perkin Elmer) and Conduct meter - [Operating Manual-multi 340i]. The received samples were analysed at two laboratories of sate institutions, Hydrometeorologic Institute of Kosovo (HIK) – Pristine and National Public Health Institute of Kosovo in Pristine. Results are set out on the tables bellow and compared with permitted values according to World Health Organization (WHO).

**Results and Discussions**

We have presented bellow the tables of five springs examined. The tables set out the name of spring, coordinates, locality, municipality, basin, status of - usable or non-usable, period of sampling, maximum permitted values (MPV) as per WHO requirements as well as results obtained for physical and chemical parameters during a summer-winter 2007-2008 periods.

The table 1 shows the physical and chemical results obtained for 16 parameters in two zones of research. As can be seen from Table 1, the spring "Kroi i Mbreitit" falls into the zone of Drenica. It is partly used by the Community. The flowing capacity of the source is larger in spring season with 4.2 l/s, while the water temperature exceeded the levels permitted by the WHO’s requirements in summer 2007. Oxygen and dissolved oxygen result in higher levels in the spring season, due to increase of bringing capacity and supply with atmospheric oxygen. No turbidity during examination was shown by the analysed spring. The levels of heavy metals run within the maximum values permitted by the WHO’s standards, except for Nickel and lead (Wenzel et.al. 2002). These two metals had higher levels in two zones of examination in 2007-2008, compared to APV as per the WHO. The high level of Ni may be attributed to geochemical phone, and high level of Pb are attributed to anthropogenic pollution, which are perhaps a result of NATO’s bombarding, high frequency of vehicles in the vicinity of the spring (10m).
Table 1. The physical and chemical results obtained for 16 parameters in Spring "Kroi i Mbretit", Place of spring 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Units</th>
<th>Series I</th>
<th>Series II</th>
<th>MPV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flowing Quantity</td>
<td>l/s</td>
<td>3 l/s</td>
<td>4.2 l/s</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>T. Water</td>
<td>ºC</td>
<td>13.7</td>
<td>10</td>
<td>8-12</td>
</tr>
<tr>
<td>3</td>
<td>Conductivity</td>
<td>µS/cm</td>
<td>749</td>
<td>613</td>
<td>1500</td>
</tr>
<tr>
<td>4</td>
<td>Turbidity</td>
<td>NTU</td>
<td>0</td>
<td>0</td>
<td>1.2-1.4</td>
</tr>
<tr>
<td>5</td>
<td>pH</td>
<td></td>
<td>7.22</td>
<td>7.7</td>
<td>6.8-8.5</td>
</tr>
<tr>
<td>6</td>
<td>Oxygen</td>
<td>mg/l</td>
<td>4.8</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Dissolved Oxygen</td>
<td>%</td>
<td>41.8</td>
<td></td>
<td>56.4</td>
</tr>
<tr>
<td>8</td>
<td>Iron</td>
<td>mg/l</td>
<td>0.0438</td>
<td>0.0335</td>
<td>0.3</td>
</tr>
<tr>
<td>9</td>
<td>Zinc</td>
<td>mg/l</td>
<td>0.0084</td>
<td>0.006</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>Manganese</td>
<td>mg/l</td>
<td>0.0043</td>
<td>0.0039</td>
<td>0.05</td>
</tr>
<tr>
<td>11</td>
<td>Chrome</td>
<td>mg/l</td>
<td>0.017</td>
<td>0.0097</td>
<td>0.05</td>
</tr>
<tr>
<td>12</td>
<td>Copper</td>
<td>mg/l</td>
<td>n.d</td>
<td>n.d</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>Nickel</td>
<td>mg/l</td>
<td>0.0155</td>
<td>0.0137</td>
<td>0.001</td>
</tr>
<tr>
<td>14</td>
<td>Cadmium</td>
<td>mg/l</td>
<td>0.0018</td>
<td>0.0017</td>
<td>0.05</td>
</tr>
<tr>
<td>15</td>
<td>Lead</td>
<td>mg/l</td>
<td>0.038</td>
<td>0.0047</td>
<td>0.01</td>
</tr>
<tr>
<td>16</td>
<td>CQA as per Ion Equilibrium</td>
<td>%l</td>
<td>99.47</td>
<td>&gt;97</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Map of the Springs Examined
The table 2 shows the physical and chemical results of 16 parameters in two zones of examination. The spring "Kroi i Fshatit" Dritan falls into the zone of Drenica, and flows into Black Sea. It is partly used by the Community. Its flowing capacity is approximately the same as in two seasons, while the temperature of water results in higher values in two seasons, exceeding the permitted values of the WHO by 1 ºC, pH of water is neutral. Oxygen and dissolved oxygen kept same levels in the two seasons examined.

Table 2. The physical and chemical results of 16 parameters examined in Spring "Kroi i Fshatit", Place of spring 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Units</th>
<th>Series I</th>
<th>Series IV</th>
<th>MPV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flowing Quantity</td>
<td>l/s</td>
<td>1 l/s</td>
<td>1.2 l/s</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>T. Water</td>
<td>ºC</td>
<td>13</td>
<td>13</td>
<td>8-12</td>
</tr>
<tr>
<td>3</td>
<td>Conductivity</td>
<td>µS/cm</td>
<td>790</td>
<td>812</td>
<td>1500</td>
</tr>
<tr>
<td>4</td>
<td>Turbidity</td>
<td>NTU</td>
<td>0.42</td>
<td>0</td>
<td>1.2-1.4</td>
</tr>
<tr>
<td>5</td>
<td>pH</td>
<td></td>
<td>7.4</td>
<td>7.3</td>
<td>6.8-8.5</td>
</tr>
<tr>
<td>6</td>
<td>Oxygen</td>
<td>mg/l</td>
<td>4.2</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Dissolved Oxygen</td>
<td>%</td>
<td>48</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Iron</td>
<td>mg/l</td>
<td>0.0654</td>
<td>0.1063</td>
<td>0.3</td>
</tr>
<tr>
<td>9</td>
<td>Zinc</td>
<td>mg/l</td>
<td>0.0053</td>
<td>0.0089</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>Manganese</td>
<td>mg/l</td>
<td>0.0013</td>
<td>0.0083</td>
<td>0.05</td>
</tr>
<tr>
<td>11</td>
<td>Chrome</td>
<td>mg/l</td>
<td>0.0061</td>
<td>0.024</td>
<td>0.05</td>
</tr>
<tr>
<td>12</td>
<td>Copper</td>
<td>mg/l</td>
<td>0.0169</td>
<td>0.0216</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>Nickel</td>
<td>mg/l</td>
<td>0.0144</td>
<td>0.032</td>
<td>0.001</td>
</tr>
<tr>
<td>14</td>
<td>Cadmium</td>
<td>mg/l</td>
<td>0.0033</td>
<td>0.0017</td>
<td>0.05</td>
</tr>
<tr>
<td>15</td>
<td>Plumbi</td>
<td>mg/l</td>
<td>0.0343</td>
<td>0.0796</td>
<td>0.01</td>
</tr>
<tr>
<td>16</td>
<td>CQA per Ion Equilibrium</td>
<td>%</td>
<td>99.18</td>
<td>99.76</td>
<td>&gt;97</td>
</tr>
</tbody>
</table>

The levels of heavy metals result in average permitted values of the WHO, except for nickel (Ni) and lead (Pb). These two metals result in higher levels in the two seasons of examination, as compared to MPV of the WHO. The higher levels of Ni may be attributed to geochemical phone, while the high levels of Pb to anthropogenic pollution came from chemical and technological processes of "Ferronickel" Smelter, which is only 2 km away from the spring. High levels of lead may be a result of burning of the City wastes only 2 km away from the spring, and higher levels in the spring season may be a result of rinsing of these pollutions by atmospheric precipitations.

The table 3 shows the physical and chemical results of 16 parameters examined in this spring. The spring "Xhurrama" falls into the zone of Drenica, and flows into Black Sea. It is partly used by the Community. The flowing capacity of the spring is higher in spring season. The temperature of water is higher in summer season, by exceeding the permitted levels of the WHO by 1 ºC, and pH is mainly neutral. The dissolved oxygen results in higher levels in spring season, which may be attributed to capacity of bringing and supply with atmospheric oxygen. The levels of heavy metals are in compliance with the permitted levels of the WHO, except for nickel (Ni), lead (Pb), manganese (Mn) and chrome (Cr). These metals result in higher levels in both seasons of examination 2008-2009, compared to MPV of the WHO. The higher levels of Ni, Mn and Cr may be attributed to geographical
structure of the zone, and high levels of Pb are attributed to geochemical phone as a result of function of limy aquifers, good dischargers of water, 1.5 km far from the spring (Cillaj, 1990).

The Table 3 shows the physical and chemical outcomes of 16 parameters examined in this spring. The spring "Kroi i Fshatit" Krasaliq falls into the zone of Skenderaj and flows into Black Sea. It is a non-usable spring by the Community. The flowing capacity of the spring does not change through seasons. The temperature of water is within the average values permitted by the WHO, pH of water is mainly neutral. The dissolved oxygen results in higher levels in spring season. Higher levels in the second season of examination may be a result of more frequent atmospheric precipitation, which may enable the supply with atmospheric oxygen. The levels of heavy metals comply with the average values permitted by the WHO, except for nickel (Ni) and lead (Pb). These two metals result in higher levels in both seasons of examination 2008-2009, compared to MPV of the WHO. High levels of Ni and Pb may be attributed to geological structure of the zone and geochemical phone [1Km far away from Ferronickel Smelter].

**Table 3.** The physical and chemical results of 16 parameters examined in spring “Xhurrama”, Place of spring 3

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Units</th>
<th>Series I</th>
<th>Series IV</th>
<th>MPV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flowing Quantity</td>
<td>l/s</td>
<td>3 l/s</td>
<td>7 l/s</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>T. Water</td>
<td>ºC</td>
<td>13</td>
<td>11.7</td>
<td>8-12</td>
</tr>
<tr>
<td>3</td>
<td>Conductivity</td>
<td>µS/cm</td>
<td>774</td>
<td>815</td>
<td>1500</td>
</tr>
<tr>
<td>4</td>
<td>Turbidity</td>
<td>NTU</td>
<td>0</td>
<td>0</td>
<td>1.2-1.4</td>
</tr>
<tr>
<td>5</td>
<td>pH</td>
<td></td>
<td>7.5</td>
<td>7.25</td>
<td>6.8-8.5</td>
</tr>
<tr>
<td>6</td>
<td>Oxygen</td>
<td>mg/l</td>
<td>1.73</td>
<td>4.85</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Dissolved Oxygen</td>
<td>%</td>
<td>18.9</td>
<td>49.5</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Iron</td>
<td>mg/l</td>
<td>0.0757</td>
<td>0.069</td>
<td>0.3</td>
</tr>
<tr>
<td>9</td>
<td>Zinc</td>
<td>mg/l</td>
<td>0.0506</td>
<td>0.0955</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>Manganese</td>
<td>mg/l</td>
<td>0.0011</td>
<td>0.0047</td>
<td>0.05</td>
</tr>
<tr>
<td>11</td>
<td>Chrome</td>
<td>mg/l</td>
<td>0.0704</td>
<td>0.0712</td>
<td>0.05</td>
</tr>
<tr>
<td>12</td>
<td>Copper</td>
<td>mg/l</td>
<td>0.0704</td>
<td>0.068</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>Nickel</td>
<td>mg/l</td>
<td>0.0461</td>
<td>0.0432</td>
<td>0.001</td>
</tr>
<tr>
<td>14</td>
<td>Cadmium</td>
<td>mg/l</td>
<td>0.0065</td>
<td>0.0064</td>
<td>0.05</td>
</tr>
<tr>
<td>15</td>
<td>Lead</td>
<td>mg/l</td>
<td>0.0112</td>
<td>0.012</td>
<td>0.01</td>
</tr>
<tr>
<td>16</td>
<td>CQA as per Ion Equilibrium</td>
<td>%</td>
<td>98.32</td>
<td>98.16</td>
<td>&gt;97</td>
</tr>
</tbody>
</table>

The Table 5 shows the physical and chemical results of 16 parameters examined with the spring "Kroi i Fshatit ", which is to be found in village Zhazhe, Municipality of Mitrovica. It falls into the basin of river Iber and is partly used by the Community. The bearing capacity of this spring is small 0.234-0.295 l/s, the water temperature is a bit higher in summer season, when compared to the WHO’ standards. The pH of water is acidic in both seasons of examination (4.0 -3.92).

The dissolved oxygen has notably a higher value in spring season. The spring “Kroi i Fshatit" results in higher levels with heavy metals, Ni and Pb. The high levels of heavy metals are mainly as a result of geomorphologic structure of the zone, since the water resources are very near the Trepça Smelter (this can be seen on the Map, Figure 1).
The Figure 2 shows that there is a light outrun with the four first springs examined, compared to MPV as per the WHO, while heavy metals exceed extremely MPV with the spring “Kroi I Fashatit”- Zhazhe. The Figure 3 shows the level of heavy metals in percentage with the spring “Kroi I Fashatit”, located in Zhazhe, Municipality of Mitrovica. As can be seen from this Graph of the spring, Mn exceeds the levels permitted by the WHO’s standards by 64 %, Ni by 26 % and Pb by 10%. The results obtained from these springs show that there is a strong connection of heavy metals to the environment through which the water flows from the studied springs.

Table 4. The physical and chemical outcomes of 16 parameters examined in this spring. The spring "Kroi i Fshatit" Krasaliq, Skenderaj, Place of spring 4

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Units</th>
<th>Series I</th>
<th>Series IV</th>
<th>M.P.A.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>03.08.07</td>
<td>01.04.08</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Flowing Quantity</td>
<td>l/s</td>
<td>0.7 l/s</td>
<td>0.9 l/s</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>T. Water</td>
<td>ºC</td>
<td>11.3</td>
<td>11.4</td>
<td>8-12</td>
</tr>
<tr>
<td>3</td>
<td>Conductivity</td>
<td>µS/cm</td>
<td>1234</td>
<td>1334</td>
<td>1500</td>
</tr>
<tr>
<td>4</td>
<td>Turbidity</td>
<td>NTU</td>
<td>0</td>
<td>0</td>
<td>1.2-1.4</td>
</tr>
<tr>
<td>5</td>
<td>pH</td>
<td></td>
<td>7.33</td>
<td>7.1</td>
<td>6.8-8.5</td>
</tr>
<tr>
<td>6</td>
<td>Oxygen</td>
<td>mg/l</td>
<td>1.48</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Dissolved Oxygen</td>
<td>%</td>
<td>14.8</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Iron</td>
<td>mg/l</td>
<td>0.0428</td>
<td>0.0415</td>
<td>0.3</td>
</tr>
<tr>
<td>9</td>
<td>Zinc</td>
<td>mg/l</td>
<td>0.0129</td>
<td>0.0199</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>Manganese</td>
<td>mg/l</td>
<td>0.0092</td>
<td>0.0071</td>
<td>0.05</td>
</tr>
<tr>
<td>11</td>
<td>Chrome</td>
<td>mg/l</td>
<td>0.0199</td>
<td>0.0209</td>
<td>0.05</td>
</tr>
<tr>
<td>12</td>
<td>Cooper</td>
<td>mg/l</td>
<td>0.0086</td>
<td>n.d</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>Nickle</td>
<td>mg/l</td>
<td>0.0433</td>
<td>0.0249</td>
<td>0.001</td>
</tr>
<tr>
<td>14</td>
<td>Cadmium</td>
<td>mg/l</td>
<td>0.0026</td>
<td>0.0041</td>
<td>0.05</td>
</tr>
<tr>
<td>15</td>
<td>Lead</td>
<td>mg/l</td>
<td>0.0379</td>
<td>0.0428</td>
<td>0.01</td>
</tr>
<tr>
<td>16</td>
<td>CQA as per Ion</td>
<td>%</td>
<td>97.98</td>
<td>98.81</td>
<td>&gt;97</td>
</tr>
</tbody>
</table>

Figure 3. The level of heavy metals in percentage with the spring “Kroi i Fshatit”, Zhazhe
Figure 2. Level of Heavy Metals, compared to MPV as per the WHO.

Table 5. The physical and chemical results of 16 parameters examined with the spring "Kroi i Fshatit", Zhazhe, Municipality of Mitrovica, Place of Spring 5

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Units</th>
<th>Series I</th>
<th>Series II</th>
<th>M.P.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flowing Quantity</td>
<td>l/s</td>
<td>0.234 l/s</td>
<td>0.295 l/s</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>T. Water</td>
<td>ºC</td>
<td>13</td>
<td>12</td>
<td>8-12</td>
</tr>
<tr>
<td>3</td>
<td>Conductivity</td>
<td>µS/cm</td>
<td>297</td>
<td>317</td>
<td>1500</td>
</tr>
<tr>
<td>4</td>
<td>Turbidity</td>
<td>NTU</td>
<td>0</td>
<td>0</td>
<td>1.2-1.4</td>
</tr>
<tr>
<td>5</td>
<td>pH</td>
<td></td>
<td>4</td>
<td>3.92</td>
<td>6.8-8.5</td>
</tr>
<tr>
<td>6</td>
<td>Oxygen</td>
<td>mg/l</td>
<td>7.4</td>
<td>8.22</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Dissolve Oxygen</td>
<td>%</td>
<td>90</td>
<td>99.2</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Iron</td>
<td>mg/l</td>
<td>n.d</td>
<td>0.008</td>
<td>0.3</td>
</tr>
<tr>
<td>9</td>
<td>Zinc</td>
<td>mg/l</td>
<td>0.4921</td>
<td>0.482</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>Manganese</td>
<td>mg/l</td>
<td>1.791</td>
<td>1.804</td>
<td>0.05</td>
</tr>
<tr>
<td>11</td>
<td>Chrome</td>
<td>mg/l</td>
<td>0.0036</td>
<td>0.0028</td>
<td>0.05</td>
</tr>
<tr>
<td>12</td>
<td>Copper</td>
<td>mg/l</td>
<td>0.0553</td>
<td>0.0641</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>Nickel</td>
<td>mg/l</td>
<td>0.712</td>
<td>0.748</td>
<td>0.001</td>
</tr>
<tr>
<td>14</td>
<td>Cadmium</td>
<td>mg/l</td>
<td>0.0042</td>
<td>0.0087</td>
<td>0.05</td>
</tr>
<tr>
<td>15</td>
<td>Lead</td>
<td>mg/l</td>
<td>0.263</td>
<td>0.294</td>
<td>0.01</td>
</tr>
<tr>
<td>16</td>
<td>Perc. of Metals * Bearing Capacity</td>
<td>mg/l sec-1</td>
<td>0.777</td>
<td>1.006</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4. The levels of heavy metals determined in the laboratory per 1 L of water (mg/L) over the two seasons of examination 2007-2008.

Figure 5. The concentration of heavy metals (mg/L) in relation to Q = 1/s for the two seasons of examination in summer 2007 and in spring 2008 for five springs.

Conclusions

- Based on this research, we have concluded that these springs fall into the resources of a contact type, whose geochemical cycle changes from some months to some decades;
- Examined water resources are partly used by the population;
- The first four springs are mainly within permitted standards of the WHO. The levels are exceeded mainly by Ni and Pb.
- The spring "Kroi i Mbreitit", Koretice e Larte exceeds the levels of Ni and Pb. The higher levels of Ni are a result of geochemical phone, and higher levels of Pb are attributed to anthropogenic pollution – as a result of the high frequency of vehicles on the highway Peja- Pristine.
The spring "Kroi i Fshatit" Dritan, exceeds the levels of Ni and Pb. The high levels of Pb are a result of chemical and technological processes of “Ferronickel “Mine as well as of burning the wastes of City.

The spring "Xhurrama" Shkabe, exceeds the levels of Mn, Cr, Ni, and Pb. The high levels of these metals may be attributed to chemical phone and anthropogenic pollution.

The spring "Kroi i Fshatit" Krasaliç exceeds the levels of Ni and Pb. The high levels of Pb may be as a result of anthropogenic pollution and be attributed to geochemical phone.

The spring "Kroi i Fshatit"- Zhazhe, located in Mitrovica, results evidently in higher levels with heavy metals such as Mn, Ni, and Pb, compared to permitted values of the WHO. Such higher levels of heavy metals are mainly a result of geomorphologic structure of the zone where the springs fall into.

References
Vaso P (2005) Elaborate of geological characteristics of Baks Mine, Case study in this region Skenderaj, Kosovo.
Lead and Zinc Contents and Distribution in Mineral Deposit of Përroi i Ngjyrosur-Artana Ore Field (Kosovo)

Bedri Durmishaj1,∗, Sylejman Hyseni1, Ferat Shala2, Bislim Fetahaj3

1Faculty of Mining and Metallurgy, Mitrovica; 2Trepça-Enterprise under PAK Administration, Mitrovica; 3Mines with flotation, Kizhnica and Artana, Prishtina, Kosovo

Received March 11, 2010; Accepted April 26, 2010

Abstract: In this paper was presented the result of study of composition and distribution of lead, zinc, as two components of most economic significance in the mineral deposit Perroi i ngjyrosur (Artana) and main element of silver. The study was made in the thickness of ore bodies, within the scope of mineral ores as well as according to vertical depth of the deposit. The importance and interest of this study concerns not only the theoretical aspect but also the fact that in current situation there are attempts for reactivating large resources of the Republic of Kosovo, thus aiming also at the possibility of extending further research of polymetallic mineralization in the ARTANA ore field.

Key words: Distribution, lead, zinc, silver, deposit, Përroi i ngjyrosur (Artana).

Introduction

The mineral deposit of Perroi i ngjyrosur (Artana) is located around 18 km eastern of Prishtina (Figure 1), where 9Mt ore reserves with average content of 2.30% Pb, 2.50% Zn and 92 ppm Ag are calculated (Radoslav et al., 1989; Klisič, 1995; Fetahaj, 2007; Durmishaj, 2007). Main metallic components in this deposit are Pb, Zn and Ag, whereas other elements such as Cd, Bi, Au, etc. can be found in smaller quantities. The study is based on the data of Artana mine (Përroi i ngjyrosur) taken during the years of exploitation. The contents of main metals of Pb and Zn were analyzed in separate assays in chemical manner in the mine laboratory, whereas the contents of Ag, Cd, Bi, etc. were analyzed only in assays.

Figure 1. Geographical position of the Artana ore field

∗ Corresponding: E-Mail: bdurmishaj@yahoo.com; Tel: +377(0)44294077; Fax:028539202
Geological setting

The geological setting of the deposit is composed of the gneisses, amphibole schists, marbles, phyllites and andesites (Radoslav et al., 1989), Figure 2. All rocks were intensively changed. In the southeast and central part of the deposit, skarns and corneites are present, and their participation grows with the depth. Hydrothermal alterations are manifested as intensive pyritization, silification, carbonatization, sericitization, kaolinitization, and argillitization of the host rocks (Klisič, 1990).

The deposit is located in the central part of the ore structure 2 (Makresh-Artane-Lagja e Bullajve), Figure 3. The composition of the deposit is a complex one and it contains lead-zinc, siderite-smithsonite and halloysite ores.

![Figure 2. Geological map of the Artana ore field](image)

**Figure 2.** Geological map of the Artana ore field

The polimetallic mineral deposit of the Përroi ngjyrosur belongs to the group of contact-metasomatic-hydrothermal deposits forming in close connection with Tertiary tectonic-magmatic processes. The deposit of mineralisation was mostly done by metasomatic processes in the marble level, whose footwall is composed of gneisses and amphibolitic schists and the hanging wall of phyllites. The ore was deposited in free space along the contacts of various rocks and smaller ore bodies were forming in faults and fault zones. The deposit generally strikes from the submeridian to the NNW-SSE direction, with a dip into the western field at an angle of 60-80°, (Klisič, 1990).

**Location and morphological characteristics of ore bodies**

The sulphur mineralisation of lead-zinc is located in the different rock types. The mineralization located in limestone is of economic importance in the mineral deposit of Perroi ngjyrosur (Artana). Other the control factor of lead-zinc mineralisation, the structural factor is evident control in ore deposit. Different morphologies of the ore bodies are observed in deposit Perroi ngjyrosur. All ore bodies have elongated shapes and a thickness which varies from 2 to 60m.
Figure 3. The structure number 2 of the Artana ore field.

Mineralogical composition

Based on the studies conducted until now the polymetallic sulphur mineralization of the mineral deposit of Perroi ngjyrosur (Artana) belongs to the subvolcanic type of pneumatholite-hydrothermal phase of tertiary metalogenesis (Rakić et al. 1978; Smejkal, 1960; Smejkal et al. 1956).

The main mineralogical paragenesis of lead-zinc ore bodies are the sulphide paragenesis with sphalerite, galena and pyroline, the siderite-smithsonite, the paragenesis of alumino-silicate minerals, group of kaolinite (Halloysite), and paragenesis of oxide minerals like psilomelane. The mineral deposit Perroi i ngjyrosur is mostly composed of pyrite, sphalerite and galenite, as well as of pyrrhotite and magnetite in the deeper parts. All other minerals (arsenopyrite, chalcopyrite, tetraedrite, boulangerite, cubanite etc) are present as mineralogical occurrences.

The main accumulation of zinc is related to the mesothermal phase, whereas that of lead is of later phase. After an evaluation based on the average mine results (Durmishaj B., et al 2003 & Durmishaj B., 2007), the Zn content is higher in Hajvali and Përroi ngjyrosur deposits (respectively 14.4 and 5.5%) with a predomination over the Pb content (9.4 and 4.4 % respectively). In contrary, in Badovc and Kizhnica deposits the Pb content (5.5 and 6.9%) is higher than Zn content (2.6 and 1.5% respectively). The Ag content is higher in Perroi ngjyrosur deposit (125 ppm) and then in Hajvali, Badovc and Kizhnica deposits (108.83 and 74 ppm respectively). Ag is correlated with Pb in all deposits except Kizhnica deposit where a correlation with Zn and As is observed.

Electron probe analysis (Durmishaj B. et al, 2006) show that galena is quite pure with sporadic high Ag content (up to 100 ppm). Sphalerite has high Fe content (up to 13%Fe in Kizhnica) with sporadic high Ag content. In pyrites Co predominates over Ni and Bi over Sb. Arsenic content in pyrite is higher (up to 1.3% As) than in chalcopyrite. Platinum group elements are found sporadically, but sometimes in high contents, in all three main minerals (galena, sphalerite and pyrite) of the mineral deposits of Hajvali, Badovc, Kizhnica and Përroi i ngjyrosur-Artana ore field.

Distribution of usable metals in mineral deposit “Përroi i ngjyrosur” (Artana)

Here we summarized the study of the distribution of main elements: lead, zinc and silver- according to thickness, within the limited scope of ore bodies and the depth of deposit- and for this we used the
results of analysis of samples taken from the deposit during the phase of exploitation. The analyses were made in the laboratory of the mine (Kizhnica and Artana), Prishtina.

Distribution according to the thickness of ore bodies

For this study we selected the ore bodies with their representation in the deposit; in particular, ore body 2 found in different excavated levels was taken for study. In figures 4 and 5 we presented the contents and distribution of the useful components of lead and zinc and relation Zn/Pb in the thickness of the ore body 2 in different levels of the deposit.

The corridors of the V-th and VIII-th level of the mineral deposit Përroi i ngjyrosur (Artana) studied by us do not show a characteristic distribution of Zn and Pb with an increase in the central parts of the ore bodies and gradual decrease on their sides. But sometimes in ore bodies and in different levels of the deposit there are cases of better correlation of Zn with Pb (Figure 5), however in general there is a lack of correlation of contents of these metals. In order to bring forth this fact, in the abovementioned figures we presented the oscillations of the relation Zn/Pb. This relation, in the cases of...
presented by us oscillates averagely from 0.9 to 2 but in separate samples we find values from 0.2 to 8.2. If the relation 0.9 to 2 can be considered a characteristic of Përroi i ngjyrosur deposit, of the chemical compositions of hydrotherms respectively, the frequent oscillations over these average values in separate samples should indicate certain local conditions (Durmishaj B., 2007).

To conclude, the distribution of main metals (Pb, Zn) usable through the thickness of ore bodies in Përroi i ngjyrosur deposit is heterogeneous, mainly controlled by lithologic factor and intensity of chemical activity of hydrotherms. There results a non correlation of Zn compositions with those of Pb in some cases (Figure 2), and relation Pb/Zn oscillates between values 0.9-2.0.

**Distribution within ore bodies along a level**

In order to observe the distribution of the abovementioned metals inside the ore bodies, we selected the most represented mineral ores in the deepest level exploited. For this purpose we studied a great number of representative samples of the studied deposit. The analyses were made in the laboratory of the mine (Kizhnica and Artana). In order to better observe the distribution of Pb and Zn we drafted maps of distribution of these elements within ore bodies according to the inverse distance method using SURFER program.

In Figures 6, 7 and 8, we presented the interpolated values of the contents of lead, zinc and silver in the limited surface of the ore bodies 1 and 2 in the deepest level exploited (Durmishaj B., 2007). In the ore body 1, we observed an area with high concentration of Pb over 15% surrounded with other areas where the Pb composition falls gradually. Often these areas directly contact with surrounding rocks. Nevertheless, the areas with the highest values of Zn over 15% do not relate with those of Pb, which shows a spatial non correlation of these two elements. In addition, in ore body 2, we observed some epicenters with high concentration, over 20%, of Zn, which are surrounded by other areas where the Zn composition falls gradually. Then we observed that often some of these epicenters directly contact with surrounding rocks. Contrary to ore body 1, in ore body we observed that epicenters with highest values of Zn, over 20%, are to some extent related to those of Pb, which shows a sort of spatial correlation between these two elements.

In Figure 6, we presented interpolated values of Pb and Zn for the ore bodies 1 and 2 in the VIII-th level. In the below maps we can observe a non homogeneous distribution of these elements within the ore bodies. Thus, we can observe an epicentre with high concentration of Zn, over 10%, which normally is surrounding by other areas where its compositions fall gradually. Also, these epicenters and areas often directly contact with the surrounding rocks. Whereas, the high values of Pb, over 6%, do not relate with those of Zn which shows that there is no spatial correlation between these two elements.

In figure 7, we presented interpolated values of Pb and Zn for the ore body 2 in the VI-th level. In the below maps we can observe a non homogeneous distribution of these elements within the ore bodies. Thus, we can observe an epicentre with high concentration of Zn, over 10%, which normally is surrounding by other areas where its compositions fall gradually. Also, these epicentres and areas often directly contact with the surrounding rocks. Whereas, the high values of Pb, over 6%, do not relate with those of Zn which shows that there is no spatial correlation between these two elements. We also studied the distribution of Ag and Au within the ore body 2 in the VI-th level and then we compiled geochemical maps for the interpolated values of Au and Ag as in figure 8.

Based on above said we conclude, the distribution of components of Pb and Zn within the ore bodies of the deposit under study is heterogeneous and apparently it is controlled by lithological factor but also by the physical-chemical conditions of crystallization. These epicentres with high values of Pb do not relate with high values of Zn, which shows a spatial non correlation of Pb and Zn compositions within the ore bodies. But, sometimes in this deposit there are cases when the epicentres with high values of Zn somewhat relate to those of Pb, which shows a weak spatial correlation between these two elements. As far as the distribution of Ag and Au within the ore bodies is correlated, from this study it results that there is a non homogeneous distribution of these very important elements in the abovementioned deposit. The epicentres with high values of Ag (over 180 ppm) do not relate to those of Au (over 1 ppm) which does not show a spatial correlation between them.
Figure 6. Interpolated values of Pb and Zn for ore bodies 1 and 2 in the deepest level exploited (VIII-th 620 m) of the mineral deposit Përroi i ngjyrosur (Artana).

Figure 7. Interpolated values of Pb and Zn for ore body 2 in the VI-th level (760 m) of the mineral deposit Përroi i ngjyrosur (Artana)
Figure 8. Interpolated values of Ag and Au for ore body 2 in the VI$^{th}$ level (760 m) of the mineral deposit Përroi i ngjyrosur (Artana).

Distribution of Pb, Zn and Ag in ore bodies from the surface towards the depth

In order to study the authenticity of the change in the hydrothermal activity in separate ores we calculated the quantity of metals (in tons) deposited in each level per meter height (Durmishaj B., 2007). In the following figures we presented the quantity deposited of main metals exploited from the hydrotherms from the deposit as well as Zn/Pb relation among them. In figure 9, we presented the quantity of the components of Pb and Zn in ore bodies provided by hydrotherms as well as the change in geochemical behavior between them according to the exploited levels.

Figure 9. The quantity of Pb and Zn deposited by hydrotherms from the surface towards the depth, ore body 1 of the mineral deposit Përroi i ngjyrosur (Artana).

Such geochemical behavior of these metals is apparent through the relation Pb/Zn in figure 10.
Figure 10. The Zn/Pb relation in ore body 1 from the surface towards the depth of the mineral deposit Përroi i ngjyrosur (Artana).

Whereas in Figure 11, we presented the quantity of Ag in ore body 1 according to the levels provided by hydrotherms.

Figure 11. The quantity of Ag in ore body 1 according to the levels provided by hydrotherms, mineral deposit Përroi i ngjyrosur (Artana).

In Figure 12, we presented the quantity of components of Zn and Pb in ore body 2 provided by hydrotherms as well as change in geochemical behavior between them according to levels.

Figure 12. The quantity of Pb and Zn deposited by hydrotherms from the surface towards the depth, ore body 2 of the mineral deposit Përroi i ngjyrosur (Artana)
Such geochemical behaviour of Pb and Zn is apparent through the relation Pb/Zn show in Figure 13.

Figure 13. The Zn/Pb relation in the ore body 2 deposited by hydrotherms from the surface towards the depth of the mineral deposit Përroi i ngjyrosur (Artana).

Whereas in Figure 14, we presented the quantity of Ag in ore body 2 according to the levels provided by hydrotherms.

Figure 14. The quantity of Ag provided by hydrotherms from the surface towards the depth, ore body 2 of the mineral deposit Përroi i ngjyrosur (Artana).

From our geochemical study we conclude: the deposit under study is not genetically closed in the deepest exploited levels. On the contrary, from the geochemical point of view there should be expected a development even in deeper areas of ore bodies, at least with the same mineralization intensity as in the deepest exploited levels. The Zn/Pb relation in mineral deposit Përroi i ngjyrosur (Artana) is different with some maximums around 2 (level 680 m) and minimums under 1.5 (levels 847 and 760 m) in the entire ore body 2, whereas in ore body 1 this relation is approximately the same around 0.5 in the entire ore body (mineral deposit) with the exception of deepest parts exploited where there is an increase in this relation approximately 1.5.

References
Durmisaj B, (2007) Perspective and potential of the ore field of “Hajvali-Badovc-Kizhnice” based in geological - geochemical study (PhD), Faculty Geology and Mining in Tirana, Albania.
Smejkal S, (1960) Structure, mineralisation, mineral paragenesis and genesis of Kopaonic district lead-zinc deposits, PhD, MGFU, Belgrade.
Effects of Lead (PbCl₂) Stress on Germination of Lentil (Lens culinaris Medic.) Cultivars

Alihan Cokkizgin

Kahta Vocational School, Adiyaman University, Kahta, Adiyaman, 02400, Turkey

Received March 09, 2010; Accepted May 21, 2010

Abstract: Heavy metals in soil, water and air are cause of pollution. They are one of the most important environmental pollutants and reaching dangerous amount requires more research. This study was conducted to investigate the effects of lead (PbCl₂) stress on germination of different lentil cultivars. Seeds of four different lentil (Lens culinaris Medic.) cultivars (Fırat-87, Sakar, Seyran-96 and Yerli Kırmızı) were placed in the temperature adjustable germination cabinet at 15°C with 10 different lead solutions (Control, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 mM) and germination percentage, mean germination time, vigour index, plumule length and radicle length were observed. Lead concentrations showed negative effect on germination percentage, mean germination time, vigour index, plumule length and radicle length. Lead concentrations decreased germination percentage, vigour index, plumule length, radicle length and increased mean germination time. Fırat-87 cultivar was determined to be more sensitive to lead pollution. On the other hand, Yerli Kırmızı cultivar compared to other varieties was found to be relatively resistant to PbCl₂.

Key Words: Lentil (Lens culinaris L.), PbCl₂, germination, vigour index, plumule and radicle length

Introduction

Rapid industrialization has led to increased disposal of wastewater into the environment, which often exceeds the admissible sanitary standards resulting in adverse impact on aquatic habitats and consequently on human health (Kapoor & Viraraghavan, 1995; Jongle rtjunya, 2008). Heavy metals in soil, water and air are cause of pollution. Heavy metals are one of the most important environmental pollutants (Kirbag & Munzuroglu, 2003). An unfortunate consequence of industrialization and industrial production is the generation and release of toxic waste products which are polluting our environment (Gondal & Hussain, 2007). Owing to industrial development and population expansion, heavy metal pollution in water environment is increasing. Heavy metals raises the concern that the surrounding environment may be adversely affected if these residues are used as material for construction or are improperly landfilled (Shimaoka et al., 2002). Lead exists in many forms in natural sources throughout the world, and is now one of the most widely and evenly distributed heavy metals (Nriagu, 1992). Lead metallurgy is one of the most important sources of Pb pollution in the environment. The impact of base metal smelting on soil contamination is a well-known phenomenon on numerous smelting sites (Dumat et al., 2001; Kabala & Singh, 2001; Morin et al., 1999; Rieuwerts et al., 1999). It has recently received much attention as a hazardous pollutant to human and animals. Pb is found in accumulator industry sludge, toy production, printing, petroleum industry, waste water and exhaust gases (Demirezen & Aksoy, 2004).

Studies showed that soils have generally major lead amounts. Exhaust gases, mines, metal plants, industrial activities, lead contaminated waste and fertilization are cause of lead pollution (Zakrzewski, 1991). Pb is not essential for plant growth and considered as toxic at the concentration of 30-300 μg g⁻¹ in plant tissues (Ross, 1994). Among the heavy metals, lead (Pb) also might exhibit a high toxicity to photosynthesis, but few studies have focused on the effects of Pb on photosynthesis (Prasad & Hagemeyer, 1999; Neelima et al., 1991).

Heavy metals are one of the most important environmental pollutants. Studies showed that lead caused decrease of seed germination, radicle and plumule elongation (Fargasova, 1994; Lane & Martin, 1980), prevention of chlorophyll biosynthesis (Hamm & Lendzian, 1974; Miranda & Ilangovan, 1996), chlorosis (Johnson et al., 1977; Johnson & Proctor, 1977), inhibition of photosynthesis (Bazzaz et al., 1974), induction or inhibition of most of enzymes (Van Assche &
deterioration of cell structure (Fargasova, 1994; Liu et al., 1994; Levan, 1945; Xiong, 1997). This studies that showed lead had negative effect on germination, growth and yield (Kiran & Munzuroğlu, 2004). This study was performed for determination of the lead pollution effects on different lentil cultivars.

Materials and Methods

Lentil Cultivars
This laboratory study was conducted at Faculty of Agriculture, Kahramanmaras Sutcu Imam University and Kahta Vocational School, Adiyaman University in 2010. Four lentil cultivars were used and their seeds were obtained from Southeast Agricultural Research Institute (Fırat-87, Seyran-96 and Yerli Kırmızı cultivars) and Dicle University, Faculty of Agriculture, Field Crops Department (Sakar cultivar).

PbCl$_2$ Solutions
PbCl$_2$ (Lead II Chloride) were obtained from Sigma-Aldrich and prepared by using of distilled water (Kiran and Sahin, 2005). Four different lentil (Lens culinaris Medic.) cultivars (Fırat-87, Sakar, Seyran-96 and Yerli Kırmızı) were placed in the temperature adjustable plant growth cabinet at 15°C with 10 different lead solutions (0.0(Control), 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 mM) during 24 hour. Having 25 seeds in each petri dish, 4 replications were used. Then, seeds were washed and placed in germination cabinet at a temperature of 15 ± 0.5 °C for 10 days. During this period the petri dishes were observed daily (Tanveer et al., 2010).

Germination Percentage (%)
Germinated seeds were counted daily according to the seedling evaluation procedure in the Handbook of Association of Official Seed Analysts. The number of germinated seeds was recorded every 24 h (Anonymous, 1990). Ten days after germination, the germination percentage (GP) was calculated using the formula in below for each replication of the treatment (Tanveer et al., 2010).

\[
GP = \frac{\text{Germinated Seed}}{\text{Total Seed}} \times 100
\]

Mean Germination Time (days)
Mean germination time (MGT) was calculated according to the equation of Ellis and Roberts (1981),

\[
MGT = \frac{\sum D \sum n}{\sum n}
\]

where, n is the number of seeds that germinated on day D, and D is the number of days counted from the beginning of germination.

Vigour index
Vigour index (VI) was calculated by using formula of Baki and Anderson (1973) as shown below,

\[
VI = [\text{MPL} + \text{MRL}] \cdot \text{GP}
\]

In formula, MPL: Mean plumule length, MRL: Mean radicle length and GP: Germination Percentage (%).

Plumule Length and Radicle Length (cm)
The length of radicle and plumule were measured in centimetres from the point where the radicle and plumule joins together at the end of the radicle and to the top of the plumule. (Tanveer et al., 2010).

Data Collection
Experimental design was a complete randomized blocks (CRD) with four replicates. Data were subjected to analysis of variance using SAS statistical software (Anonymous, 1997) and mean
separation was performed by Fisher’s least significant difference (LSD) test if F test was significant at P < 0.01.

**Results and Discussion**

Significant differences was determined between cultivars and PbCl₂ treatments. Lead affected germination percentage, mean germination time, vigour index, plumule length and radicle length. All these parameters were decreased with increasing lead (II) chloride level, except mean germination time. On the other hand, cultivar x PbCl₂ concentration interactions were found to be statistically significant for all parameters studied (Table 1).

**Table 1.** Analysis of variance for germination percentage (GP), mean germination time (MGT), vigour index (VI), plumule length (PL) and radicle length (RL) of lentil

<table>
<thead>
<tr>
<th>Source</th>
<th>Degree of freedom</th>
<th>GP</th>
<th>MGT</th>
<th>VI</th>
<th>PL</th>
<th>RL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cultivars</td>
<td>3</td>
<td>392.090**</td>
<td>2.030**</td>
<td>602686**</td>
<td>5.383**</td>
<td>0.268**</td>
</tr>
<tr>
<td>PbCl₂ Concentration</td>
<td>9</td>
<td>436.680**</td>
<td>1.016**</td>
<td>1040309**</td>
<td>10.424**</td>
<td>6.677**</td>
</tr>
<tr>
<td>Cultivars X PbCl₂</td>
<td>27</td>
<td>18.00**</td>
<td>0.799**</td>
<td>18344.6**</td>
<td>0.156**</td>
<td>0.326**</td>
</tr>
<tr>
<td>Error</td>
<td>117</td>
<td>17.456</td>
<td>0.076</td>
<td>1278.6</td>
<td>0.026</td>
<td>0.015</td>
</tr>
<tr>
<td>Total</td>
<td>159</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CV (%)</td>
<td></td>
<td>7.010</td>
<td>5.339</td>
<td>7.430</td>
<td>3.827</td>
<td>3.602</td>
</tr>
<tr>
<td>Means</td>
<td></td>
<td>59.60</td>
<td>5.17</td>
<td>481.24</td>
<td>4.19</td>
<td>3.37</td>
</tr>
</tbody>
</table>

**, Significant at 0.01

**Germination percentage**

The results indicated that differences among treatments and cultivars were significant (Table 2 and Table 3). The highest germination percentage was obtained from control (99.5%) whereas the lowest was obtained from 4.5 mM PbCl₂ solution (28.3%). The germination percentage was decreasing while the lead concentration was increasing, which shows that higher lead concentrations inhibit the germination (Fargasova, 1994; Kiran & Munzuroglu, 2004; Wierzbicka & Obidzinska, 1998). This can be also due to the toxic effects of ions on the germination process (Khajeh-Hosseini et al. 2003). Cultivar Yerli Kırmızı (73.2%) showed the highest germination percentage while Firat-87 (46.5%) had the lowest one. Germination patterns could be different between species and between different varieties (McWilliam & Phillips, 1971; Therios, 1982).

**Table 2.** Effect of PbCl₂ concentrations for all parameters

<table>
<thead>
<tr>
<th>PbCl₂ concentrations (mM)</th>
<th>Germination percentage (%)</th>
<th>Mean germination time (days)</th>
<th>Vigor index</th>
<th>Plume length (cm)</th>
<th>Radicle length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 (Cont.)</td>
<td>99.5 a</td>
<td>4.95 c</td>
<td>944.5 a</td>
<td>5.24 a</td>
<td>4.25 a</td>
</tr>
<tr>
<td>0.5</td>
<td>86.3 b</td>
<td>4.98 c</td>
<td>811.8 b</td>
<td>5.14 a</td>
<td>4.23 a</td>
</tr>
<tr>
<td>1.0</td>
<td>70.5 c</td>
<td>5.06 c</td>
<td>620.5 c</td>
<td>4.83 b</td>
<td>3.88 b</td>
</tr>
<tr>
<td>1.5</td>
<td>63.8 d</td>
<td>5.04 c</td>
<td>546.1 d</td>
<td>4.73 b</td>
<td>3.75 c</td>
</tr>
<tr>
<td>2.0</td>
<td>58.5 e</td>
<td>5.03 c</td>
<td>466.8 e</td>
<td>4.41 c</td>
<td>3.48 d</td>
</tr>
<tr>
<td>2.5</td>
<td>56.3 e</td>
<td>5.03 c</td>
<td>411.7 f</td>
<td>4.14 d</td>
<td>3.13 e</td>
</tr>
<tr>
<td>3.0</td>
<td>51.5 f</td>
<td>5.09c</td>
<td>354.0 g</td>
<td>3.82 e</td>
<td>3.01 f</td>
</tr>
<tr>
<td>3.5</td>
<td>47.0 g</td>
<td>5.46 b</td>
<td>295.5 h</td>
<td>3.50 f</td>
<td>2.73 g</td>
</tr>
<tr>
<td>4.0</td>
<td>34.5 h</td>
<td>5.29 b</td>
<td>208.7 i</td>
<td>3.28 g</td>
<td>2.70 g</td>
</tr>
<tr>
<td>4.5</td>
<td>28.3 i</td>
<td>5.73 a</td>
<td>153.0 j</td>
<td>2.90 h</td>
<td>2.49 h</td>
</tr>
<tr>
<td>LSD</td>
<td>2.9</td>
<td>0.19</td>
<td>25.0</td>
<td>0.11</td>
<td>0.09</td>
</tr>
</tbody>
</table>

_Different letters show that significant differences at 0.01 level_

**Mean Germination Time**

The highest mean germination time was observed in 4.5 mM PbCl₂ solution (5.73 days). It showed that average velocity of germination in this treatment is the slowest. The shortest mean number of days
of germination was observed in control with 4.95 days, followed by other treatments (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mM PbCl₂ solution). When we compared the control treatment to the 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mM PbCl₂ treatments, the observations there are significant differences among the treatments. (Table 2). The highest mean germination time increases when the lead concentration increased which meant increased lead concentration caused a decrease in germination velocity. Inhibitions of germination and increase in germination time of lentil are supported by Stavrianakou et al. (2004), Dongre and Yadav (2005), Kadioglu et al. (2005), Tanveer (2010).

Significant variation on mean germination time was found among the lentil cultivars. The highest mean number of days of germination belonged to Firat and Sakar cultivars (5.37 and 5.33 days respectively). It showed that mean velocity of germination in this cultivars was very slow. The shortest number of days of germination was observed in Yerli Kırımızı (4.89 days) indicating its high germination velocity (Table 3). This cultivar had highest velocity of germination, resulted from its high genetic potential. Similar findings were stated by Tanveer (2010).

**Table 3. Effects of lentil cultivars for all parameters**

<table>
<thead>
<tr>
<th>Cultivars</th>
<th>Germination percentage (%)</th>
<th>Mean germination time (days)</th>
<th>Vigour index</th>
<th>Plumule length (cm)</th>
<th>Radicle length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Firat-87</td>
<td>46.5 d</td>
<td>5.37 a</td>
<td>351.9 d</td>
<td>3.69 c</td>
<td>3.27 c</td>
</tr>
<tr>
<td>Sakar</td>
<td>50.5 c</td>
<td>5.33 a</td>
<td>405.5 c</td>
<td>4.24 b</td>
<td>3.35 b</td>
</tr>
<tr>
<td>Seyran-96</td>
<td>68.2 b</td>
<td>5.08 b</td>
<td>554.6 b</td>
<td>4.27 b</td>
<td>3.36 b</td>
</tr>
<tr>
<td>Yerli Kırımızı</td>
<td>73.2 a</td>
<td>4.89 c</td>
<td>613.0 a</td>
<td>4.58 a</td>
<td>3.47 a</td>
</tr>
</tbody>
</table>

LSD 1.9 0.12 15.8 0.07 0.05

Different letters show that significant differences at 0.01 level

**Vigour Index**

There was a direct relation between lead (II) concentration and reduction in vigour index because the PbCl₂ concentration level increased while the vigour index decreased (Table 2). The highest vigour index was obtained from control (944.5) whereas the lowest vigour index was obtained from 4.5 mM PbCl₂ solution (153.0). Similar results were observed by Channappagoudar et al. (2005). There were significant differences among lentil cultivars in terms of vigour index. The highest vigour index belonged to Yerli Kırımızı cultivars (613.0) and the lowest vigour index belonged to Firat-87 (351.9). These rates could be resulted from their genetic potentials which support the report of Ganesh et al. (2009).

**Plumule length**

The highest plumule length was observed in control and 0.5 mM PbCl₂ treatments with 5.24 and 5.14 cm respectively. The seeds treated with lead showed significant difference to control and 0.5 mM PbCl₂. The shortest plumule length was observed less than 4.5 mM lead concentration (2.90 cm). When comparing the control and 0.5 mM lead treatment with the other treatments, particularly to the high lead concentrations, the observations showed significant differences (Table 2). The plumule length decreases while the lead concentration increased. The presence of inhibitory chemicals in higher concentrations might be the reason for differential behaviour of the extracts and maximum reduction in seedling growth (Fargasova, 1994; Kumar & Singh 1991; Shukla et al. 2003).

Substantial variation on plumule was found between lentil cultivars (Table 3). Among cultivars the highest plumule length belonged to Yerli Kırımızı (4.58 cm) but least plumule length belonged to Firat-87 cultivar (3.69 cm). Similar results were observed by Ganesh et al. (2009). Germination patterns could be different between species and between different varieties (McWilliam & Phillips, 1971; Therios, 1982).

**Radicle length**

There were significant differences among PbCl₂ concentrations and cultivars for radicle length. The highest radicle length was observed in control with 4.25 cm, followed by 0.5 mM PbCl₂ treatment (4.23 cm), whereas the lowest radicle length was obtained from 4.5 mM PbCl₂ concentration with 2.49 cm. The radicle length decreases while the lead concentration increased, which shows that higher
concentrations inhibit radicle length (Table 2). The highest concentration of lead (4.5 mM) showed the least radicle length (2.49 cm). Our findings are similar to ones of Kiran and Munzuroglu (2004).

On the other hand, the tallest radical one belonged to Yerli Kirmizi cultivars with 3.47 cm and the shortest radical one belonged to Firat-87 with 3.27 cm (Table 3). These rates could be resulted from their genetic potentials. The result was in parallel to the findings of Bybordi and Tabatabaei (2009). In conclusion, the use of the PbCl₂ caused significant decreases in germination percentage, vigour index, plumule length and radicle length while mean germination time increase. The negative effect of high concentration of the PbCl₂ was clearly observed. The results also revealed that significant variation is found between cultivars in all parameters. Firat-87 cultivar was determined to be more sensitive to lead pollution. On the other hand, Yerli Kirmizi cultivar compared to other varieties was found to be relatively resistant PbCl₂.

References


Photosynthesis Rates and Growth Responses of the Desert Shrub *Calotropis procera* to NaCl Salinity

Tahar Boutraa* and Abdellah Akhkha

Department of Biology, Faculty of Sciences, University of Taibah, Al-Madinah Al-Munawarah, Kingdom of Saudi Arabia

Received March 28, 2010; Accepted May 10, 2010

**Abstract:** Soil salinity is a major environmental constraint that limits plant growth and development. *Calotropis procera* is one of the plant species in vast areas of semiarid and arid regions worldwide subjected to harsh environments typically known with severe drought, high temperature and salt stress. To examine the effects of salinity on this plant species, a pot experiment was carried out in growth chamber at the Department of Biology, University of Taibah, at Al-Madina Al-Munwara, Kingdom of Saudi Arabia. Plants grown in plastic pots containing compost were subjected to four salt treatments; 0, 75, 150 and 300 mM NaCl. Photosynthesis and growth parameters, including plant height, number of leaves, leaf area and dry weight were evaluated. Growth was progressively declined, as salt concentration increased. Significant reductions were recorded in plant height, number of leaves and leaf area and plant biomass of all plant parts (stem, leaves and roots). NaCl significantly reduced the total fresh weight, but no effects on total dry weight were found. The photosynthetic capacity was significantly decreased under high saline condition.

**Keywords:** *Calotropis procera*, salt stress, photosynthesis efficiency, growth.

**Introduction**

The extension of irrigated agriculture using extensive water resources, which is characterized by low rainfall and high evapo-transpiration rates, has greatly contributed to the salinity effects in soil and ground water (Lambers, 2003). Salinity is a major problem in semi arid and arid regions, where soil salt levels are high and accompanied by low precipitation that reduces the leaching capacity of salts (Heidari-Sharifabad and Mirzaie-Nodoushan, 2006). Soil salinisation is considered to be a major cause of desertification, and elevated salinity affects approximately 1 billion ha of land worldwide (Maas and Hoffman, 1977; Abrol et al., 1988). It has been also estimated that soils of 32 million ha out of 500 million ha of dry land are affected by salt accumulation (FAO, 2005), resulting in large reduction in plant productivity. One of the approaches to diminish the risks of salts is plantation of salt species that can improve the remediation of salts (Oba et al., 2001). The establishment of vegetation in saline areas is likely to combat desertification and play a major role in remediation of certain saline soils (Imada et al., 2009). One of the most acceptable approaches to reduce salinity problems is the domestication of halophytes in saline areas (Koyro, 2006). Salts levels might be also reduced through the uptake of salts by the root systems of salt tolerant plant species (Lambert & Turner, 2000; Stirzaker et al., 2002).

A number of processes are affected by plants grown under salinity conditions. These include photosynthesis, protein synthesis and lipid metabolism. High concentrations of salts cause damage at the molecular level that result in reducing plant growth and might cause plant death (Tijen and Ismail, 2006). *Calotropis* plant species are one of the most drought (Akhkha, 2009, Boutraa, 2010) and salt (Al-Sobhi et al., 2006) tolerant plant species that dominates a vast areas in semi arid and arid regions. Thus, it might be an important potential plant candidate for forestation. Plant species differ in their responses to salinity stress; therefore, it is important to study the effects of salinity on the different physiological processes in order to enhance the understanding of mechanisms of salt tolerance (Koyro, 2003). Salt stress tolerance in plants is one of the complex phenomena that involve developmental, physiological and biochemical changes (Delauney & Verma, 1993).

*Calotropis procera* is a desert shrub grows uncultivated and is widespread in the tropics. The plant has been widely used in the traditional medicine in Asia and Africa (Kumari et al., 2004). All the plant parts contain active medicinal compounds, although most of them are found in the milky latex.

*Corresponding: E-Mail: tboutraa@yahoo.co.uk; Tel: 0096648460008 (1430); Fax: 0096648454770
that exudate from broken leaves and stems. For example, the roots are used as carminative in the
treatment of dyspepsia (Kumar and Arya, 2006). The roots also possess anti-inflammatory and
analgesic properties (Basu and Nag Choudhuri, 1991). The aerial plant parts contain the milky latex,
that is highly abundant in leaves and can be collected only from the green parts, has been shown to
produce antidiabetic, hepatoprotective, antiarthritic, cytotoxic and anticancer effects in rats (Padhy et
al., 2007; Kumar and Roy, 2007). Most studies on C. procera deal with the pharmacological and
medicinal aspects. There is little information on the effects of the different environmental stresses on
the growth and physiology of C. procera, including water stress (Al-Zahrani, 2002; Aziz and Khan,
2003; Boutraa, 2010; Akhkha, 2009) and salt stress (Al-Sobhi et al., 2006). Thus, the objective of the
present study was to evaluate the effect of salt stress on growth and photosynthetic responses of the
desert shrub C. procera. The results might contribute to the understanding of physiological
mechanisms involved in salt tolerance that lead to the improvement of the desert environments.

Materials and Methods

Plants materials and experimental design

Research was carried out in the Department of Biology, Faculty of Sciences, Taibah University,
Al-Madinah Al-Munawarah in the Kingdom of Saudi Arabia. Seeds of C. procera were collected in
June 2009 from Al-Mustarah, at Al-Madinah Al-Munawarah district. Dried seeds were soaked into
distilled water for 24 hours to facilitate germination process. Seeds were planted in small plastic pots
containing compost. Seven days after emerging, seedlings were transferred to 12 cm x 20 cm plastic
pots filled with 700g sand:compost mix (1:3 v:v). Two-week old plants were subjected to one of the
following NaCl treatments; 0 mM (distilled water, control), 75 mM, 150 mM and 300 mM NaCl.
Plants were kept in a growth chamber with 16 hours photoperiod and watered every two days. Plants
were harvested after 2 weeks of imposing salinity treatments (Huang et al., 2010).

Plant weights determination

Three plants of each NaCl treatment were harvested, divided into roots, stem and leaves. All
plant parts were oven-dried at 85°C for 48 h and weighed to determine the dry weights.

Leaf area and specific leaf area (SLA) measurements

Leaf area was measured with a portable leaf area meter (LiCoR LI-3100C Portable Area Meter,
Biosciences, USA). The specific leaf area (SLA) was calculated as leaf area per leaf dry weight using
the following equation (Huang et al., 2010).

\[
SLA = \frac{\text{Leaf area (cm}^2\text{)}}{\text{Leaf dry weight (g)}}
\]

Leaf area ratios (LAR) were calculated by dividing the leaf area by the total dry weights as follows:

\[
LAR = \frac{\text{Leaf area (cm}^2\text{)}}{\text{Total Plant dry weight (g)}}
\]

Leaf chlorophyll content measurement

Leaf Chlorophyll content was measured using a hand-held chlorophyll content meter (CCM-200,
Opti-Sciences, USA). The chlorophyll content was measured three times for each leaf and the average
was used for analysis.

Photosynthesis measurements

Photosynthesis rates were measured on the forth fully expanded leaves using a portable
photosynthesis analyzer (LiCoR 6400 - XT, Lincoln, USA). Net photosynthesis rate (A) were
determined at ambient CO₂ concentrations (300 -350 μmol), temperature of 30°C and relative humidity
of 40% ± 5%. The steady state light response curve was measured at photosynthesis photon flux density levels at 0, 100, 150, 500, 1000 and 1500 µmol photon m⁻² s⁻¹.

Statistical analysis

The experiment was designed in a completely randomized design with three replicates for each salt stress treatment. Analysis of variance (ANOVA) was performed using Minitab (version 13) to determine if the means were significantly different.

Results and Discussion

Plant height

Salt stress induced significant (< 0.001) decrease in plant height at all NaCl concentrations with the highest reduction at 300 mM NaCl (Fig. 1). The decrease in plant height caused by the two treatments; 75 and 150 mM NaCl was not significantly different compared with the control plants. The mean values of plant heights were 9.7±0.44 (±SE), 7.8±0.44, 7.5±0.29 and 5.1±0.17 cm for treatments of 0, 75, 150 and 300 mM NaCl, respectively. The salinity stress caused a reduction in plant height of 19%, 22% and 47% at 75, 150 and 300 mM NaCl respectively. These results were in accordance with a number of investigations of salinity on plant height. For example, da Siva et al., (2008) reported a reduction in plant height of umbu plants subjected to NaCl treatments. The increasing salt concentration induced a progressive decline in shoot length of the desert plant Atriplex hortensis (Sai Kachout et al., 2009). The reduction in plant height caused by salinity stress is probably due to the perturbation of water relations created by salinity stress and to the salt specific ions-excess effects (Munns, 2002). Marshner (1990) reported that reduction of plant growth under similar salinity stress environment was more likely to be due to osmotic and ionic effects on soil solution.

Different plant species reacted differently to salinity stress; for example, a treatment of seedlings of Leucaena leucocephala with 100 mM NaCl caused a reduction of 60% in shoot growth, while, under similar NaCl stress conditions, seedlings of Prosopis julifora plants reduced by only 15% (Viégas et al., 2003). These differences could be due to differences in the level of salt tolerance within different plant species.

![Figure 1](image_url)

**Figure 1.** Plant height (cm) of *C. procera* grown under four levels of NaCl concentrations. Vertical bars are ± SE for three replicates.

Number of leaves

Although plants grown under the highest level of NaCl concentration, 300 mM, showed a significant reduction (< 0.005) in the number of leaves compared to the control plants; plants subjected to 75 and 150 mM did not show significant differences compared to control plants (Fig. 2). The mean values of number of leaves per plant were 10.0±0.00, 9.3±0.67, 8.6±0.67 and 7.0±0.58 leaves for treatments of 0, 75, 150 and 300 mM NaCl, respectively. The percentage reduction in the number of leaves caused by the salinity stress was 7%, 13% and 30% at 75, 150 and 300 mM NaCl respectively. The number of leaves in umbu plants subjected to salt stress showed a significant reduction after 7
days of incubation. The decrease in the number of leaves was reported at a range of NaCl levels; 25, 50, 75 and 100 mM (da Silva et al., 2008).

Figure 2. Number of leaves of C. procera plants grown under four levels of NaCl concentrations. Vertical bars are ± SE for three replicates.

**Plant Fresh and Dry Weights**

Salt stress significantly (< 0.01) reduced the fresh weight of root, stem, leaf (Fig 3 A) and total fresh weight (< 0.001) (Figure 3 C). Salinity stress also significantly reduced the dry weight of root (< 0.001), stem (< 0.01), and leaf (< 0.05) (Fig 3 B), but total dry weights were not affected (data not shown). The most affected plant part by NaCl was leaves followed by stem and roots, with the highest reduction at the 300 mM NaCl treatment. The NaCl treatments at 75, 150 and 300 mM resulted in the following reductions; leaves; 15%, 25% and 60%, stem; 0%, 32% and 57% and roots; 20%, 40% and 67% respectively. A similar effect was observed on a number of plant species subjected to salt stress; wheat, barley, canola and chickpea. For example, Grewal (2010) reported that shoot and root dry weights of plants treated with salinity stress were severely decreased. The less effects of salinity stress were expressed in roots. Our findings suggested that shoot growth was more sensitive to salinity than root growth, and this is supported by a number of studies reporting that high concentration of salts restricts roots growth (Rengasamy et al., 2003; Grewal et al., 2004). In Atriplex hortensis, salinity stress reduced dry weights of stems and roots (Sai Kachout et al., 2009). The sensitivity of shoot growth to salinity stress could be due to an imbalance in cations in the xylem transport system (Munns, 1993). This phenomenon might be associated with the faster osmotic adjustment that is accompanied with slower turgor loss in the roots (Shalhevet et al., 1995).

**Leaf Area and Leaf Indices**

Leaf area was significantly (< 0.01) reduced in plants grown under salinity stress, although the reduction in leaf area did not differ significantly among NaCl treatments, except for 300 mM NaCl (Fig. 4A). The reduction values were 20%, 28% and 65% at 75, 150 and 300 mM NaCl respectively. Reduction in leaf area was observed earlier than other growth parameters. This was previously observed in Asteriscus maritimus plants treated with salinity (Rodríguez et al., 2005). In umbu plants grown under salinity conditions, da Silva et al., (2008) reported that leaf area reduced as salt concentrations increased. They found that 75 and 100 mM caused a reduction of 46% and 55% respectively compared with the control plants. Salinity stress also reduced leaf area in Atriplex portulacoides plants (Redondo-Gomez et al., 2007). They subjected plants to 0, 20, 200, 400 and 700 mM and found that only 700 mM NaCl treatment caused a significant reduction in leaf area. In two varieties of Atriplex hortensis (red and green) increasing NaCl concentrations significantly decreased the total leaf area. At 15 g/l NaCl the total leaf area was reduced by 13 and 47% for red and green varieties, respectively (Sai Kachout et al., 2009). The reduction in the leaf area of plants grown under saline conditions might be explained by a decrease in leaf turgor and/or changes in cell properties or lowering photosynthesis rates (Franco et al., 1997; Rodríguez et al., 2005).
Figure 3. Fresh weights of stem leaf and root (A), dry weights of stem, leaf and root and total fresh weigh (C) of *C. procera* plants grown under four levels of NaCl concentrations. Vertical bars are ± SE for three replicates.
Figure 4. Leaf area (A), leaf area ratio (B) and specific leaf area (C) of *Calotropis procera* plants grown under four levels of NaCl concentrations. Vertical bars are ± SE for three replicates.
Specific leaf area (SLA), which is a measure of leaf thickness, was not affected by salt treatments at any of the NaCl concentrations (Fig. 4B). This may suggest that whether the plants are under stress or not, the amount of dry matter accumulated per unit leaf area was not affected by increasing salt concentrations. These findings are in full accordance with previous results on umbu plants reported by da Siva et al. (2008). Leaf area ratio, which is a measure of the leafiness of the plant, was significantly (< 0.001) affected by salinity treatment at the highest NaCl concentration, 300 mM NaCl; the treatment caused a reduction of 53%. This indicates that the amount of dry matter allocated to the development of photosynthetic tissues (leaves) was decreased with increasing salt concentrations. This was not in accordance with the findings reported by Rodríguez et al. (2005), who observed that LAR remained unchanged with increasing salt concentrations in Asteriscus maritimus plants. However, the highest salt concentration used in this study did not exceed 140 mM NaCl.

**Photosynthesis Rates**

Photosynthesis rates were reduced significantly with increasing salinity stress (Fig. 5). The average reductions in photosynthesis capacity, as a result of salt stress, were 13%, 37 and 90% at 75, 150 and 300 mM NaCl, respectively. The reduction in the photosynthesis rate explains the reduction in growth including the photosynthetic tissues. Other plant species showed similar effect when exposed to high salt levels (Yeo et al., 1985; Lin and Sternberg, 1993; Ashraf, 2004, Dubey, 2005). The mechanism by which the photosynthesis is reduced could be related to stomatal behavior in response to high salinity. For example, increasing external salinity in Atriplex hortensis plants reduced the stomatal conductance by 50% (Sai Kachout et al., 2009). Increasing salinity stress in halophyte plants may cause a partial stomatal closure, which result in limiting both transpiration and salts transport to the leaves (Véry et al., 1998). The partial closure of the stomata results in lowering the CO₂ diffusion rates, which can lead to reducing the photosynthesis capacity (Redondo-Gómez et al., 2007). The effects of salinity on photosynthesis rates might be mediated by the individual effects on the enzymes assimilation capacity, photochemical processes or resistance to gas exchange (Redondo-Gómez et al., 2007). Salt stress affects the photosynthesis efficiency through the peroxidation of lipids in the thylakoids, the damage to the photosystem II (PSII) and the reduction in the activity of the electron transport chain of PSII (Lu and Vonschak, 1999). The excessive salt absorption causes premature leaf aging as a result of the reduction in the photosynthetic area that maintains growth (Munns, 2002). High concentrations of Na⁺ and Ca²⁺ in the cytoplasm should be kept at low level, because high concentrations of these ions are toxic (Epstein and Bloom, 2005). The previous authors added that; “the photosynthesis apparatus, in particular, must be protected from high concentrations of these ions”.

Chlorophyll Content

No difference in chlorophyll content was detected in plants grown under 75 and 150 mM NaCl concentrations compared with the control plants. Plants treated with 300 mM NaCl resulted in 30% increase in chlorophyll content (Fig. 6). There have been contradictory reports on the effects of salinity on chlorophyll content. For example, salinity stress at 5, 10 and 15 g/l NaCl resulted in significant reduction in the photosynthesis pigments; Chl a and b (Sai Kachout et al., 2009). Netondo et al., (2004) reported that the chlorophyll content in sorghum plants started to decline in plants grown at 100 mM NaCl and higher concentrations. The reduction in chlorophyll content under salinity conditions could be due to the effect of salinity that cause inhibition of chlorophyll synthesis or enhance chlorophyll degradation (Reddy and Vora, 1986). Redondo-Gomez et al., (2007) found that concentration of photosynthesis pigments in leaf tissues were not affected by salinity treatments at 0, 20, 200, 400 and 700 mM. An increase in chlorophyll content under salinity conditions was also reported by Kirst (1989), and this increase might be due to the accumulation of NaCl in the chloroplast. Furthermore, it was observed in chlorophyllous systems that cells respond to saline stress developing more chlorophyll when grown under photautotrophic conditions (Chang et al., 1997).
Figure 5. Net photosynthesis rates (µmol CO₂ m⁻² s⁻¹) of *C. procera* plants grown under four levels of NaCl concentrations. Vertical bars are ± SE for three replicates.

Figure 6. Chlorophyll content in leaves of *Calotropis procera* plants grown under four levels of NaCl concentrations. Vertical bars are ± SE for three replicates.

Explaining why plants under saline conditions in the lab have higher chlorophyll content is more complicated especially when plants under salinity stress in their native environments do not appear greener (Streb and Feierabend, 1996). Therefore, the mechanism(s) responsible for the increase of chlorophyll content in plants under salt stress are not fully understood. However, using chlorophyllous cells, García-Valenzuela *et al* (2005) demonstrated that increases in chlorophyll accumulation previously observed in salt-adapted dicot cells may be the result of the osmotic shock (water deficit),
rather than the ionic effect of salt on the physiology of chlorophyllic cells of dicots. Similar mechanism may be responsible for the increase in chlorophyll content in *C. procera* when exposed to high salt concentrations.

**References**


Study by Modelling the Scenarios of CO₂ Emissions Mitigation Related to Households Energy Demand in Dakar

Cheikh Diop¹,²*, Marie Ndiaye Seck¹, Mamadou Adj³, Karim Konate⁴, Isselmou Ould H’medy², Mame Diabou Gaye Seye, Atanasse Coly², Alphonse Tine²

¹Institute of Environmental Sciences (ISE), Faculty of Sciences and Techniques, University Cheikh Anta Diop – BP 5005 Dakar- Senegal; ²Laboratory of photochemistry and analysis, Faculty of Sciences and Techniques, Département of Chemistry, Faculty of Sciences and Techniques, University Cheikh Anta Diop – BP 5005 Dakar- Senegal; ³Polytechnic Higher School, University Cheikh Anta Diop – BP 5005 Dakar- Senegal; ⁴Department of Mathematics and Computer Science, Faculty of Sciences and Techniques, University Cheikh Anta Diop – BP 5005 Dakar- Senegal

Received January 12, 2010; Accepted April 2, 2010

Abstract: The reduction of greenhouse gas (GHG) emissions is an objective of the United Nations Framework Convention on Climate Change and the Kyoto Protocol to fight against climate change related primarily to CO₂ emissions from fossil fuels. Many scenarios have been developed based on simulation of CO₂ emissions and their reductions. But none of them was interested in traditional use of domestic fuels from biomass in relation to African Climate Change. The objective of this present study is the mitigation of CO₂ emissions from domestic fuel from a model of energy planning. This modelling was done along three axes: the simulation of future demand for domestic fuels; proposals of intervention strategies and assessment of environmental impacts of strategies. The Scenarios or the case studies in this model correspond to either a strategy or a combination of defined strategies. The data needed to run the model are three categories: data on population, data on household consumption and data relating to wood carbonization. The simulations were performed, first with the input of the model to see the evolution of future demand for household fuels in the Dakar region and then from the identified strategies to assess their impacts.

Keywords: greenhouse gas, Climate Change, CO₂ emissions, mitigation, modelling, household,

Introduction

The Earth's climate undergoes significant changes following an accumulation in the atmosphere of gases like CO₂, CH₄, N₂O, CFCs and O₃ as shown by (Caro, 2000). These so-called greenhouse gases (GHG) emissions come not only from human activities in industry, transport and agriculture, but also by deforestation and burning of domestic fuels. These modifications known as climate change have many consequences like the melting of polar and mountains glaciers, changes in rainfall patterns, the rising of sea levels with the gradual inundation of coastal lowlands and some productive deltas, the salinization of soils and the contamination of some groundwater (Caro et al., 2007). These phenomena lead also to a reduction of water resources and land degradation, thus causing a decline in agricultural production (Rivard et al., 2003; Caro et al., 2007). New diseases are emerging in places where they were not known before; old ones are in progress (Githeko et al. 2000; Rivard et al., 2003, GIEC, 2007).

The projections of the scientists indicate that the global surface temperature is likely to rise a further 1.4 to 5.8 °C, associated with a doubling of CO₂ concentration in the atmosphere (Caro et al., 2007). Indeed, climate changes are associated with CO₂ emissions, mainly from fuel and particularly fossil fuels. Therefore the reduction of GHG emissions is a key objective of the Convention of the United Nations Framework for Climate Change (United Nations, 1992) and the Kyoto Protocol (United Nations, 1998; Nations Unies, 1998; Bressol, 2006).

In order to reduce CO₂ and other greenhouse gases emissions many scenarios have been developed, particularly by Akimoto et al. (2004), Matsumoto, (2002), Perrels et al. (2000), Hayashi et al. (2005), Shrestha, (2002), Ekholm et al. (2009), Nakata et al. (2003), Masui et al.(2002), Worell et al. (1999), Avami et Farahmandpour, (2008) and Nickerson, (2004). Yet none of these scenarios has really investigated the impact of domestic fuels on climate changes and the relation between them. The

*Corresponding: E-mail: namorydiop@yahoo.fr; Tel: 00 221 77 501 42 61 Fax: 00 221 825 41 97
aim of the present work is to study the mitigation of CO₂ emissions from domestic fuel in Dakar, Senegal, using a model of energy planning.

According to Sokona & Revet (1995) one African consumes 7 times less energy than an European, 1.5 kilograms of oil equivalent (koe) per day. This is an average in the continent, yet some countries like Senegal consume about ten times less. More than half of the energy is consumed in the form of biomass, what is theoretically twice the amount consumed by a European. For the IAE (IAE, 2006), the ratio of the African populations’ access to electricity is 8% by now. And among the 1.5 billion of people who have not yet access to electricity an important part lives in Africa. According to the agency, Africa has consumed 435 millions of tons-equivalent oil (teo) in 2004. This confers on Africa the lowest ratio per inhabitant of the planet, with 0.5 teo per year, against 1.2 teo on average in the world.

The primary energy balance of Senegal in 1998 is as follows: transport 21%, industry 20%, tertiary 5%, households 54% (MEH, 2000). In Senegal wood energy represents 61% of energy balance, 1 against 37% for oil and only 2% for vegetable waste, households being the most energy-consuming sector. Urban wood fuels (wood 28.5% and charcoal 56%) represent more than 84% of domestic consumption and cover nearly 87% of cooking needs (MMEH, 2000). In Dakar, the capital of the country, where nearly 25% of the population is living, fuel consumption will exceed 50% for charcoal, compared to the country’s total consumption (DE/MPN/SN, 1997). The growth of the population of Dakar could increase from 2.4 million in 2006 to 5.4 million in 2021 (Adjamagbo & Antoine, 2002; Comité National Habitat II SN, 2002). This population increase could be accompanied by a sharp increase in fuel requirements for domestic households.

To save the forest and take into account the importance of domestic fuel in the consideration of global emissions of CO₂ from the perspective of mitigating climate change, sustainable intervention strategies must be found to reduce consumption of wood energy while ensuring a proper supply of household with domestic fuels.

**Material and Methods**

1. **Material**

   The present work is related to the area of the Dakar region. The energy sources include wood fuels (fuel wood, charcoal), butane gas, kerosene, gel fuel, peat briquettes, rice husk coal, peanut shell coal and solar energy. The analysis of CO₂ emissions from households is conducted according to an energy planning model. The main axes of the study are:
   1-simulation of future demand for domestic fuels;
   2-proposals and intervention strategies;
   3-assessment of the strategies environmental impacts.

2. **Methodology**

   The methodology is based on the classification of households according to the way they use fuels and on the strategies.

2.1. **Classification of households by mode of use of fuels**

   Households are classified by mode of use of fuel into the seven types below:
   - Type 1 = charcoal + gas;
   - Type 2 = charcoal + wood;
   - Type 3 = charcoal only;
   - Type 4 = gas + charcoal;
   - Type 5 = gas + wood;
   - Type 6 = gas only;
   - Type 7 = mainly Wood.

   The first element of each type is the mainly used fuel and the second element is the auxiliary fuel.

2.2. **Proposed strategies**

   The strategies are aimed at reducing the negative impacts of wood energy consumption. They are based on scenarios which take into account the orientations of the domestic fuels subsector. They are derived from a baseline scenario taken as the initial situation of domestic fuel consumption. The ecological impacts of these scenarios are related to the levies on forest resources and the CO₂ emissions resulting from their implementation. Four strategies have been identified:
• **Strategy 1: Substitution of charcoal by kerosene.**

Assuming that fuel consumption will rise by 8% per year up to 2014, the estimated amount of substitutable charcoal is given by the following relation:

\[
C_{sub} = \frac{C_{ker} \times P_{ker} \times R_{ker}}{P_{cb} \times R_{ch}}
\]  

(1)

where

\( C_{sub} \) = quantity of substitutable charcoal per year;
\( C_{ker} \) = quantity of kerosene used per year;
\( P_{ker} \) = calorific value of kerosene;
\( P_{cb} \) = calorific value of charcoal;
\( R_{ker} \) = yield of the considered kerosene stove;
\( R_{ch} \) = yield of the considered coal stove.

• **Strategy 2: Substitution of charcoal by peanut hulls coal**

The estimation of the quantity of substitutable charcoal is given by the following relation:

\[
C_{sub} = \frac{C_{ca} \times P_{ca}}{P_{cb}}
\]  

(2)

\( C_{ca} \) = quantity of peanut hulls coal produced per year;
\( P_{ca} \) = calorific value of peanut hulls coal.

• **Strategy 3: Popularization of improved charcoal stoves**

The dissemination of improved stoves can significantly reduce the amount of fuel wood at regional level.

• **Strategy 4: Improved weight yield of carbonization by widespread use of the Casamance kiln**

The introduction of the Casamance kiln with a yield of 25 to 30% is the best strategy for the weight yield improvement. The most widely used traditional kiln has a weight yield of only 18 to 23% (Caho, 1993, Stassen, 2002, Ducenne, 2001).

2.3. Operating Model Overview

The scenarios studied in this model correspond to either a strategy or a combination of strategies as defined below:

• Substitution: strategy 1 + strategy 2;
• Dissemination of improved stoves: Strategy 3;
• Improved carbonization: Strategy 4;
• Combination of substitution, improved stoves and improved carbonization: strategy 1 + strategy 2 + strategy 3 + strategy 4.

Our model is inspired by MESAP (Modular Energy System Analyst and Planning), an energy planning software developed by IER University of Stuttgart in Germany. The model is divided into two main parts. The first part is used to assess current and future demands for fuel in the Dakar region. The second part is dedicated to a deeper analysis of the proposed scenarios. This part allows us to vary the scenarios’ inputs and see their effects at global level.

This model gives way to simulations related to the defined energy policies. In order to run the model three types of data are needed: Data on population (population size of Dakar, average household size, rate of population growth), data on household consumption (household distribution in types of consumers, fuel consumption by type of household, cooking equipment used by households) and data on wood carbonization (used carbonization techniques, percentage of use, performance, quantity of emitted CO₂ according to the carbonization mode). These data are the results of various investigations conducted in the Dakar region. In this model, the year 1992 was chosen as the baseline year, because it is the year from which the data needed to feed the model exist. The chosen horizon of the study is up to 2014, year during which (period in the course of which) we believe to be in control as far as the stability of events is concerned. In this model, simulations were made, first with the input of the model to see the evolution of future demand for household fuels in the Dakar region, and then from the identified strategies to assess their impacts, in particular CO₂ emissions.

2.4. The algorithms

The algorithms of the main functions are the following ones:

- calculation of the population size and the number of households;
- calculation of domestic fuels consumptions for the various types of consumers
- calculation of the annual domestic fuels consumptions;
- calculation of the wood-energy consumptions;
- calculation of carbon dioxide emissions.

Each of these algorithms is implemented in a program module. And then all the modules are put together to realise the simulation program.

2.4.1. Example of algorithm for calculating emissions of carbon dioxide (CO₂)

The algorithm for calculating carbon dioxide (CO₂) emissions is given in Figure 1. The input variables are: F trad and F casa; all other variables are calculated by the function for a given year t.

![Flow chart for calculating CO₂ emissions](image)

**Figure 1.** Flow chart for calculating CO₂ emissions

- CO₂_charbt: quantity released by the consumption of charcoal;
- CO₂_wood: quantity released by the consumption of fuel wood;
- CO₂_gas: quantity released by the consumption of butane gas;
- CO₂_ker: quantity released by the consumption of kerosene;
- CO₂_ca: quantity released by the consumption of peanut hulls coal;
- CO₂_comb: quantity released by the consumption of domestic fuels;
- CO₂_trad: amount of CO₂ released by carbonization with the traditional kiln
- CO₂_casa: quantity of CO₂ released by carbonization with the Casamance kiln;
- CO₂_carbt: total amount of CO₂ released by carbonization;
- CO₂_tot: quantity released by carbonization and fuel consumptions;
- F trad: CO₂ emission factor of the traditional kiln;
- F casa: CO₂ emission factor of the Casamance kiln.

The input variables entered are: F trad and F casa; all other variables are calculated by the function for a given year t.
Results and Discussion

3. Modelling of CO₂ emissions

3.1. Reference Case

The Reference case shows the evolution of the situation when there is no policy aimed at reversing the trend and consumers’ behaviour remains unchanged. The initial input values in this scenario are some observed values.

The analysis of Table 1 shows that household consumption of wood fuels in Dakar may lead to deforestation of about 1,200,000 tons of wood in 2014 with 1,098,472 tons for the production of charcoal (more than 90% of cuts of wood energy). A comparison between different sources of carbon dioxide emissions shows that the mainly used method of charcoal production is harmful to the environment and contributes to the exacerbation of climate change because it releases more CO₂ than all other sources combined. With the Reference case, we see that the needs of households in charcoal are important, and that the use of charcoal has many negative effects.

<table>
<thead>
<tr>
<th>Years</th>
<th>Charcoal (t)*</th>
<th>Wood for Charcoal (t)*</th>
<th>Total wood (t)</th>
<th>CO₂ from fuels (t)</th>
<th>CO₂ from carbonization (t)</th>
<th>Total CO₂ (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992</td>
<td>152856</td>
<td>851101</td>
<td>873449</td>
<td>554821</td>
<td>1087657</td>
<td>1642478</td>
</tr>
<tr>
<td>1994</td>
<td>111504</td>
<td>620853</td>
<td>643914</td>
<td>504011</td>
<td>793414</td>
<td>1297425</td>
</tr>
<tr>
<td>1996</td>
<td>119086</td>
<td>663071</td>
<td>704219</td>
<td>577396</td>
<td>847365</td>
<td>1424761</td>
</tr>
<tr>
<td>1998</td>
<td>124454</td>
<td>692960</td>
<td>737209</td>
<td>612009</td>
<td>885561</td>
<td>1497570</td>
</tr>
<tr>
<td>2000</td>
<td>129831</td>
<td>722899</td>
<td>770438</td>
<td>647943</td>
<td>932821</td>
<td>1580764</td>
</tr>
<tr>
<td>2002</td>
<td>135186</td>
<td>752716</td>
<td>803740</td>
<td>685171</td>
<td>961925</td>
<td>1647096</td>
</tr>
<tr>
<td>2004</td>
<td>133415</td>
<td>804771</td>
<td>859323</td>
<td>732553</td>
<td>1028449</td>
<td>1761002</td>
</tr>
<tr>
<td>2006</td>
<td>142119</td>
<td>857099</td>
<td>915198</td>
<td>780184</td>
<td>1095321</td>
<td>1875505</td>
</tr>
<tr>
<td>2008</td>
<td>151320</td>
<td>912829</td>
<td>974706</td>
<td>830917</td>
<td>1166540</td>
<td>1997457</td>
</tr>
<tr>
<td>2010</td>
<td>161038</td>
<td>972190</td>
<td>1038090</td>
<td>884948</td>
<td>1242400</td>
<td>2127348</td>
</tr>
<tr>
<td>2012</td>
<td>170930</td>
<td>103339</td>
<td>1103449</td>
<td>900625</td>
<td>1320621</td>
<td>2221246</td>
</tr>
<tr>
<td>2014</td>
<td>181334</td>
<td>1098472</td>
<td>1172932</td>
<td>999893</td>
<td>1403781</td>
<td>2403674</td>
</tr>
</tbody>
</table>

Table 1: Evolution of wood energy consumption and CO₂ emissions from domestic fuel

3.2. Case Studies: The case studies are likely scenarios for assessing the future by following strategies.

3.2.1. Case of substitution: Table 2 shows that the substitution of wood by kerosene or peanut hulls coal had no significant influence on the evolution of charcoal and wood consumption over the reference case. However, if the substitution is done for the two fuels together, the amount of wood energy would lower around to 88,804 tons and 5920 ha of forest are preserved.

<table>
<thead>
<tr>
<th>Years</th>
<th>Charcoal (t)*</th>
<th>Kerosene (l)*</th>
<th>Peanut hulls coal (t)</th>
<th>Fuels (toe)</th>
<th>Total Wood (t)*</th>
<th>CO₂ from fuels (t)*</th>
<th>CO₂ from carbonization (t)*</th>
<th>Total CO₂ (t)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992</td>
<td>152856</td>
<td>0</td>
<td>0</td>
<td>145805</td>
<td>873449</td>
<td>554821</td>
<td>1087657</td>
<td>1642478</td>
</tr>
<tr>
<td>1994</td>
<td>111504</td>
<td>0</td>
<td>0</td>
<td>141741</td>
<td>643914</td>
<td>504011</td>
<td>793414</td>
<td>1297425</td>
</tr>
<tr>
<td>1996</td>
<td>119086</td>
<td>0</td>
<td>0</td>
<td>162380</td>
<td>704219</td>
<td>577396</td>
<td>847365</td>
<td>1424761</td>
</tr>
<tr>
<td>1998</td>
<td>124454</td>
<td>0</td>
<td>0</td>
<td>172619</td>
<td>737209</td>
<td>612009</td>
<td>885561</td>
<td>1497570</td>
</tr>
<tr>
<td>2000</td>
<td>129831</td>
<td>0</td>
<td>0</td>
<td>194437</td>
<td>803740</td>
<td>685171</td>
<td>1028449</td>
<td>1761002</td>
</tr>
<tr>
<td>2002</td>
<td>135186</td>
<td>1368550</td>
<td>11861</td>
<td>206090</td>
<td>797407</td>
<td>728816</td>
<td>949324</td>
<td>1673137</td>
</tr>
<tr>
<td>2004</td>
<td>133415</td>
<td>1368550</td>
<td>11861</td>
<td>219309</td>
<td>849418</td>
<td>770040</td>
<td>1011257</td>
<td>1781296</td>
</tr>
<tr>
<td>2006</td>
<td>124454</td>
<td>1368550</td>
<td>11861</td>
<td>233358</td>
<td>904427</td>
<td>819137</td>
<td>1076278</td>
<td>1895863</td>
</tr>
<tr>
<td>2008</td>
<td>129831</td>
<td>1368550</td>
<td>11861</td>
<td>248286</td>
<td>962560</td>
<td>871258</td>
<td>1145877</td>
<td>2017134</td>
</tr>
<tr>
<td>2010</td>
<td>170930</td>
<td>2533090</td>
<td>11861</td>
<td>263625</td>
<td>1021788</td>
<td>924744</td>
<td>1216264</td>
<td>2141005</td>
</tr>
<tr>
<td>2012</td>
<td>181334</td>
<td>295459</td>
<td>11861</td>
<td>279882</td>
<td>1084128</td>
<td>981373</td>
<td>1290294</td>
<td>2271666</td>
</tr>
</tbody>
</table>

The CO₂ emissions will also decrease compared to baseline, from 2,400,000 tons to 2,300,000 tons, as illustrated reported in Figure 2, with a decline rate of approximately 5%.
3.2.2. Case of improved stoves: In this case of widespread use of improved stoves the results, as reported in Table 3, show the efforts to reduce charcoal consumption. Some models of improved stoves have been developed for charcoal with a yield (30% to 35%) higher than the one for traditional "Madagascar" stoves (18% to 20%) (Affoudji Ehemba, 2009).

Table 3. Fuel consumption and CO2 emissions in the case of the widespread use of improved stoves from 2006

<table>
<thead>
<tr>
<th>Years</th>
<th>Charcoal (t)</th>
<th>Fuel (toe)</th>
<th>Wood for charcoal (t)*</th>
<th>Total Wood (t)</th>
<th>CO2 from fuels (t)</th>
<th>CO2 from carbonization (t)</th>
<th>Total CO2 (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992</td>
<td>152856</td>
<td>145805</td>
<td>851102</td>
<td>873449</td>
<td>554821</td>
<td>1087657</td>
<td>1642478</td>
</tr>
<tr>
<td>1994</td>
<td>111504</td>
<td>141741</td>
<td>620854</td>
<td>643914</td>
<td>504011</td>
<td>793414</td>
<td>1297425</td>
</tr>
<tr>
<td>1996</td>
<td>119086</td>
<td>162380</td>
<td>663071</td>
<td>704219</td>
<td>577396</td>
<td>847365</td>
<td>1424761</td>
</tr>
<tr>
<td>1998</td>
<td>124454</td>
<td>172619</td>
<td>692960</td>
<td>737209</td>
<td>612009</td>
<td>885561</td>
<td>1497570</td>
</tr>
<tr>
<td>2000</td>
<td>129831</td>
<td>183305</td>
<td>722899</td>
<td>770438</td>
<td>647943</td>
<td>923821</td>
<td>1571764</td>
</tr>
<tr>
<td>2002</td>
<td>135186</td>
<td>194437</td>
<td>752716</td>
<td>803740</td>
<td>685171</td>
<td>961925</td>
<td>1647096</td>
</tr>
<tr>
<td>2004</td>
<td>144535</td>
<td>207883</td>
<td>775216</td>
<td>837409</td>
<td>732553</td>
<td>1028449</td>
<td>1761002</td>
</tr>
<tr>
<td>2006</td>
<td>112884</td>
<td>192665</td>
<td>628537</td>
<td>686636</td>
<td>662726</td>
<td>803232</td>
<td>1465958</td>
</tr>
<tr>
<td>2008</td>
<td>120224</td>
<td>205194</td>
<td>669406</td>
<td>731283</td>
<td>705821</td>
<td>855459</td>
<td>1561280</td>
</tr>
<tr>
<td>2010</td>
<td>128042</td>
<td>218537</td>
<td>712937</td>
<td>778837</td>
<td>751717</td>
<td>911090</td>
<td>1662807</td>
</tr>
<tr>
<td>2012</td>
<td>136103</td>
<td>232296</td>
<td>757821</td>
<td>827871</td>
<td>799044</td>
<td>968449</td>
<td>1767493</td>
</tr>
<tr>
<td>2014</td>
<td>144674</td>
<td>246922</td>
<td>805543</td>
<td>880003</td>
<td>849357</td>
<td>1029434</td>
<td>1878791</td>
</tr>
</tbody>
</table>

(t)*: in tons

Figure 3 shows that in the case of widespread use of improved stoves beginning from 2006, there was a significant decrease in the use of wood. In 2014 the charcoal consumption will drop from 200,000 tons in the reference scenario to 140,000 tons. The use of improved stoves could also help reduce carbon dioxide emissions, which could decrease by 15% compared to the baseline scenario, as reported in Figure 4.

3.2.3. Case of improved carbonization: Among all the methods used for carbonization, the most appropriate one is the Casamance kiln. Compared with the most widely used traditional kiln, the Casamance kiln offers the following advantages:
- weight performance of the Casamance kiln is 25 to 30% whereas it is 18 to 23% for the traditional kiln as shown by Affoudji Ehemb (2009). The difference of 7% can be important in terms of reduction of the annually deforested area;
- the traditional kiln releases much more carbon dioxide than the Casamance kiln;

The analysis of wood taking for charcoal production following the two methods of carbonization (traditional and Casamence) in Figure 5, highlights the waste of forest resources because of poor performance during processing with the used traditional techniques.
Using the Casamance kiln is very interesting in terms of CO₂ emissions. Its implementation could lead to a significant reduction in CO₂ emissions thanks to the wood carbonization compared to baseline as reported in Figure 6.

**Figure 3.** Evolution of the total wood consumption in the case of the use of improved stoves from 2006

**Figure 4:** Evolution of carbon dioxide emissions in the case of the use of improved stoves from 2006

**Figure 5.** Evolution of wood consumption in the case of the widespread use of the Casamance kiln since 2006

3.2.4. **Combination of substitution, improved stoves and improved carbonization**

In the case of joint implementation of all strategies (substitution, widespread use of improved stoves and use of Casamance kiln) beginning from 2006, we can see in Figure 7 that the amount of collected
wood is reduced by 48% thanks to the massive use of improved stoves. This scenario could also lead to a significant reduction in CO₂ emissions. This reduction, as reported in Figure 8, would be around 40% beginning from 2006. The amount of emitted carbon dioxide would thus drop from 2,403,673 tons to 1,106,827 tons in 2014.

**Figure 6.** Evolution of carbon dioxide emissions in the case of the widespread use of the Casamance kiln since 2006

**Figure 7.** Evolution of wood consumption in the case of substitution, the widespread use of improved stoves and Casamance kiln since 2006

**Figure 8:** Trends in emissions of carbon dioxide in the case combining the substitution, the widespread use of improved stoves and Casamance kiln use since 2006
Conclusion

The aim of the present study was the mitigation CO₂ emissions from domestic fuel from an energy planning model. The results show that the households’ consumption of wood fuel in Dakar causes deforestation. The comparison of the different carbon dioxide emission sources shows that the mainly used charcoal production method releases more CO₂ than other techniques. With the substitution of fuel wood by kerosene and peanut hulls charcoal, the amount of wood energy is reduced, and 5920 ha of forest are preserved. There is a 5% reduction of CO₂ emissions compared to the baseline. In the case of widespread use of improved stoves beginning from 2006, there would be a decrease in the use of charcoal, and carbon dioxide emissions could also decrease by 15% in 2014. Using Casamance kiln could lead to a significant reduction in CO₂ emissions compared to the baseline. In the case of joint implementation of all strategies (substitution, widespread use of improved stoves and Casamance kiln) from 2006, the amount of collected wood would fall by 48% and lead to significant reduction in CO₂ emissions of around 40% from 2006 compared to baseline.

The results of this study show that the current trend of use of wood fuels is a factor of deforestation, but also a source of pollution through emissions of carbon dioxide (CO₂), the major source of greenhouse gas emissions for climate change. To fight against climate change, make the exploitation of forest resources more efficient and sustainable while supplying the domestic household fuels, we must take some measures revealed by the modelling. This modelling shows also that there is a close relationship between several factors, including those related to urban growth and wood energy consumption. It allowed proposing appropriate solutions to the identified problems. Thus, the results of various scenarios studied in this model have shown that there are several effective strategies to curb the increasing trends in consumption of wood energy. However, the projections here are only made on the basis of energy demand. For better planning of this sector, it should involve sub-sectors of the supply and demand for domestic fuels. The integration of these factors could contribute to enrichment of the model and can better influence the scenarios here developed.

Acknowledgements: We wish to thank the IER University of Stuttgart in Germany and GTZ in Dakar for their supports.

References


Quantitative Comparison of the Abundance of Insects between Ecological and Conventional Farms in the Region of Tirana, Albania

Anila Paparisto1,∗, Elton Halimi1, Etleva Hamzaraj1, Margarita Ihi2, Odeta Laknori1

1Department of Biology, University of Tirana, Faculty of Natural Sciences; Bul. Zogu I, Tirana, Albania;
2Department of Physics, University of Tirana, Faculty of Natural Sciences; Bul. Zogu I, Tirana, Albania

Abstract: The aim of this study is a comparison of the abundance of insect fauna between two farms in the region of Tirana (Fushë-Preza), on lots with similar abiotic conditions: one of them is managed ecologically, while the other one is managed conventionally. We intend to see how much are the number and the growth rate of insect populations affected by the presence of insecticides. During 12 months (October 2007-October 2008) we collected insects (following prescribed procedures), and identified them according to genus or family. This way we were able to determine 1491 individuals, from which 1280 (85.84%) in the ecological farm, and only 211 (14.16%) in the conventional one. By analyzing different species of insect fauna, it appears that more carabides (Carabidae, Coleoptera) and aphids (Aphididae, Homoptera) were found in ecological farm. That indicates to the fact that they have better living conditions in ecological farm. We observed that during the spring-summer period, the populations of all insects follow an exponential growth law, where the populations of predators grow faster than those of the prey. The populations of insects found in the ecological farm are several times larger than those found in the conventional one.

Key words: insect fauna, conventional farm, ecological farm, Coleoptera, Homoptera, PPP.

Introduction

Insects influence the ecosystem, being an important part of biota. Insects' activity is strongly related to the development of crops (Birkhofer et al., 2008; Fuller et al., 2005; Gaxho, 1967; Murraj, 1970; Peja, 1995). Lucern (alfalfa) is quite important in the study of the relationship between plants and insects. This is due to the biological aspects of cultivation of this plant. Some harmful insects that damage lucern belong to the orders of Coleoptera, Orthoptera, Hemiptera, Homoptera, etc. One of the ways to fight harmful insects is the use of insecticides, which are toxic substances that kill harmful insects. They are used in specific dosages and in accordance with the species present in the system (Letourneau et al., 2009; Hanaj, 1990). Several kinds of harmful insects are exhibiting resistance to these substances, thus forcing humans to change the dosage used to fight them. The goal of this work is to study the impact of insecticides on the number and growth rate of insect populations, by means of comparing the rates of change of the density of insectofauna in two farms in otherwise identical abiotic conditions in the region of Tirana (Fushë-Prezë), of which one is an ecological farm, while the other is a conventional one.

Main text

Our study included the period from October 2007 to October 2008. We analyzed two agricultural farms of the Fushë-Preza region (near Tirana), of which one is a conventional farm, where insecticides are used, and the other is an ecological farm, oriented toward organic products. In each of the farms we chose a lot with dimensions 200mx100m or an area of 2000m². These two lots are in the same abiotic conditions (Buzo, 2000; Grup autorësh, 1991). They are surrounded by draining ditches (Figure 1).

One of these lots has been treated with insecticides (Kolaci, 1997; Zehnder et al., 2007). The treatment has been done in the months October, February, and March. Below (Table 1) we give the names of the insecticides and the corresponding dosages.

In order to evaluate the insectofauna in two lots which have identical structure and type of soil, we used the method of Pitt traps (Letourneau et al., 2008; Kuu et al., 2004). We set 10 traps in 10 plastic cups of base diameter of 7cm. On the ground the traps were placed inside a small hole of 10 cm height. Traps were distributed uniformly along the diagonal of the lot. On the threshold of the cups

∗Corresponding: E-Mail address: anila_paparisto@yahoo.com; Tel: +355 672004022
were placed substances that attract insects, such as candies, raisins, etc. Inside the cups was poured a blend of 20 parts white vinegar, 80 parts ethylic alcohol 70°, and a few drops of ether. We added two drops of dish detergent, in order to increase the surface tension, so the insects would not be able to escape (Paparisto, 2001). In order to analyze the presence of insects at a height equal to that of the plants, we used the technique of entomological net along the diagonals of the lot we were studying (10 times for each diagonal).

**Figure 1.** Schematics of the area from which material was collected (1. The conventional lot; 2. The ecological lot; 3. Draining ditch)

**Table 1.** Insecticides and dosages used during the period of study

<table>
<thead>
<tr>
<th>Insecticide</th>
<th>Time of Use</th>
<th>Dosage</th>
<th>Active ingredients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lambda-Cyhalothrin</td>
<td>10.10.2007</td>
<td>40ml/100 liter water</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>01.02.2008</td>
<td>Were used 15 litters solution</td>
<td></td>
</tr>
<tr>
<td></td>
<td>06.03.2008</td>
<td>Dosage used 4.56 ml karatë</td>
<td>5%</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>10.10.2007</td>
<td>Dosage 25-30kg/ha</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Were used 150 g sevin</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Active ingredients</td>
<td></td>
</tr>
<tr>
<td>Esfenvalerate</td>
<td>01.02.2008</td>
<td>Dosage 50ml/100 lit water</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Were used 3.8 lit solution</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dosage used 1.9 ml sumialfa</td>
<td></td>
</tr>
<tr>
<td>Methomyl</td>
<td>08.10.2007</td>
<td>Dosage 40-50gr/100 l water</td>
<td>90%</td>
</tr>
<tr>
<td></td>
<td>01.02.2008</td>
<td>Were used 3.8 lit solution</td>
<td></td>
</tr>
<tr>
<td></td>
<td>06.03.2008</td>
<td>Dosage used 0.19 gr lanate</td>
<td></td>
</tr>
</tbody>
</table>

Samples were collected during the period October 2007 to November 2008. The frequency of collection was three times in the months of October, April, May, June, July, August, and September, and once in the months November till March. They were taken in the time interval from 10am to 3pm, depending on the weather conditions. The collected material was stored in sealed entomological vessels. The collected samples were identified with the aid of the stereomicroscope, and the definition keys found in “Praktikumi i Entomologjisë Bujqësore” (Grup autorësh, 1991; Mader, 1996; Misja, 2003; Zahradnik, 1977).

**Conclusions**

The ecological indicator chosen for the evaluation of the dynamics of different species of class *Insecta*, processed by the month in which the samples were collected from the lots, was their density, which measures the number of individuals of each species per unit area. Based on the data obtained
after the identification of the collected individuals, we calculated the densities of different species for each month and lot in study. We identified 1491 individuals, of which 1280 (85.84%) in the ecological farm, and only 211 (14.15%) in the conventional one. Analysis of different species of insecto-fauna showed that in the ecological farm were found more individuals of orders Carabidae, Coleoptera, and Aphididae, Homoptera.

Within each species we observe growth of their populations from February till September, followed by a decrease in the fall and winter months. The population growth observed for the months of spring and summer follows the exponential law: \( N = N_0 e^{\alpha t} \). The Coleoptera population grows according to \( N = 1.97 e^{3.18t} \) in the ecological lot, and \( N = 0.34 e^{2.64t} \) in the conventional one. As we see, \( N_0 \) of the ecological lot is several times higher than that of the conventional one, but the characteristic time \( 1/\alpha \) decreases as well (the characteristic time is the time interval during which the population grows \( e \) times). This indicates an increase of the rate of population growth. The same behaviour is observed in the populations of other orders, as well as for the total number of insects. This can be seen in the graphs (Figures 2, 3, 4).

![Figure 2. The evolution of the Coleoptera population from October 2007 to November 2008](image)

![Figure 3. The evolution of the Homoptera population from October 2007 to November 2008](image)
A comparison of figures 2 and 3 shows that the growth rate of the *Coleoptera* population is higher than those of all the other insect populations. The populations of insects that serve as prey grow at a slower rate than those of predators, which was to be expected. E.g., the population of the order *Homoptera* grows according to \( N=8.78 e^{2.42t} \) in the ecological lot, and \( N=2.15 e^{1.17t} \) in the conventional one. The fact that other populations grow slower reduces the overall growth rate of the total insect population, which can be noticed when we compare the growth laws: \( N=16.05 e^{2.47t} \) in the ecological lot, and \( N=12.75 e^{1.12t} \) in the conventional one. This can be seen when we compare Figures 2 and 4.

Similar studies have been conducted elsewhere, but they have run over shorter periods of time; consequently they lack the present mathematical processing of data, and hence conclusions on the long-term behavior of insect populations [3, 4, 10]. However, in those studies, as in the present one, have been observed decreases by several times of the insect populations when crossing from the ecological farms to the conventional ones [19].

In the future we plan to extend this study in two directions: (i) conducting more measurements, in order to obtain data with higher accuracy, and (ii) building a mathematical model of this system, which would enable us to verify the actual (real-world) values of the parameters that influence the dynamics of this system.

References


The Main Recreative Areas in Podujeva Municipality

Florim Isufi*, Fitim Humolli, Shpejtim Bulliqi

University of Prishtina, Faculty of Maths and Natural SCIENCIES, 10000 Prishtina-KOSOVA

Received February 15, 2010; Accepted April 09, 2010

Abstract: Recreation is time available to human kind, excluding normal working hours that are a time for physiological and physical needs of human kind and time for sleep, which is used for entertainment, sport, hobby, rest etc. Well known fact is that recreation is a need of contemporary man, which is at the same time the reason for elaborating this subject. Podujeva Municipality is one of Republic of Kosova’s municipality, and likewise all other municipalities, offer possibilities and have similar problems to other municipalities. Making distinctions between different recreations and identifying them within a scope of this research, made possible to closely see their advantages and deficiencies in the current situation. Current political, social and economic situation is main factor that has affected already unsatisfactory treatment and level of recreation as available time to man, as well as recreational areas as places that generate good things out of recreation itself. Final conclusion emphasises a need for general public awareness with regard to more professional approach, which presumes involvement of institutions as well, for building up new recreational areas, and maintaining of those that already exist, by implementing professional local and international standards.

Key Words: Recreation areas, Physical recreation, Psychological recreation, Locality, Municipality, GIS.

Geographical Position of Podujeva Municipality

The Municipality of Podujeva is located on the north-east part of Kosovo in geographical coordinates 42°45'29" to 43°08'18" in the north part and 20°58'01" to 21°26'14" in the east part. Having 632,58 km² (5.80 % surface of Republic of Kosovo; www.komuna-podujeve.org), after Prizren with 637,81 km², the Municipality of Podujeva has a second largest surface in Kosovo. In the aspect of geographical-physical position, the Municipality of Podujeva mainly belongs to the grub valley of Llap, including the sides of this dam.

The grub valley of Llap and other areas offer good condition to cultivate different agriculture cultures (Bulliqi 2000). This reminds to us that climate conditions, litology and pedological content as well as relatively the frequent hydric net have created pre-conditions or pre-disposals for good conditions for agriculture use. The Motorway M25, which connects Kosovo and Albania in North-East and Serbia is a very important communication axis not only in Municipality of Podujeva and Kosovo, but for the whole region and more. Although, located in the remote parts of Kosovo, Podujeva has a good position which should not be underestimated (Bulliqi 2000), especially when we asses the entries and above mentioned roads (Figure 1).

Definition of term “Recreation”

Regarding the term “recreation”, there are different opinions which have many similarities and differences between themselves. In many languages it is used almost the same word or something different for the same aim, e.g. Rekreacion (Albanian), Recreation (English), Rekreacija (Croatian, Serbian and Bosnian), the origin of word is from latin “recreatio”, which means renovation (to create again) (Isufi, 2008).

Recreation is the time on disposal for human, excluding the regular time of work, the time for physical-philological needs of human and the time of regular sleep, which is used for the entertainment needs, sports, hobbies, rest-stay, etc.

The needs for recreation change continuously in time, as well as forms and manners for its realization. Starting from the para-classical forms of recreation and following the trends of time, the forms of recreation have been changed.

*Corresponding: E-mail: florim.Isufi@yahoo.com; Tel. +381(0) 44 241 463; fax: +381(0)38 540 705
The time, the daily, weekly, monthly, and yearly schedule have also changed permanently until it is achieved a today’s schedule that today it is considered as a regular, 8 hours daily work. This schedule it is not fixed (unchangeable), but it is generally accepted that today, the general schedule is considered 8-hours daily work. This schedule is not fixed (unchangeable), but it is generally accepted by the majority of countries.

So, we have to understand that in favor of recreation (the time out of necessary regular obligations), the schedule is shorten. While noticing these changes, we come to conclusion that the definition or the understanding manner along with the need for recreation have been and continue to be dynamical, changeable and continuously developing.

Types of recreation

We have these types of recreation:

- Physical recreation
- Psychological Recreation
- Healing from the recreation and a special type of recreation which generates physical and psychological activities.
- Hobby recreation or utilitarian recreation (Gashi 1986).

The above mentioned numbering is base of its content, respectively based on activities which are developed in each of these types of recreation as well as the manner for realization of recreation.
Example: if we take any sports activity of any type, than from this play (sport event), we can have two groups of direct participants (that extend psychological recreation). This is one example how one recreation area or environment can conduct recreation activities, two or many dimensional.

Table.1. Functional recreation spaces in the Municipality of Podujeva.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>The recreation space-Locality</th>
<th>Recreation space</th>
<th>Type of recreation</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Podujeva</td>
<td>Football Stadium</td>
<td>Physical</td>
<td>FC. Llap and FC Besiana</td>
</tr>
<tr>
<td>2</td>
<td>Podujeva-Shtedim</td>
<td>Football Stadium</td>
<td>Physical</td>
<td>FC. Hysi</td>
</tr>
<tr>
<td>3</td>
<td>Podujeva</td>
<td>Small football stadium</td>
<td>Physical</td>
<td>“Llapi Sport”</td>
</tr>
<tr>
<td>4</td>
<td>Podujeva</td>
<td>Small football stadium</td>
<td>Physical</td>
<td>Te Beselicët</td>
</tr>
<tr>
<td>5</td>
<td>Podujeva</td>
<td>Small football stadium</td>
<td>Physical</td>
<td>“Bernabeu”</td>
</tr>
<tr>
<td>6</td>
<td>Podujeva</td>
<td>Small football stadium</td>
<td>Physical</td>
<td>Outside of Podujeva, the road to Merdar</td>
</tr>
<tr>
<td>7</td>
<td>Podujeva</td>
<td>Small football stadium</td>
<td>Physical</td>
<td>Te Hotel Besiana</td>
</tr>
<tr>
<td>8</td>
<td>Llapashticë e Poshtme</td>
<td>Small football stadium</td>
<td>Physical</td>
<td>“Alianz Arena”, near the Llapashtica Cherry</td>
</tr>
<tr>
<td>9</td>
<td>Llapashticë e Poshtme</td>
<td>Small football stadium</td>
<td>Physical</td>
<td>“Nderimi”</td>
</tr>
<tr>
<td>10</td>
<td>Lluzhan</td>
<td>Small football stadium</td>
<td>Physical</td>
<td>Between Sfeqal and Lladoç</td>
</tr>
<tr>
<td>11</td>
<td>Sfeqal</td>
<td>Small football stadium</td>
<td>Physical</td>
<td>Te Hotel Besiana</td>
</tr>
<tr>
<td>12</td>
<td>Podujeva</td>
<td>Swimming Pool</td>
<td>Physical</td>
<td>At the Mosque</td>
</tr>
<tr>
<td>13</td>
<td>Podujeva</td>
<td>Swimming Pool</td>
<td>Physical</td>
<td>At the Mosque</td>
</tr>
<tr>
<td>14</td>
<td>Podujeva</td>
<td>Swimming Pool</td>
<td>Physical</td>
<td>Te malokët</td>
</tr>
<tr>
<td>15</td>
<td>Podujeva</td>
<td>Cultural Hall</td>
<td>Physical</td>
<td>In the center</td>
</tr>
<tr>
<td>16</td>
<td>Podujeva</td>
<td>Park</td>
<td>Psychological</td>
<td>“Peace Park”</td>
</tr>
<tr>
<td>17</td>
<td>Podujeva</td>
<td>Park</td>
<td>Psychological</td>
<td>The old town park near the river Llap</td>
</tr>
<tr>
<td>18</td>
<td>Podujeva</td>
<td>Park-Square</td>
<td>Psychological</td>
<td>The square in the center near the green market</td>
</tr>
<tr>
<td>19</td>
<td>Podujeva</td>
<td>Sports Hall</td>
<td>Physical, Psychological, Fizik, Fizik</td>
<td>New Sports Hall, the only in the Municipality</td>
</tr>
<tr>
<td>20</td>
<td>Batllava, Orllan, Ballaban</td>
<td>Artificial Lake</td>
<td>Psychological, Physical</td>
<td>The known lake of Batllava</td>
</tr>
<tr>
<td>21</td>
<td>Sibovc</td>
<td>The inner swimming pool, Sauna</td>
<td>Physical-Psikik, Fizik</td>
<td>It is used in the winter season</td>
</tr>
<tr>
<td>22</td>
<td>Shakovica</td>
<td>Bath</td>
<td>Curative</td>
<td>Known as Sallabaja Bathe (New Bathe)</td>
</tr>
<tr>
<td>23</td>
<td>Shakovica</td>
<td>Bath</td>
<td>Curative</td>
<td>Known as Sallabaja Bathe (New Bathe)</td>
</tr>
</tbody>
</table>

Explanation:

- Physical recreation (14)
- Physical recreation (4)
- Physical recreation, Psychological (3)
- Curative Recreation (2)
Recreation areas in the Municipality of Podujeva

The Municipality of Podujeva is having 632.58 km² which includes 6% of the territory of Republic of Kosovo. The main centers in this municipality are the Podujeva town itself, approximately in the central part of the mentioned municipality. In the course, we will get to know about the most recreation centers, while in statistical manner we will introduce all those centers that in different forms serve for recreation activities of the inhabitants of all age of this municipality and more.

In above mentioned paragraphs, we mentioned the types of recreation, while now we will get to know with their types in Podujeva Municipality. In due course we will analyze the recreation areas in Podujeva Municipality and we will see as how much these areas fulfill the needs of clients, etc.

The Spaces with high recreation potency in the Municipality of Podujeva

Cultural Hall, Podujeva-

This hall is no doubt the only national or social place, where the youth from town and other places conduct cultural and artistic activities (Figure 2).

The Cultural Hall was built right after the WWII during the years of 1948-1950 (Interview, Balaj N. 2009). The Cultural Hall of the Municipality of Podujeva is adaptable for these activities and or cultural - artistic manifestation: Theater, Chorus, Assemblies and other cultural and artistic organization.

![Figure 2. Cultural Hall, Photo F. Humolli, Podujeva, 07.10.2009](image)

The Hall has a capacity of 420 seats (Interview, Balaj N. 2009), eventhough is the only of this type in Podujeva, again is not being used in a proper way. Here, we should first mention the fact of lack of adequate equipment- machinery for realization of films (activation of ancient cinema)

Up today this cultural hall is not functional as a cinema, since 90-ties. Since, then does not exist the required equipment for showing movies in a big screen and as it is known, such investing is very expensive.

Within this cultural hall, exist the separated annex (small hall), which serves for youth activities and for preparing different programmes.

The large space which offers the cultural hall made it possible for the Podujeva Municipality to offer several necessary spaces for this amateur theater of Podujeva:

- Teatri i Qytetit (Town Theater)
- Theater “Alo”,
- Theater “Ndryshe (Different)”,
- Theater “Besiana”,
- Theater “Qëndresa” (Resistance) and
- Theater “Dielli” (Sun) (Interview, Balaj N. 2009).
The activities of these theaters, which sometimes are functional also with other manifestations except theater is time to time. The reasons can be many, as; the lack of finance, high number of theaters and their coordination among themselves, the lack of interest for watching movies also in other towns which are having more professional theater than this in Podujeva, etc.

Three are NGO-s that conducts their activities in this cultural hall; engagement of those is focused on realization of some youth projects for cultural, environmental aims and other alternatives: 1. Eko Vision, 2. New Alternative of Llap, 3. The Youth Group for human rights (Interview, Balaj N. 2009).

Since, we are mentioning the culture and arts, we know also about two Assemblies in Podujeva Municipality.

**Cultural Center of Podujeva and the Assembly of Adults** (Interview, Balaj N. 2009).

These Assemblies take always part in artistic events of youth all over Kosova, in all National Albanian Festivals, as well as in regional festivals and South-East Europe as well. These Assemblies, while taking part in this festivals many times are crowned with prices, which for participants-children and for organizers is a large satisfaction.

In fact, the cultural life in Podujeva Municipality is poor, due to the general poverty, starting from economical poverty to the lack of adequate environment and the lack of authentic organizations. It’s a pity that sometime ago this town was having the cinema and today is not having it.

**The Park of Peace, the Main Park, Podujeva-**

The park located in the east part of the town, established immediately after the WWII, during the years of 1948-1950 in a hill it is very interesting in a middle of the Llap Hollow, and it is interesting for its morphological aspect. This park is a very valuable environmental reservoir in which is filtrated the large part of the polluted air in the town. This pollution comes as a result of vehicles in the traffic, chimneys from the locality, and little or at all from the industry, as well as result of bad road infrastructure.
The mentioned park has a surface of 16 hectares and it is located on the sea level height of 646 m with a medium height difference from the town of 30 m (615 m). The park with considerable number of falling and keeping leave trees as well as with other vegetative established in this terrain. It offers very convenient conditions for recreation of inhabitants of the town. The park has medium capacities for this town, which of course does not use in an appropriate level. The park in many parts is having natural seats from wood, created from the wood, very natural, trying in every condition to save the originality of the cultivated nature in time in the recreative zone (Figure 6). **Pedestrian Path:** The park posses a number of paths which serve for athletics, walking, standing and movement on a clear air (Figure 6 and 7).

**Figure 6.** Seats and pedestrian path. Photo: F. Humolli, Podujeva 29.09.2009

**Figure 7.** Sport Tool. Photo: F. Humolli Podujeva, 26.09.2009.

**Special Annex of the Park of Peace**

It is financed by donors from Manchester-England and also from the Municipality of Podujeva. This park has improved a lot. This photo and some seats as well as other
Infrastructure in the park (see the photos above) is a result of these contributes that have started mainly in 2003.

**Figure 8.** Annex of the Park of Peace. Photo: F. Humolli, Podujeva, 26.09.2009.

**Batllava Lake, Batllava, Orllan and Ballaban**

Batllava Lake is located on the eastern part of Podujeva Municipality and in the northeastern part of Republic of Kosovo. It is the second largest lake in Republic of Kosovo. Located between two towns Podujeva (about 20 km) and Prishtina (about 35 km) and close to many rural places, with vilas and different kind of seats, with natural attraction of the surrounding forest as well as with a summer freshness of water, etc, this area also offers also potential and tourist destination. You have to go across through the path near the lake and you will see a large number of visitors with their cars, motorcycles, bicycles and on foot walking (the walk in the nature and on the fresh air), playing different games, resting, sailing with boats of different kinds and mostly by refreshing themselves inside the water of the lake. Being so, this recreation area is without doubt the most used of this kind in Kosovo.

**Figure 9.** Batllava Lake. Photo: www.panoramio.com, Designed by, F. Humolli, 2009

1- “Beach”; 2- Fresh resting places- shadows; 3- Curve road which follows the hill lake line; 4- Forest, falling leaves vegetation; 5- Forest- keeping leaves vegetation.
From the explained material until now and on visits conducted in every recreation area as well as the fact of analyze and research of areas in Podujeva Municipality, we come to some results that if in case of plan realization, then we would create better conditions for regeneration of psycho-physical abilities of the citizens of this area, and would strengthen the health of the population and we would increase the collective and environment culture, etc.

Weaknesses:
1. The Municipality of Podujeva has enough recreation area (total 23 recreative areas towards 78 localities (Osmani 2005), which results with around 30 % of coverage of localities with recreation areas). This in reality is not the case, because in some localities as Podujeva and Shakovica, we have more than one recreation area. Total 23 recreation areas for a territory of 632,58 km². Divided in this surface it means that we have one recreation area in 27,50 km².
2. The deviation of these recreation areas is not the same, but there is a pointed concentration. In 7 (seven) localities, we have all recreation areas (Podujeva 15, Shakovica 3, Llapashtica e Poshtme 2, Sfeqla 1, Sibovci 1, Batllava 1 and Merdari 1 (Anonymus 1995).
3. While dividing these recreation areas were not conducted the professional and administrative criterias. For this reason, we can say that their establishing was done based on individual readiness of the owners, who are at the same time the owner of the land in which a recreation area has been established (this is regarding the football terrenes and swimming pools). There is no logic or reason, except on undeveloped countries and those in development where in every condition, you have to exposed directly to the main road, which in main arteria in our case is highway. Excluding some old recreation areas dhe some others, the majority are builded in less than 30 meters distance from the main road, where the frequentation of vehicles is very high.
4. The majority of localities do not have even a zone, area or recreation point in their territory. 71 localities have not established any center.
5. The Municipality of Podujeva at least until now did not have on agenda sufficient treatment regarding the issue of recreation and I belive that also the cadrovic capacities of the Municipality are not sufficient and don’t have the sufficient knowledge to treat this issue, so sensitive and needful for the welfare of the citizens among all.

Priorities:
1. The Park of Peace as it is now, with all need to be in the good level, after all offers an enviroment which can satisfy the curiosity of many simpatizans of the enviroment and nature.
2. The Batllava Lake, after all has achieved several steps forward. By putting the entrance stamps for summer season, now there is more clean enviroment, eliminating more from the garbage of unceraful people and securing a better commodity for many people who rest and come from other municipalities in summer season.
3. The Cultural Hall in Podujeva, eventhough not being used properly, again has its own priority, because at least exist as an object and as such with a little renovation and maintenance can
technically to become as a pikant object in Podujeva Municipality. The fact of possession of the theatrical hall and other annex objects has made it possible that different generation to make first steps of arts in these facilities.

4. The demographic structure of our population is a premis among many others also for recreation and potential possibility of implication for good, in increasing the general awareness and establishing the recreation potential in the near future.

5. In Podujeva Municipality are potential natural zones and others with pre- natural disposition, which in near future would be used for physical, psychological recreation, etc. We are mentioning only some of these potentials:

The zone of the valley of river Kaqandoll, or better to say the dam of this river, with its beaty and premises is desirable for everyone. This area is located on the southern part of Kopaunik Mountain. These Mountains offer in Municipality of Podujeva also other beatiful and natural recreation areas, as we will mention the mountain part of the boundary with Mitrovica Municipality (Bajgora). Other zones in a very northern part and western part of the municipality offer premises for mountain recreation, etc.

Conclusion

Our society in general, Municipality of Podujeva, political structures, who are running to get the power, the intellectual class, different NGO-s mainly those for enviorment, as well as educational structures (schools of law and medium levels) have absolutely to do more than actual engagements to achieve another level, where also a professional and science critic would give other conclusions. Institutions and the society should prove that they are for different enviroment, more clean, healthy and stable, where each person has a possibility to enjoy or to find himself in his circle or away.

We request strongly to change the current approach of establishing new recreation areas. The leading municipal organs but also those central, very soon should lead the private initicatives. They should plan zones and municipal territories, where later, only with small investments from the private sector, the investment would have legitimacy and larger benefit. Planning would understand the rational distribution of those towards localities, where more would be invested in socializing the whole territory and decreation of the difference between the village and a town.

References

Bulliqi Sh. (2000) Magistral Work, UP, FMNS (Faculty of Mathematical and Natural Science), Departament of Geography, Prishtina, Spetember.


www.llapi.com, (commercial and information local web page).

www.panoramio.com, (Kosovo commercial and information web page).
Antibacterial Activity of Coumarin Derivatives Synthesized from Hydroxy-4-2H-[1]-Benzopyran-2-one. The Comparison with Standard Drug

Aziz Behrami1, Kozeta Vaso2*, Islam Krasniqi1

1Chemistry Department, University of Prishtina, Kosovo; 2Chemistry Department, Faculty of Natural Sciences, University of Tirana, Albania

Received March 11, 2010; Accepted April 19, 2010

Abstract: In present paper, we report the organic syntheses of three compounds from 4-Hydroxy-2H-[1]-benzopyran-2-one and describe the results of antibacterial activity of purified compounds. Compounds 4-Hydroxy-3-nitro-2H-[1]-benzopyran-2-one (1a); 4-[N-Ethylhydrazino]-2H-[1]-benzopyran-2-one (2a); 4-Butylamino-2H-[1]-benzopyran-2-one (3a), have been synthesized and characterized using melting points, IR spectra, 1H-NMR and 13C-NMR spectra. The antibacterial activity of synthesized compounds and streptomycin at concentrations of 1mg/ml; 3mg/ml and 5mg/ml have been evaluated against three strains of bacterial culture; Staphylococcus aureus, Escherichia coli and Klebsiella. The compounds show bacteriostatic and bactericidal activity.

Keywords: 4-Hydroxy-2 H-[1]-benzopyran-2-one, coumarin derivatives, antibacterial activity, Staphylococcus aureus, Escherichia coli, Klebsiella, streptomycin.

Introduction

Starting from 4-Hydroxy-2-H-[1]-benzopyran-2-one (a); 2H-[1]-benzopyran-2-one derivatives (1a, 2a, 3a) are synthesized. The identification of 2H-[1]-benzopyran-2-ones derivatives 1a, 2a, 3a is made by using melting points, Infrared(IR) spectrum, 1H-NMR spectrum, 13C-NMR spectrum and elemental analyses. Melting points were determined on an Electrothermal apparatus in an open capillary tube and are uncorrected. Infrared (IR) spectrums were recorded in cm\(^{-1}\) for KBr pellets on a Buck Scientific Spectrophotometer. 1H-NMR spectra were recorded on a Varian 300MHz spectrometer using DMSO-d\(_6\) as the solvent and TMS as the internal reference standard. Chemical Shifts are expressed in \(\delta\) ppm. Mass spectra were taken on a LKB 9000 mass spectrometer. Elemental analyses were preformed on a Perkin – Elmer 240 B CHN analyzer. The purity of the compounds (synthesized) was routinely checked by TLC using Silica G and the spots were exposed in iodine vapour for visualization.

Material and Methods

Experimental, Chemistry

Compounds 4-Hydroxy-3-nitro-2H-[1]-benzopyran-2-one (1a); 4-[N-Ethylhydrazino]-2H-[1]-benzopyran-2-one (2a); 4-Butylamino-2H-[1]-benzopyran-2-one (3a), are synthesized. The identification of 2H-[1]-benzopyran-2-ones derivatives 1a, 2a, 3a is made by using melting points, Infrared(IR) spectrum, 1H-NMR spectrum, 13C-NMR spectrum and elemental analyses. Melting points were determined on an Electrothermal apparatus in an open capillary tube and are uncorrected. Infrared (IR) spectrums were recorded in cm\(^{-1}\) for KBr pellets on a Buck Scientific Spectrophotometer. 1H-NMR spectra were recorded on a Varian 300MHz spectrometer using DMSO-d\(_6\) as the solvent and TMS as the internal reference standard. Chemical Shifts are expressed in \(\delta\) ppm. Mass spectra were taken on a LKB 9000 mass spectrometer. Elemental analyses were preformed on a Perkin – Elmer 240 B CHN analyzer. The purity of the compounds (synthesized) was routinely checked by TLC using Silica G and the spots were exposed in iodine vapour for visualization.

Synthesis of 4-Hidroksi-3-nitro-2H-[1]-bezopyran-2-one (1a) To realize this synthesis is used the former well known method Huebner and Link (Huebner et al 1945) which consists in the reaction

* Corresponding: E-Mail: kozeta_y@yahoo.it, Tel.: + 355- 69 2276071; Fax:+35542229590
between 4-Hydroxy-2-H-[1]-benzopyran-2-one and nitric acid in the presence of acetic acid as catalyst. In a 100ml flask are mixed together 5g 4-Hydroxy-2-H-[1]-benzopyran-2-one solved in 10ml glacial acetic acid with the nitration mixture (3ml concentrated nitric acid with 2.6ml glacial acetic acid). The flask with this mixture is placed in water bath and is refluxed under temperature until red nitrogen oxides vapours are released. The mixture is further cooled with ice until yellow crystals are formed. The crystals are filtered and rinsed first with water and then with a saturated solution of sodium bicarbonate, again with water and finally with absolute ethanol. Recrystallization from absolute ethanol gave a yellow product 85% yield. Melting point 171-172°C (Scheme 1)

Scheme 1: Synthesis of 4-Hydroxy-3-nitro-2H-[1]-benzopyran-2-one (1a)

Synthesis of 4-[N-Ethylidrazino]-2H-[1]-bezopyran-2-one (2a) In a 100ml flask are mixed 2g 4-Hydroxy-2-H-[1]-benzopyran-2-one with the equivalent quantity of 0.85ml ethyl hydrazine. First is added the 4-Hydroxy-2-H-[1]-benzopyran-2-one and then ethyl hydrazine with a pipette and the reflux continuous. After one hour of reflux at 250-300°C a yellow precipitate begins to appear in the flask. Filtration, recrystallization from ethanol and N,N-Dimethylformamide(N,N-DMF) gave a yellow product 80% yield. Melting point 205-207°C (Scheme 2)

Scheme 2: Synthesis of 4-[N-Ethylhydrazino]-2H-[1]-benzopyran-2-one (2a)

Synthesis of 4-Butylamino-2H-[1]-bezopyran-2-one (3a) 2g of 4-Hydroxy-2-H-[1]-benzopyran-2-one is placed in a 100ml flask and then the respective amount of 1.5ml 1-Aminobutane is added. The flask is placed under reflux for several hours at 300°C. At the end of the reaction some brown crystals appears at the walls of the flask. The crystals are filtered and rinsed with methanol in order to remove oil. Recrystallization from methanol gave a brown product 62% yield. Melting point 104.7°C (Scheme 3)

Scheme 3: Synthesis of 4-Butylamino-2H-[1]-benzopyran-2-one (3a)

**Antibacterial activity**  
The purified synthesized compounds 1a, 2a, 3a were subjected to test their antibacterial activities against bacterial cultures; *Staphylococcus aureus, Escherichia coli* and *Klebsiella*. Antibacterial activities of compounds were examined applying the disc method.
Results and Discussions

By reacting equimolar amounts of 4-Hydroksi-2-H-[1]-benzopyran-2-one (a) and corresponding reagents (according schemes 1, 2 and 3), under reflux reaction conditions products 1a, 2a and 3a are synthesized in 85%, 80 and 62% yield. The structures of 2H-[1]-benzopyran-2-one derivatives 1a, 2a and 3a were determined from their IR, $^1$H-NMR, $^{13}$C-NMR spectra and their melting points as follows:

For (1a); IR bands (KBr, cm$^{-1}$): 3300-3600 (OH vibration); 1735(C=O α-pironi); 1603 (C=C aromatic); 1330 NO$_2$; 1550 (C-NO$_2$); 750 (C-H aromatic).

$^1$H-NMR (DMSO-d$_6$) δ ppm: 8.0-7.1 m (4 H aromatic).

$^{13}$C-NMR (DMSO) δ ppm: 137-115 (6C aromatic); 177-174 (C =O); 160-159 (C-NO$_2$); 115-137 (CH aromatic).

For (2a); IR bands (KBr, cm$^{-1}$): 3390-3174 (NH-NH); 3318 (N-H); 1664 (C=O α piron); 3069(C-H aromatic); 1606-1546 (C=C); 782 (C-C).

$^1$H-NMR (DMSO-d$_6$) δ ppm: 9.6-8.9 s (1H; NH); 8.6-8.1 s (1H; NH); 7.9-6.9 m (4H aromatic); 4.9-4.5 s (1H; CH$_3$); 3.6-3.2 s (2H; CH$_2$); 2.4-1.8 s (3H; CH$_3$).

$^{13}$C-NMR (DMSO) δ ppm: 161.3 (C=O); 153.4-153.1 (C-N); 136.2-114.2 (12C aromatic); 132.2-117.0 (8-CH aromatic); 17.1 CH$_3$; 40.3-38.6 (DMSO); 83.5 (CH-3).

For (3a); IR bands (KBr, cm$^{-1}$): 3414 (N-H); 3078 (C-H aromatic); 2940 (C-H alifatic).

$^1$H-NMR (DMSO-d$_6$) δ ppm: 8.2-7.9 d (1H; NH); 7.9-7.2 m (4H aromatic); 3.4-3.0 t (6H; 3CH$_2$); 2.2-1.8 s (3H; CH$_3$); 6.6-5.9 s (1H, C-3)

$^{13}$C-NMR (DMSO) δ ppm: 177(C=O); 136-124 (7C aromatic); 100.8 (C3); 40.3-34.5 (DMSO); 28(CH$_2$); 22 (CH$_2$); 12 (CH$_2$); 10.9 (CH$_3$); 7.7 (CH$_3$); 8 (CH$_3$); 116 (CH aromatic); 24.1 (CH$_2$); 9.2 (CH$_2$).

Antibacterial activity against Staphylococcus aureus, Escherichia coli and Klebsiella

The purified synthesized compounds 1a, 2a, 3a were subjected to test their antibacterial activities against bacterial cultures; *Staphylococcus aureus*, *Escherichia coli* and *Klebsiella*. Antibacterial activity of compounds were examined applying the disc method (d=5,5mm, max. capacity 10mikrogram). The disc was wetted with N,N-DMF solutions of the synthesized compounds with concentration 1mg/ml; 3mg/ml and 5mg/ml and then are placed in petridish(d=15cm). The old subculture *Escherichia coli* and *Klebsiella* were poured and spread in petridish in Agar-Mc-Conkey while *Staphylococcus aureus* in Agar-maltoze (Barry 1991). The discs were incubated at 35°C for 48h, the control was also maintained with DMF and streptomycin in similar manner and, the zones of inhibition of the bacterial growth were measured in mm and the results are summarized in Table 1, Table 2 and Table 3 and graphically in Figures 1, 2 and 3.

Table 1. The diameters of the inhibition zones (mm) of the discs wet with various concentration of the synthesized coumarin derivatives for *Staphilococcus aureus* and the comparison with streptomycin

<table>
<thead>
<tr>
<th>Coumarin derivatives</th>
<th>Concentration and the inhibition zones</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1mg/ml</td>
</tr>
<tr>
<td>1a</td>
<td>17.3mm</td>
</tr>
<tr>
<td>2a</td>
<td>11.6mm</td>
</tr>
<tr>
<td>3a</td>
<td>13.4mm</td>
</tr>
<tr>
<td>Streptomycin</td>
<td>21mm</td>
</tr>
<tr>
<td>N,N-DMF</td>
<td>4mm</td>
</tr>
</tbody>
</table>
Figure 1. Diameters of the inhibition zones (mm) for S. aureus and the comparison with streptomycin

Table 2. The diameters of the inhibition zones (mm) of the discs wet with various concentration of the synthesized coumarin derivatives for Escherichia coli and the comparison with streptomycin

<table>
<thead>
<tr>
<th>Coumarin derivatives</th>
<th>Concentration and the inhibition zones</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1mg/ml</td>
</tr>
<tr>
<td>1a</td>
<td>15.2mm</td>
</tr>
<tr>
<td>2a</td>
<td>18.3mm</td>
</tr>
<tr>
<td>3a</td>
<td>18.7mm</td>
</tr>
<tr>
<td>Streptomycin</td>
<td>19.9mm</td>
</tr>
<tr>
<td>N,N-DMF</td>
<td>4mm</td>
</tr>
</tbody>
</table>

Figure 2. Diameters of the inhibition zones (mm) for E. coli and the comparison with streptomycin

Table 3. The diameters of the inhibition zones (mm) of the discs wet with various concentration of the synthesized coumarin derivatives for Klebsiella and the comparison with streptomycin

<table>
<thead>
<tr>
<th>Coumarin derivatives</th>
<th>Concentration and the inhibition zones</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1mg/ml</td>
</tr>
<tr>
<td>1a</td>
<td>16.6mm</td>
</tr>
<tr>
<td>2a</td>
<td>15.5mm</td>
</tr>
<tr>
<td>3a</td>
<td>12.5mm</td>
</tr>
<tr>
<td>Streptomycin</td>
<td>18mm</td>
</tr>
<tr>
<td>N,N-DMF</td>
<td>4.1mm</td>
</tr>
</tbody>
</table>
Conclusions
From the results we may draw the following conclusions:

1. The chemical structures of synthesized compounds were determined according to extensive NMR experiments and published data.

2. This study provided the first evidence that these compounds 1a, 2a, 3a showed a significant antibacterial effect against Staphylococcus aureus, Escherichia coli and Klebsiella.

3. Compounds 1a, 2a and 3a have bacteriostatic and bactericidal activity.

4. The increasing of concentration of compounds 1a, 2a and 3a shows higher activity against Staphylococcus aureus. The antibacterial activity for compounds 1a and 2a is almost the same to that of streptomycin, while compound 3a shows antibacterial activity always lower compared to streptomycin.

5. The increasing of concentration of compounds 1a and 2a shows almost bacteriostatic activity against Escherichia coli, while compound 3a shows lower bactericidal activity compared to streptomycin.

6. Compounds 1a and 2a show higher antibacterial activity that of compound 3a against Klebsiella, almost the same to that of streptomycin.

7. Compounds 1a and 2a in concentrations 3mg/ml and 5mg/ml show antibacterial activity higher than that of streptomycin.

References


Sanghyun Lee 1, Dong-Sun Shin 1, Ju Sun Kim 1, Ki-Bong Oh, Sam Sik Kan, (2003) Antibacterial Coumarins from *Angelica gigas* Roots. Archives of Pharmacal Research. 26, Nr.6, 449-452.
Spectral Separation of Uranine, SRG Extra and Rhodamine WT Fluorescence in Binary Mixtures in Water Samples

Liljana Kola*, Pranvera Lazo

Tirana University, Faculty of Natural Sciences, Tirana, Albania

Received April 2, 2010; Accepted June 15, 2010

Abstract: The fluorescence ability of Uranine, Rhodamine WT and SRG Extra (Sulphorhodamine G Extra) enables their using as artificial tracers in the water system studies. These fluorescent can be injected in a water system to trace and determine water movements within the carstic system and underground waters. Related with the aims of the study one can inject one, two or more dyes in the different points of the same water system. The artificial tracer experiment in water system studies was first applied in our country; in the carstic system study of Mali me Gropa, in 2002. In four different places of the system were injected four artificial tracers in the same time. One can detect the maxima of the fluorescence of each tracer in water samples separating them from each other. The separation of the fluorescent dyes needs chemical supplementary treatments. In this paper only spectral separation of fluorescent dyes in binary mixtures and treatments based on pH-variations are described. The concentration and synchronous scan methods were used for the measurement of the Uranine, Rhodamine WT and Sulphorhodamine G Extra fluorescence by means of a Perkin Elmer LS 55 Luminescence Spectrometer. These results help us to decide which dyes can be used together in the same water system study. According to these results one can decide how to detect the maxima of their fluorescence in water samples, as well.

Key words: Synchronous scan, Fluorescence Intensity (IF), Artificial tracer, Uranine, SRG, Extra, Rhodamine WT.

Introduction

Modern techniques of tracers in hydrology are elaborated to know and study aquatic systems in order to assess their water suitability as well as to find the optimum and sustainable ways of water management. The introduction of fluorescent tracers has led to enormous methodological and instrumental developments (Behrens, 1983; Behrens, 1986). The problems they deal with when applied in studying various water systems might be grouped into different groups, according to where is groundwater flowing from, from where it comes, whether exist underground hydraulic connections between different points of the system or not, how is flowing the groundwater in(to) and/or through the system under the study, etc. (Käss, 1994).

Water system is labeled through fluorescent dyes as artificial tracers and then their presence is monitored from time to time in various parts of the system under the study. Related with the aims of the study one can inject one, two or more tracers in the same experiment.

The greatest advantage of the synchronous scan method is the detection of almost all dyes used in hydrology in one spectrum. With this method a better spectral resolution and a diminished Rayleigh and Raman scatter is obtained. But it is not possible to analyze quantitatively a mixture of dyes only by instrumental measurement. According to the close vicinity of the fluorescence emission maxima spectral overlapping occurs. In practice this happen if two or more tracers are used in the same experiment. To separate the dyes from each other, as Benischke (1991) and Käss (1994) have shown, supplementary chemical treatments of the sample are necessary. This paper presents the obtained results in our lab from the spectral separations of fluorescent dyes in binary mixtures, Uranine-Rhodamine WT, Uranine-SRG Extra and treatments based on pH-variations of the water samples. These results can help us to decide which dyes can be used together in the same water system study and how to detect the maxima of their fluorescence in water samples, too.

Materials and Methods

Some “blanks” been sampled from the different water system, were previously analyzed in order to assess the natural presence of dyes fluorescence, the so called “background”. A special
software package (FL WinLab) manages different application programs that the instrument LS 55 offers. Tracer’s content in water samples was detected and measured by using the Concentration and Synchronous Scan Applications. First the instrument validation should be realized through Raman spectra (Raman Peak Wavelength, Raman Peak Intensity and Raman S/N ratio) from a sealed water cell (Perkin Elmer-1, 2000) and a reference material, Anthracene (Perkin Elmer-2, 2000). The instrument stability was checked with regard to fluorescence intensity by the means of a reference material (Anthracene) (Perkin Elmer 1 and 2, 2000). The method elaborated to measure dyes content in water samples is made up of the following parameters: Uranine-Excitation wavelength-491 nm; Emission wavelength- 512 nm; Rhodamine WT- Excitation wavelength- 554 nm; Emission wavelength- 580 nm; SRG Extra- Excitation wavelength- 531 nm; Emission wavelength- 552 nm. The other parameters are the same for these tracers: Ex. slit- 10.0 nm; Em. slit- 10.0 nm; Δλ– 21 nm; etc. The instrument was previously calibrated with standard solutions by means of the calibration application (Lazo, 2002) for Uranine, Rhodamine WT and SRG Extra (Kola, 2008). Chemical treatment procedure has been applied for both samples and standards.

Results and Discussion

Separations of Uranine and Rhodamine WT Fluorescence in Binary Mixtures in Water Samples

When Uranine and Rhodamine WT are injected together as artificial tracers in the same water system, it is possible that these tracers may be together in the same water samples collected in different points of the system. In this paper only separation of fluorescent dyes in such binary mixtures and treatments based on pH-variations is described. Standard solutions of Uranine (concentration=1ppb) and Rhodamine WT (concentration=1ppb) in distilled water were prepared. Mixture of these standard solutions in equal quantity (1:1) was prepared to supervise practically the behaviour of these dyes during their measurements and separations.

Fluorescence of Uranine and Rhodamine WT standard solutions (conc.=1ppb) and their mixture were measured applying the concentration method of Uranine and of Rhodamine WT, to compare the results between them and the obtained results by applying synchronous scan method, too. Uranine gives its fluorescence maximum in a basic medium at pH> 8.3 (see: Figure 1, Kola, 2008) therefore the measurements were made after the treatment of the standard solution with EDTA-Na 0.5 mol/dm³, in order to create a basic medium (according to Uranine concentration method), as is shown by Benischke (1991) and Käss (1994).

![Figure 1. Influence of pH on Uranine, Rhodamine WT and SRG Extra Fluorescence Intensity](image)

Measurements of the fluorescence in the same samples, using Rhodamine WT concentration method, were done directly in above samples, without preliminary treatment for changing the pH value, because Rhodamine WT gives the maximum of fluorescence at pH > 5.5 (Figure 1). Obtained results using the concentration method of Uranine are presented in table 1, whereas table 2 presents the obtained results using the concentration method of Rhodamine WT.

The above results show that the application of the concentration method is not a good way to measure the fluorescence of these mixed dyes in the water samples. The synchronous scan method was applied to detect Uranine and Rhodamine WT in above standard solutions and their mixture in equal quantity. Their spectra are presented in figure 2.
**Table 1:** Results obtained by concentration method of Uranine.

<table>
<thead>
<tr>
<th>Nr</th>
<th>Sample</th>
<th>Fluorescence Intensity</th>
<th>Conc. (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Standard solution 1ppb Uranine</td>
<td>159.259</td>
<td>1.011</td>
</tr>
<tr>
<td>2</td>
<td>Standard solution 1ppb Rhodamine WT</td>
<td>0.176</td>
<td>0.000</td>
</tr>
<tr>
<td>3</td>
<td>Mixture: Uranine+Rhodamine WT (1:1)</td>
<td>59.539</td>
<td>0.360</td>
</tr>
<tr>
<td>4</td>
<td>Mixture: Uranine+Rhod.WT (1:1), pH&gt; 8</td>
<td>160.062</td>
<td>1.024</td>
</tr>
</tbody>
</table>

**Table 2:** Results obtained by concentration method of Rhodamine WT.

<table>
<thead>
<tr>
<th>Nr</th>
<th>Sample</th>
<th>Fluorescence Intensity</th>
<th>Conc. (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Standard solution 1ppb Uranine</td>
<td>0.083</td>
<td>0.001</td>
</tr>
<tr>
<td>2</td>
<td>Standard solution 1ppb Rhod. WT</td>
<td>45.001</td>
<td>1.02</td>
</tr>
<tr>
<td>3</td>
<td>Mixture: Uranine+Rhodamine WT (1:1)</td>
<td>45.688</td>
<td>1.044</td>
</tr>
<tr>
<td>4</td>
<td>Mixture: Uranine+Rhod.WT (1:1), pH&gt; 8</td>
<td>44.013</td>
<td>1.012</td>
</tr>
</tbody>
</table>

**Figure 2.** Synchronous scan of the standard solutions of Uranine (conc.=1ppb) and Rhodamine WT (conc.=1ppb) and their mixture at equal quantity.

Spectrum 1 in figure 2 shows fluorescence emission of Rhodamine WT standard solutions 1ppb which has the peak at $\lambda = 554$ nm with fluorescence intensity $I_F = 47$. Spectrum 2 presents fluorescence emission of the Uranine standard solutions (1ppb) at $\lambda = 491$ nm and $I_F = 168$. Synchronous scan of the mixture of Uranine and Rhodamine WT standard solutions 1ppb in the ratio range of 1:1 gave spectrum 3. One can see clearly that the fluorescence peak of Uranine is depressed ($I_F = 48$) because of the pH $< 8$ of the sample. Synchronous scan of this mixture in pH $> 8$ (after adding EDTA-Na) gave spectrum 4. Fluorescence intensity of Uranine in this spectrum has maximum value ($I_F = 173$), whereas fluorescence peak of Rhodamine in spectra 4 remains unaffected ($I_F = 47$). So, both tracers can be well determined under alkaline conditions, which give full fluorescence for Uranine and Rhodamine WT. Because the fluorescence peaks of both tracers are far distant in the spectrum from each other no spectral overlapping occurs (Spectrum 4 in Figure 2).

These results confirm clearly that Uranine and Rhodamine WT can be used together in the same tracer experiment in water system studies.

**Separations of Uranine and SRG Extra Fluorescence in Binary Mixtures in Water Samples**

The same way mentioned above was applied to supervise practically the behaviour of Uranine and SRG Extra when they are used together as artificial tracers in the same water system study.
Mixture of Uranine and SRG Extra standard solutions 1ppb (solvent: distilled water) in equal quantity (1:1) was prepared. Fluorescence of the standard solutions and their mixture was measured using the concentration method of Uranine and of SRG Extra. Uranine gives its fluorescence maximum in a basic medium at pH > 8.3 (Figure 1) (Kola, 2008), therefore the measurement are made before and after the treatment of the standard solution and their mixture with EDTA-Na 0.5 mol/dm³, in order to create a basic medium according to Uranine concentration method (Benishke, 1991; Käss, 1994). Obtained results using the concentration method of Uranine are presented in table 3.

**Table 3. Results obtained by concentration method of Uranine.**

<table>
<thead>
<tr>
<th>Nr</th>
<th>Sample</th>
<th>Fluorescence Intensity</th>
<th>Conc. (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Standars solution 1ppb Uranine</td>
<td>156.392</td>
<td>0.985</td>
</tr>
<tr>
<td>2</td>
<td>Standard solution 1ppb SRG Extra</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Standard sol. 1ppb SRG, pH&gt; 8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Mixture: Uranine+SRG (1:1)</td>
<td>63.560</td>
<td>0.389</td>
</tr>
<tr>
<td>5</td>
<td>Mixture: Uranine+SRG 1:1, pH&gt; 8</td>
<td>156.719</td>
<td>0.988</td>
</tr>
</tbody>
</table>

**Table 4. Results obtained by concentration method of SRG Extra.**

<table>
<thead>
<tr>
<th>Nr</th>
<th>Sample</th>
<th>Fluorescence Intensity</th>
<th>Conc. (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Standars solution 1ppb Uranine</td>
<td>0.590</td>
<td>0.007</td>
</tr>
<tr>
<td>2</td>
<td>Standard solution 1ppb SRG Extra</td>
<td>74.858</td>
<td>0.845</td>
</tr>
<tr>
<td>3</td>
<td>Mixture: Uranine+SRG (1:1)</td>
<td>68.102</td>
<td>0.769</td>
</tr>
<tr>
<td>4</td>
<td>Mixture U+SRG (1:1), pH&gt; 8</td>
<td>67.320</td>
<td>0.76</td>
</tr>
</tbody>
</table>

The above results show again that the application of the concentration method is not a good way to measure these mixed dyes in the water samples. The synchronous scan method was applied to detect Uranine and SRG Extra in above solutions. Figure 3 shows fluorescence emission spectra of the solutions mentioned above.

![Figure 3](image-url). Synchronous scan of a mixture Uranine :SRG Extra 1:1 in water and their standard solutions 1 ppb.

Synchronous scan of the standard solution of SRG (conc.=1ppb) gave the spectrum-1, with fluorescence intensity $I_F = 43.41$. Synchronous scan of the standard solution of Uranine (conc.=1ppb) gave the spectrum-2 with maximum of the peak at $\lambda = 487.24$ nm with fluorescence intensity $I_F = 103.78$. Uranine-SRG mixture (1:1) was synchronous scanned without prior treatment with EDTA-Na (spectrum-3). First peak in this spectrum has the form of a shoulder in the waves length interval $\lambda = 475-500$ nm with $I_F = 10.48$ because Uranine don’t give its maximum of fluorescence at these
conditions (pH < 8). The second peak of this spectrum at $\lambda_2 = 525.16$ nm with $I_F = 40.65$ belongs fluorescence intensity of SRG Extra.

Synchronous scan of this mixture in pH > 8 (after added EDTA-Na) gave spectrum-4. Fluorescence of Uranine in the first peak of this spectrum at $\lambda_1 = 487.24$ nm has the maximum value of fluorescence intensity $I_F = 104$, which is equal with maximum of Uranine peak of its standard solution (spectrum-2). So, it is necessary to increase pH value of the water samples until pH > 8.3, to take the maximum of Uranine fluorescence. The small peak in spectrum-4 at $\lambda_2 = 524.86$ nm with $I_F = 39.05$ belongs to SRG Extra fluorescence. In water samples containing together Uranine and SRG Extra, one can measure SRG Extra acidifying the water sample. By acidification of the sample to pH<3, Uranine fluorescence will disappear almost completely, so SRG Extra can be well detected (Figure 1). Total separation of the Uranine fluorescence can not be achieved through manipulation of pH value of the water sample. As a result, Uranine and SRG Extra can be used together as artificial tracers in aquatic environments when there is no opportunity for other choice.

Conclusions

Measurements of Uranine, Rhodamine WT and SRG Extra in water samples, when they are used together in the same tracer experiment, should be done only by synchronous scan method. Uranine and Rhodamine WT spectra don’t interfere at fluorescence intensity of each other, when they are present in the same water sample. Uranine and Rhodamine WT are suitable to be used together in the same tracer experiment. Uranine and SRG Extra can be used together as artificial tracers in aquatic environments when there is not other choice, for e.g. when you don’t have the possibility to use another artificial tracer more suitable than SRG Extra.

References

Trepça Ore Belt and Beloberdo Mineral deposit—Geological Overview and Interpretation, Kosovo

Sylejman Hyseni*, Bedri Durmishaj, Mursel Rama, Muharrem Zabeli

University of Prishtina Faculty Mining and Metallurgy Mitrovicë 40000 Kosovo

Received January 18, 2010; Accepted May 12, 2010

Abstract: The Trepça Belt of Pb-Zn-Ag mineralization is located the NNW-SSE trending Vardar zone. The Belt extends for over 80 km, and supports five mines during the period 1930-2010, and contains a number of the other Pb-Zn occurrences. The replacement and vein type mineralization is hosted primarily by Mesozoic carbonates, but also occasionally by amphibolites, and it display a clear structural control. Mineralization is spatially and genetically related to Neogene andesite-dacite extrusive and sub volcanic intrusive. We use for this paper only Beloberdo mineral deposit.

Key Words: Kosovo, Trepça Belt, deposit, lead, zinc, Vardar zone, Skarn type mineralization.

Introduction

The history of silver, lead and zinc mining in Kosovo is intervened with the history of Kosovo itself. In the modern era, the production of silver, lead and zinc has been synonymous with Trepça. This briefing note describes the current situation at Trepca and examines its future outlook.

Mining activities and smelting of the silver-bearing lead-zinc ore in Kosovo has a long history and can be dated back to even pre-Roman times as relics of tools and diggings show. From the Roman period to the middle Ages, the area between Serbia and Greece - and especially the southern part of Kosovo was intensively exploited for its lead-zinc and silver ores and at that time was one of most important sources of its kind. The Roman and Ottoman Empires fought to take control of silver mines in Kosovo and at a later stage the Serbian Middle Kingdom produced much of its coinage from silver mined at Artana (Novo Berdo).

The British company Seltrust founded at one stage, in Trepca operated nine mines as shown on the map (Figure 1). Currently, only five of these have significant remaining resources although all have the potential for extensions to known mineralization, the mining and processing infrastructure following the conflict was in a very poor condition; however, after major efforts and significant investment, four of the mines have restarted limited production.

The successful industry of the 60s and the historic mines were founded on the quality of the lead-zinc deposits that occur in the Trepca Mineral Belt running in a NW-SE direction from Beloberdo in the North to Kizhnica in the South. Whilst the 80's and 90's were characterized, at least partly, by a lack of exploration, the known deposits are not exhausted and mine able reserves and measured resources (Wheeler, 2003) at the five key mines totalling at 7.068 million tones at 5.46 wt% lead, 5.64 wt% zinc and 116 g/tonne silver. All deposits are open at depth or extend on strike. Recent geological work strongly indicates that the deposits within the Trepca Mineral Belt are considered highly prospective regarding additional reserves and resources as the mineralization is structurally and/or fault controlled. Consequently, the Trepca Mineral Belts (Hyseni & Large, 2003) holds a high potential, not only for lead, zinc and silver but also for copper and gold (Hyseni & Durmishaj, 2007).

Regional Geology

The linear Trepca “Belt” of lead-zinc mineralization extends for over 80 km in northern Kosovo, and includes numerous mines and occurrences (Figure 1). Although evidence of mining dates back to the Romans, who were primarily interested in the small gold occurrences, modern mining started in 1930 at the Stan Terg lead-zinc mine, which is located on the Trepca stream.

The Trepca Belt, which comprises part of what has been previously described as the Kapaonik District (Forgan, 1948; Jankovic et al., 1997), includes numerous lead-zinc deposits. On a regional

*Corresponding: E-mail: sylejmanhyseni3@hotmail.com; Tel+377(0)44136020
scale, the Trepca Belt belongs to the Kosovo sector of the Serbo-Kosovo-Macedonian-Rhodope metallogenic belt of Oligocene-Miocene age, which includes the base and precious-metal districts in Kosovo, southern and western Serbia, Macedonia, northern Greece and southern Bulgaria (Heinrich & Neubauer, 2002). The Trepca Belt lies within the NNW-SSE trending Vardar tectonic zone (Figure 2).

Figure 1. Map of Kosovo showing Trepça with the Mineral deposit of Belobrdo, and Mines, Concentrators and final Processing Facilities

Figure 2 Vardar tectonic zone

Regional structure marks the fundamental suture between the Serbo-Kosovaro-Macedonian Massif, which is underlain by late Proterozoic metamorphic, and the Dina rides, which are comprised of Mesozoic successions with typical Alpine deformation. The Vardar Zone contains fragments of Paleozoic crystalline schist and phyllite, with unconformable overlying Triassic clastics, phyllites,
volcanoclastic rocks and Upper Triassic carbonates. Serpentinized ultrabazic rocks, gabbros, diabases and sediments of the ophiolite association characterize the Jurassic. The Cretaceous sequence consists of a complex series (sometimes described as mélange) of clastics, serpentinite, mafic volcanics and volcanoclastic rocks, and carbonates. The Tertiary (Oligocene-Miocene) andesite, trachyte and latite sub volcanic intrusives volcanics and pyroclastic rocks occur at several centers within the Trepca Belt, and cover large areas and is particularly well developed in the eastern sector (so-called Inner Vardar sub-zone) of the Vardar zone. Miocene and Pliocene shallow water sediments fill the Kosovo Basin, which borders the central and southern sectors of the Trepca Belt to the west.

Figure 3. The Trepca Mineral Belt

The structure of the Trepca Belt is dominated by NNW-SSE trending structures. Overthrusts with SE vergence are dominant, some of which are demonstrably post-Oligo-Miocene in age while others are clearly older. Congruent WSW-ENE structures link the dominant NNW-SSE trending structures. It is considered that many of the Vardar structures may be reactivated Variscan structures marginal to the Serbo-Kosovar-Macedonian Massif. The possible influence of the NW-SE structures in the Drina-Ivanjica (Drenica) structural block, which is an external unit of the Dinarides and forms the western margin of the Vardar zone, are overprinted on the dominant NNW-SSE trend. Trepça geologists recognized three regional (NNW-SSE) trending zones of mineralization within the Belt (Figure 3).

Zone I – includes Artana (Novoberdo) – Batllavë. Zone I follows the boundary between the Kosovo sector of the Serbo-Kosovar-Macedonian Massif, which is marked here by extensive Neogene calc-alkaline volcanics and intrusive, with the Vardar Zone.

Zone II – extends from the Hajvalia – Kizhnica district in the south to Belo Berdo in the north, and includes the Stan Terg mine and numerous other occurrences. Zone II follows the major fault that marks the eastern margin of the Miocene Prishtina basin, and its extension to the NNW and the intrusive and volcanic complexes (Figure.3) in northern Kosovo.

Zone III – includes the Crnac mine, and extends along a number of lead-zinc occurrences on the western border of the Vardar Zone, where it is in contract with the Dinaride-Drina-Ivanjica (Drenica) structural block (Pruthi, 2005).

Regional Geology and setting mineral deposit Beloberdo

The Beloberdo mineral deposit area falls within the Trepca Mineral Belt of the Vardar Zone. Various litho-stratigraphically and structural units of Triassic to Pliocene age can be geologically distinguished. The oldest rocks in the Beloberdo Mine area belong to the Suva Rudžiste Series, which
in the mine area is also called Footwall Series. These metamorphic rocks are composed of argillic phyllite, phyllite, meta-sandstone, crystalline limestone and marble, meta-dolerite (diabase) as well as chlorite-, chlorite-epidote- and argillo-schist. One of the most characteristic and dominant rock types is the serpentinite of the Iber Massif and its relationship with younger rocks is mostly of tectonic origin.

The northern part of the Beloberdo deposit is characterised by the transgressive Upper Cretaceous contact on Triassic schist, which extends in a north-easterly direction towards Brzeća. This structure controls numerous and almost all continuous lead-zinc mineralization and ore bodies of the exhausted old Beloberdo Mine, Zaplanina, Strmac, and Čelići, Kula, Karaula and Brzeće. The Upper Cretaceous sediments includes, from bottom to top: Reef limestone, impure limestone and Flysch. All economic mineralization and high-grade ore bodies of the deposit occur within the stratigraphy level of the reef limestone.

Rocks of Tertiary age are widespread in the Beloberdo area and occur as sediments of the Red Series and rocks of volcanic origin. Rocks of the Beloberdo volcanic complex are several hundreds of meters in thickness and can be chemically related to two magmatic cycles. The first volcanic phase has produced mainly rocks of andesite composition and also represents the largest part of the Beloberdo volcanic complex. Sub-volcanic rocks of andesite composition are widespread and also occur within the Beloberdo mining area and have intruded into fault and fracture zones. Significant Pb-Zn mineralization often occurs adjacent to these dykes. Consequently the sub-volcanic rocks have a great importance as ore traps. The second volcanic phase at the upper level of the volcanic complex is quartz latitic in composition and occurs as lava flows and dykes. The quartz latitic dykes, like the andesite, follow pre-existing structural directions and also have acted as ore traps for mineralizing fluids.

**Figure 5** Ore body GII Beloberdo mineral deposit

**Figure 4** Geology of Beloberdo area

**Geology of Beloberdo mineral deposit**

The mineral deposit includes three ore bodies, which display several styles of mineralization (Figure 6). Replacement mineralization (GII and GIII ore bodies) is located on or close to the tectonic contacts of the carbonates (both Triassic and Cretaceous) with volcanoclastic rocks and/or serpentinite. The contact between serpentinite and Cretaceous limestone (Figure 6, section 2) is the Major controlling feature, with the mineralization being best developed beneath the overlying Tertiary
clastic and volcanoclastic rocks. The GII ore body is irregularly shaped and plunges to the SE at 20°-30°. The ore mineralogy is complex – dominated by pyrite, sphalerite, galena, it also includes arsenopyrite, chalcopyrite and a number of sulpho-salts. Quartz and (Mn-Fe) calcite are the main hydrothermal gangue minerals.

Vein-type mineralization of GII/12 ore body (Figure 6) consists of a quartz-carbonate-sulphide vein with a strike length of 400 m. It penetrates into the overlying Tertiary volcanoclastic rocks.

Skarn-type mineralization: Skarn mineralization is spatially separated from the replacement and vein-type mineralization and is best developed in Cretaceous carbonate consisting of magnetite, pyrrhotite, galena, sphalerite and chalcopyrite.

Figure 6. Ore bodies in Beloberdo mineral deposit

Estimated Reserves
These reserves derive from detailed reviews of previous estimates to which economic cut-off calculations and mining factors have been applied. The reserves given below (Table 1) are based on 3D modelling using Data Mine (Wheeler, 2003), Software and a recent re-evaluation; however do not strictly comply with CIM reporting standards due to a lack of reconciliation data. The reserves given below refer only to ore bodies located on the Kosovo side of the deposit. The deposit (abandoned parts) extends in to Serbian territory.

Table 1. Estimated Reserves and contents lead, zinc and silver in mineral deposit of Beloberdo

<table>
<thead>
<tr>
<th></th>
<th>Tones</th>
<th>Pb %</th>
<th>Zn %</th>
<th>Ag g/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proven Reserves</td>
<td>261,000</td>
<td>6.21</td>
<td>5.56</td>
<td>89.5</td>
</tr>
<tr>
<td>Probable Reserves</td>
<td>1,079,000</td>
<td>6.68</td>
<td>5.78</td>
<td>95.6</td>
</tr>
<tr>
<td>Total Mine able Reserves</td>
<td>1,340,000</td>
<td>6.59</td>
<td>5.74</td>
<td>94.4</td>
</tr>
<tr>
<td>Total Resources</td>
<td>3,720,000</td>
<td>7.65</td>
<td>6.50</td>
<td>109.0</td>
</tr>
</tbody>
</table>

References


Geochemical-Geophysical Studies for Tecnogen Pollution in Porto Romano, Albania and Their Integration in GIS

Fatbardha Vinçani1,*, Fatbardha Cara1, Piro Leka1
1Department of Geophysics and Georisk, Institute of Geosciences, UPT, Rruga Don Bosko, Nr. 60, Albania

Received 10 February, 2010; Accepted April 22, 2010

Abstract: The area around the former chemical plant in Porto Romano is contaminated by high-risk chemical components composed by Lindan, Sodium Bichromate, accumulated in tailings. They have the ability not only to pollute the water, but also are easily absorbed by agricultural cultures. The two chemicals are pollutants at high risk for the health of nearby residents, because they cause cancer in the liver, nervous system and lung of human being. The important place in the studying of tecnogen pollution spreading around the region of Porto Romano have occupied the following methods: Applying Electrometry with resistivity method, electrical sounding array-Schlumberger, with AB up to 1000 m; Well Logging with observations of electrical resistivity and spontaneous polarization into the drilling and the Geochemical method of soil samples of the Quaternary deposits with sampling density every 250 m, in the 5 and 40 cm depth. Through the use of geochemical-geophysical methods complexity is achieved to be determined: depth, thickness and lithologic composition of Quaternary deposits, chemical elements as pollutants and is consequently judging above the risk of spreading and distribution of pollution in surface and in depths of geological environment. Geochemical-geophysical studies carried out for tecnogen pollution in Porto Romano are integrated in GIS with the help of software Arc View GIS 8.2. GIS in the above studies will serve in the future to conduct further reinterpretation and reprocessing to help solving problems of scientific research required.

Keywords: Tecnogen pollution, chemical elements, electrical sounding, well logging, drilling, GIS, Porto Romano.

Introduction
The former chemical plant in Porto Romano until its closure in 1990, has produced pesticides consisting by Lindan (hexclorant) and Sodium Bichromate. In the neighborhood of this plant have been deposited from 15 to 25 thousand tones of Sodium Bichromate (Cr 6+), which have the ability not only to pollute the water, but are also easily to be absorbed by agricultural cultures.

Currently in the territory of Durres district are 2500 tones of material particles, which together with atmospheric air are absorbed to the lungs, becoming an internal source of continuous ionizing radiation, which causes lung cancer. The higher level of toxic-industrial pollution appears in areas of former chemical plant, which occupies a territory of about 3000 ha. In different soil samples and water samples analyzed at the Institute of Hygiene in Tirana, has resulted that the content of Lindan in water is up to 5 mg/l, which means 4000 times above the allowed limits of drinking water. Analysis of contaminated surfaces has shown high content of Lindan, from which it results that concentrations of HCH Ion are from 1.29 mg/kg up to 3.14 mg/kg. The samples taken in cultivated products of this area, have shown that they have a high risk to be used from the people, living there (Cara et al., 2003).

Lindan is known as very stable chemical element in the environment and has the ability to be easily accumulated in the food and in the human chain water-plant-animal-human being. So, it appears as a contaminant of high risk, and causes the cancer in the liver and nervous system of human. Sodium Bichromate is another contaminant of high risk in this area, because chromium 6-valent causes lung cancer.

The Porto Romano zone is identified and assessed as one of the most polluted territory in Albania and in the Balkans and needs to urgently be intervened rehabilitating this environment. It is necessary to emphasize the fact that in this area live about 12000 inhabitants, who are at risk to their

* Corresponding: E-mail: bardha_vin@yahoo.com; Tel/Fax: +355 42 250 601
health. The worst is that building materials of destroyed chemical plants, are putting in use to build their houses. Children of this community play in the contaminated territories, while domestic animals are using the plants and the waters in these territories.

If no rehabilitation and protective immediately measures will be taken by the authorities, high risk would be presented to the flora and fauna in the continent and the sea, in a territory larger than today (Ulitin et al., 2003).

To determine the spreading of Sodium Bichromate and Lindan pollution in the surface and in terms of depth around the former Chemical plant in Porto Romano, were used geochemical and geophysical methods.

**Defining of the boundaries of technologic contamination spreading in surface**

**Geochemistry**

To assess the spreading of technologic contamination in the surface soils in the region of Porto Romano is used the geochemical method of Quaternary deposits mapping, based on the soils sampling. Each soil sample is presented from a mixture of 4 sample towards the northeast-southwest, in the distance from the central point every 250 m, in 5 and 40 cm depth, in an area of 30 km² (Figure 1).

![The studied area](image)

**Figure 1.** The topographic map of Albania with the studied area

Geochemical maps, processed for the chemical elements as Co, Cu, Pb, Fe, Na, K shows that local outlined anomalies are of low intensity and limited sizes. In the geochemical maps of elements Cr, Ni, Zn, Mn are noted anomalous values from 300 to 500 ppm, mainly near the former Chemical Plant and in the sectors of waste discharging of Durresi town. It is to be noted and very interesting the behavior of Cr element. Its levels in soils and water, near the former Chemical plant, are very high with prevalence of Cr⁶⁺, which poses a serious cancerous risk (Cara et al., 2003), (Figure 2).
As seen in Figure 2, according to sampling in depth 5 cm, almost in the whole territory of Porto Romano-Fllakë is observed spreading of technologic pollution in surface, with the anomalous values from 350 to 400 ppm. The centers of the anomalies with highest values that 350 ppm of Cr are mainly related with former industrial discharging, localized in the northern and northeastern part of the former chemical plant. Penetration in depth of Cr $^{+6}$ is controlled by marshy clay and pH values (Tashko, 2006), (Figure 3).

Study of the distribution of technologic pollution in terms of depth

**Geoelectrics**

To judge the possibility of pollution distribution in terms of depth around the former Chemical plant in Porto Romano were interpreted the initial data of VES, carried out with quadratic regular network 500 x 500 m, array AB up to 1000 m, in an area of 12 km$^2$ (Leka et al., 2005). Graphic material processed has helped in the geological-geophysical interpretation of the results of VES, carried out in the region of Lalzi Gulf (Leka & Vinçani, 2005).
Map of electrical resistivity for the studied various depths

In electrical resistivity maps processed for the studied various depths, based to the electrical soundings-array from AB=80 m up to 1000 m, is shown that the parameter values of electrical resistivity vary from 2 to 50 ohm.m, reflecting the non-uniform distribution of sediments in depth (Vinçani et al., 2005).

Alluvial sediments of the first terrace, consisting of clay, alevrolite are presented by increasing values from 5 to 10 ohm.m, while the values 10 to 20 ohm.m are presented by fluvial and alluvial sediments, consisting of clay, sand and their mixture. Higher values from 20 to 30 ohm.m, are located in the most northern and southern part of this region and represent sediments composed with sand, gravels, clays and alevrolite alternation (Figure 4 a).

Map of electrical resistivity studying depth of 12 m

In the map of electrical resistivity processed to depth study of h = 12 m is noted that the values of this parameter are low from 1 ohm.m up to 30 ohm.m. Values about 0-1 ohm.m represent the marine, lagoonal, swamp sediments, mainly of silky clay composition, while the values from 1 to 5 ohm.m represent sediments in which it is added the presence of sand (Figure 4 b).

Figure 4 Electrical resistivity map for: a) studied various depths, b) studied depth h =12m, former Chemical plant, Porto Romano-Durrës region

To assess the spreading of Sodium Bichromate and Lindan pollution and their impact in the underground water, in the region around the chemical plant, is presented geoelectrical image according to VES of surveyed profile I, Porto Romano-Fllake.

Profile I, Porto Romano – Fllakë

In this geoelectrical cross-section are delineated 5 geoelectrical layers of different lithological composition.

First layer of electrical resistivity values from 6-20 ohm.m and the thickness 0.9-3 m, represents marine, lagoonal, swamp sediments of clay and sand composition, while the second layer of electrical resistivity values from 4-9 ohm.m and the thickness up to 100 m, represents the alluvial sediments of first terrace, consisting of clay and alevrolite.

Third layer with interruption in pickets 6-11, with the values of electrical resistivity from 2-4 ohm.m and the thickness up to 100 m represents sediments of clay and sand composition, while the fourth layer with interruption in pickets 1 to 4 and pickets 7, with the values of electrical resistivity
from 20-45 ohm.m and the thickness up to 70 m represents sediments, consisting of gravels, sand and clay combination.

Fifth and last layer of electrical resistivity values from 10-20 ohm.m represents the sediments of basement with clay and sand composition (Figure 5). Drilling carried out in this profile: W-141, W-88, W-120, W-121, W-42, W-41, W-8/1, W-37, W-36 and W-38 have helped the quantitative interpretation of electrical resistivity curve, defining exactly the borders of geoelectrical layers.

![Figure 5](image-url)  
*Figure 5. Geological–geophysical cross-section by VES in Profile I, former Chemical plant, Porto Romano-Fllake*

**Well-logging**

In this region are carried out surveys of well-logging, applying the electrical resistivity method, 3-electrodes AMN array (gradient-potential) to delineate exactly depth and thickness of sediments consisting of sand and gravels combination (Koçiaj *et al.*, 1985). These observations have helped supporting the 1-D quantitative interpretation curve of electrical resistivity of VES carried out between the above drilling. Coordination of the results, obtained by achievement of surveys in depth with those in surface issued results with theoretical-practical values to study the spreading of tecnogen pollution in terms of depth in groundwater (Leka, 2007; Figure 6).

In the curve of electrical resistivity, obtained through the drilling No.12, clearly distinguished values of this parameter from 0.5-3 ohm.m, up to 12 m depth, which represent the marine, lagoonal, swamp sediments, mainly of silky clay and sand composition. Below, to the depth 20 m, the value of electrical resistivity increases from 5 ohm.m to 10 ohm.m and represents alluvial sediments of first terrace consisting of clay and alevrolite. In depth above of 20 m, the electrical resistivity values are increasing over 10 ohm.m and represent combination of clay, clay-sand and sand near the basement of Quaternary deposits, consisting of clay with sandy content.

Levels of electrical resistivity above-mentioned are conformed to the values of electrical resistivity determined by quantitative interpretation of electrical resistivity curve of this parameter, obtained by performing of VES in the vicinity of this drilling.

Geochemical, elektrometric and well logging data show that the presence of the sands, gravels in the area around the former Porto-Romano Chemical plant testify the risk of spreading and distribution of Sodium Bichromate and Lindan pollution in underground waters.
Integrating of geochemical-geophysical studies in GIS

Geochemical-geophysical studies performed for tecnogen pollution in Porto Romano are integrated in GIS with the help of Arc View GIS 8.2 software (http://GisRockware/ArcView software).

For representation in Arc View GIS 8.2 of the results geochemical-geophysical studies carried out in Porto Romano area is used the following methodology:

1. Compilation of database with “initial data” for each electrical sounding perform (region, Profile, No. of VES, topographic coordinates X, Y, H, Array AB/2, MN, electrical resistivity value \( \rho_d \)) by the computer program written in Microsoft Office Access for this purpose.

2. Compilation of database with “data interpreted” for each electrical sounding perform (No., electrical resistivity, thickness, depth and lithology of layer according to program “Resist”) by the computer program written in Microsoft Office Access.

3. Compilation of database for chemical elements: Cr, Zn, Ni, Mn, Co, Cu, Pb, Fe, Na, K (topographic coordinates X, Y, No. of sampling, the content of chemical element).

4. Processing and informatization of graphic material according to any topographic sheet at 1:25000 scale (the location plan of sampling of chemical elements, electrometric surveys of VES, the geoelectrical and geological-geophysical cross section of observed profiles, the geochemical maps for above mentioned elements and the maps of the electrical resistivity, of the thickness and the depths of geoelectrical layers etc. and) according to softwares Surfer 8, Graph 3, AutoCad Map 6 etc.

5. Representation in the Arc View Gis 8.2 software of geochemical studies and the electrometric studies of VES for the topographic sheet K-34-87-D-d (Vrinas), at 1:25000 scale.

Processing and informatization of graphic material in this topographic sheet includes (Vinčani et al., 2009):

- Summary database “The initial and interpreted data” of VES.
- Database of chemical elements: Cr, Zn, Ni, Mn.
- The location plan of sampling of chemical elements and electrometric surveys of VES.
- Geological-geophysical cross-section of VES according to the profile I, Porto Romano-Fllake.
- Geochemical map of Cr element for sampling in 5 cm depth.
- Maps of electrical resistivity for studied various depths and depth h = 12 m.
The representation in the Arc View Gis 8.2 software of geochemical studies and the electrometric studies of VES for the topographic sheet K-34-87-D-d (Vrina), at 1:25000 scale.

In Figure 7 are presented the results of geochemical-geophysical studies for topographic sheet K-34-87-D-d (Vrina), at 1:25000 scale, including: "initial data", "interpreted data", geochemical data, curve of electrical resistivity, topographic maps with the location plan of geochemical sampling points and VES surveys, geological-geophysical cross-sections, geochemical map of Cr element in 5 cm depth, electrical resistivity maps for studied different depths and maps of Quaternary deposits contours.

With the implementation of complex of geochemical-geophysical methods to study the spreading of tecnogen pollution in Porto Romano was achieved some conclusions.

Conclusions
Geochemical and geophysical methods have helped in determining of spreading boundaries of the tecnogen pollution in the soil surface and in studying of their distribution in underground waters around Porto Romano.

Levels of 400 ppm Cr element, with the highest prevalence of Cr 6⁺, are obtained at the soil and water near the former chemical plant, while the anomalous epicenter with the values over than 350 ppm in the northern and its northeastern part, should be former toxic-industrial discharging.

Electrometric applying the method of electrical resistivity, VES-Schlumberger array, has defined depth, thickness of Quaternary deposits up to about 150 m and their lithological composition.

Geoelectrical layer of electrical resistivity values from 20 to 45 ohm.m and thickness from 20 to 100 m, which represents mixed sediments consisting of gravels, sand, clay and silk combination is penetrable from the tecnogen pollution in Porto Romano area.
Well logging applying with electrical resistivity method, 3 electrode AMN array (gradient-potential), has exactly determined the depth and the thickness of sediments consisting of sand, gravels combination and has helped in the quantitative interpretation of electrical resistivity curves, according to VES in this region.

To prevent major risks that are threatening community, flora and fauna in the continent and the sea, protective measures should be taken by the competent authorities.

References


Abstract: Kosovo has a great potential for future economic development. It is a fact that, within this economic development, industrial, energetic, traffic and other facilities of capital importance and importance for the social standard are being built. Considering the high seismicity and the frequency of occurrence of earthquakes in this region, these structures are permanently exposed to the risk of being damaged or destroyed. Developed countries and particularly developing countries like Kosovo endeavour to protect these costly structures against catastrophic earthquake effects since it is clear that conservative construction may cause serious economic consequences. To conceive the facts on the economy of development and construction in seismic areas, it is necessary to perform scientific and applicative investigations for assessment of the seismic risk, definition of economically justified and technically consistent criteria for design and construction of structures as well as selection of structures and their upgrading for the purpose of sustaining the expected earthquakes. In doing so, one should start from the fact that preventive protection, if harmonized with the level of development and future needs of the society, represents the best way to protect social goods and human lives. For that its need to expansion of seismic station network, therefore geophysical investigations are necessary.

Key words: Geophysics, seismic, investigations, refraction, reflection, station.

Introduction

Geophysical investigations are of a particular importance for the behaviours of engineering structures and other structures of interest for the society under earthquake effects. This refers not only to the location of the structures themselves but also to their wider surrounding. The experience from the last earthquake that took place in the surrounding of Gjilan in April 2002 has shown that a network for detailed monitoring of the local seismic activity needs to be installed in Kosovo. For that purpose, a proper distribution and selection of sites/locations for installation of the seismological stations will be necessary. According to the spatial configuration and the relatively high seismic activity originating from the seismic foci in Kosovo and the neighbouring countries, a network consisting of 8 seismological stations distributed over the entire territory is proposed to be installed. This network of seismological stations will enhance the accuracy of definition of earthquake parameters necessary for the study of the seismicity of the Kosovo territory. The selected locations of seismological stations are compatible and would fit into the seismological networks of the neighbouring countries. Anticipated is a real time on-line transfer of data to the main centre, i.e., the Institute of Seismology in Pristina where the data will be processed. The seismological stations are located in the following places: Prizren, Zatriq, Zatra-Peje, Llapushnik, Leposaviq, Smrekoniq, Pristina and Gjilan. Their micro locations have been defined based on geological (Christopher, (2005) The Mechanics of Earthquakes and Faulting, Cambridge, Great Britain), geophysical and seismological investigations. Also, the selection of the locations complies with the requirements set by the producer of the seismological and the accessory equipment regarding communication, power supply and physical protection of the structures in which the equipment will be installed.

Geophysical Seismic Investigations

The investigations have been performed by complex application of the following methods:

- Standard seismic refraction method for measuring velocities of seismic P and S waves and definition of the thickness of the surface cover that should be eliminated during foundation of the seismometers (Aki K, Richards PG, (1980) Quantitative seismology - theory and methods.

*Corresponding: E-Mail: nazmi_hasi@hotmail.com; Tel +3813820021547

The seismic investigations have been carried out by using the following set of equipment (Havskov J, Gerardo A, (2004) Instrumentation in Earthquake Seismology”, Springer, Netherlands):

- 12-channel seismic digital recording system (TERRACOL MARK-3, ABEM-ATLAS COPCO, Sweden)
- Vertical and horizontal geophones with natural frequency of 14 and 28 Hz;
- Hammer with a mass of 10 kg for signal excitation.

The excitation of the seismic waves has been done by hammer blows on a metal plate at each 25 or 60 meters, while the signals have been received at each 5 or 10 meters (depending on the presence of surface disintegrated cover or fault zones). Numerical analysis and interpretation of the measured data has been done by applying the Reflex set of computer programmes. The investigations have been carried out at individual, normally placed refraction and reflection seismic research profiles (Fig. 2). The refraction profiles involved a research depth of 30 – 40 m. The reflection profiles served for scanning the general geological structure of the location down to a depth exceeding 200 m. The interpretation of the measured data enabled definition of the values of the seismic Vp and Vs velocities in the present geological media and the thickness of the surface quaternary or disintegrated rock layer as well as location of the fault structures that directly affect the selection of the micro location for the seismological station and the intensity of the seismic noise. The results from the investigations performed per locations are given in the subsequent text of this work.

According to the geological map of the region presented in Fig. 1, the terrain of the Strong Motion station location is composed of Triassic limestone and dolomites. The seismic investigations were performed on a refraction profile with a length of 120 m (RP-1 in N-S direction) and a reflection profile with a length of 65 m (RL-1 in W-E direction).

Figure 1. Geological map of the region

According to the results from the refraction investigations (Figure 3), two elastic media of limestone were confirmed to exist in the higher part and three in the lower part of the terrain. The seismological station is located in the higher part of the first half of the refraction profile where the surface disintegrated layer has a thickness of 2 m and values of seismic velocities $V_p = 630 \text{ m/s}$ and $V_s = 330 \text{ m/s}$, while the compact limestone below is characterized by values of seismic velocity of $V_p = 4650 \text{ m/s}$ and $V_s = 2500 \text{ m/s}$. According to the investigations performed by using the reflection
method (Fig. 4), the thickness of the limestone and the dolomites is about 160 – 180 m. A tectonic dislocation (reverse fault with approximate north-south stretching direction) that can produce an increased seismic tremor was recorded in the west initial part of the reflection profile, at a distance of about 10 meters from the seismological station. According to the geological map, Palaeozoic shale’s are expected to be found below the limestone and the dolomites. According to the values of seismic velocities and the thickness of the limestone and the dolomite as well as expression $T = 4h/Vs$, dominant micro seismic vibration with predominant periods of about 0.3s ($f = 3.33$ Hz) are expected at this location.

Figure 2. Prizren Seismic Station-Disposition of seismic profiles 1:1000

Figure 3. Prizren Seismic Station [RP-1 (N-S) Seismic Refraction Profile; a) Time distance Curve; b) Velocity model]; Legend: $IT_{2-3}$ - Limestone, dolomite, partly cherty; $IT'_{2-3}$ - Limestone, dolomite, partly cherty, Disintegrate and weaken; $IT''_{2-3}$ - Surface wandering layer 4650/2500 - $Vp/Vs$ [m/s]; $\Delta$ - $S$ - Seismic Station
Conclusions
The selection of the new locations for seismological station of Prizren was influenced by the geological conditions in the wider surroundings, distance from larger urban areas, busy roads, railways, etc. To acquire knowledge about the natural resources at the locations, geological, geophysical and seismological analyses were performed and geological age were defined. The seismological station is located on a compact rock surface (Figure 5).

References
Research the Possibility of Transforming the Ferronickel Slag in the Product with the Economical and Environmental Importance

Izet Ibrahimi¹,*, Musa Rizaj ² Agim Ramadani ³

¹Korporata Energetike e Kosovës-Prishtinë; ²Universiteti i Prishtinës, Fakulteti i Xhetarisë dhe Metalurgjisë, Kosovë; ³Xella-Kosova L.L.C. Kosovë

Received November 11, 2009; Accepted June 08, 2010

Abstract: Kosovo is facing huge challenges in terms of industrial waste treatment. Generation growth and bad management in Drenas slag dump is made from polluting concerns that exceeded local character. The volume of deposits of over 2.6 million m³, (over 7 mil. t), exposed to atmospheric precipitation and wind, turning the waste into permanent environmental pollutants. Riffraff of slag appeared with the fine fractions, where dust particle in the slag behave in size between 30 μ and 5 μ and which have high emissions affinity and imitating in the environment. The Ferronickel slag dump in the Drenas according to reports by environmental organizations, calculated as “environmental hotspot”. The best way to reduce volume and pollutant level of these landfills is it for between reuse/recycling of slag. The aim of our research consists in the argument of fact, since the technological aspect is possible the process of slag transformation from potential polluting in new accessible material.

Keywords: waste management, ferronickel slag, construction materials.

Introduction

Modern waste management along with programs for waste reuse / recycling is now one of the basic objectives of environmental protection and sustainable economic development. Behaviour fairly in relation to the environment and save natural resources will be possible only when we reach a sustainable level of recycling and industrial waste.

Ferronickel benefit from the oxide mineral of nickel used in Foundry of "Ferronickel" in Drenas is slag process, since 75% of the clinker passes in slag. Design capacities of existing infrastructure, enable to processed over 1,200,000 t minerals/year, which are expressed in the product over 11,000 t Ni/year, and about 800,000 t slag/year.

The concepts of production so far focused only on immediate profits, have resulted in enormous increase in the volume of waste and pollutant concentration of components, and thus compromising environmental sustainability and sustainable economic development. From research of chemical and physical characteristics, it is proved that these slags are related or meet standard requirements for the qualities of raw silicate materials. Observe from the context of chemical physical and mechanical characteristics, the slag can be easily transformed from reproductive polluting in products or raw materials, very valuable for application in industry

Ferronickel Slag

The technological process of Ferronickel benefit in Drenas comes off under very complex technological scheme. Slag obtained by electric furnace is a very important component of the process. Main slag Settings as oiled system depends on its chemical composition. As shown in tab.1, the main slag components are: SiO₂, CaO, MgO, FeO, Fe₂O₃, MnO, etc. parallel with these may be present also P₂O₅, Cr₂O₃, CAS, MnS, FeS and in small concentrations participate a large number of other oxides and sulphide also metals with colour etc.

Table 1. Slag average chemical composition of the electric furnace

<table>
<thead>
<tr>
<th>Elements</th>
<th>MgO</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>MnO</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>9.34</td>
<td>58.51</td>
<td>9.72</td>
<td>1.25</td>
<td>0.404</td>
<td>13.77</td>
<td>0.016</td>
<td>0.094</td>
</tr>
</tbody>
</table>

* Corresponding: E-Mail: izet.ibrahimi@kek-energy.com; Tel: +377 (0) 44 174 266; Fax:+381(0)38 580 164
Silicates are important components of the slag, SiO$_2$ gives the dip acidic character. To neutralize this acidity report is necessary of CaO growth, therefore, these two oxide must respond to each other, and appeared in the composition of gelenites, okermanites, dikalisiumsilicates, tridimites, wollastonites and other minerals which are main carriers of the most physical-mechanical characteristics. These two oxides also are key components of this type of slag. The proportional ratios level is determining of the most slag properties and basic criterion to be separated technological groups of this type of slag.

CaO, constitutes the bulk of basic oxides, its presence plays a crucial role in promoting the connecting activities. Other basic oxides such as FeO, MgO, MnO entered in chemical compounds with the SiO$_2$, thus forming systems: CaO-FeO-SiO$_2$, MgO-SiO$_2$-FeO, CaO-MgO$_2$-SiO$_2$ etc. Settings of clinker in the first place are dependent on the situation of these systems equilibrate, but largely depends on structural settings of SiO$_2$ and silicate ions. Coefficient of acidity in some cases brought up to 4.5, which means that those slag entered in slag group with high viscosity and the high melting temperature (Fig.1.). Iron is mainly in the form of FeO, and the concentration was not the extreme boundary.

Slag discharged from the furnace periodically and through specific channels subject pass through the process of separation with water. Research in the field of slag production; confirm that with partial modifications is possible processing of Ferronickel slag as the: granular slag, crystal slag and effervescent slag.

![Figure 1. Slag chemical character of electric furnaces for producing Ferronickel](image)

Developing recycling programs for the slag under global processing practices would allow the use of slag in the construction industry or the chemical of 100%.

**Application Possibilities of Ferronickel Slag**

From extensive current research and from global practices processing slag of colour metals are determined that the acid slag, can be used as a subject important in building material industry.

According to chemical-physical characteristics, bibliographic data and experiences from the practice of using similar types of slag over the world, electrical furnace slag of Drenas, have broad application possibilities, (Table2). The process of processing and application of these slags does not require any special processing technology. Ferronickel slag of the Drenas have affinity to create strong cementers links with components mainly consist from hidroaluminates, hidroferit calcium and materials with low concentrations of hidrosilicates.
For the chemical-physical characteristics these slags entered in the group of silicates raw materials and with many characteristics advance in report with traditional silicates subjects. Drawing up schemes for application of slag necessarily have found its qualities, requirements resulting from standards for raw materials or ancillary subjects, economic and environmental effects.

**Table 2. Application possibilities of electric furnace slag for producing ferronickel**

<table>
<thead>
<tr>
<th>Nr</th>
<th>Type of slag’s processing</th>
<th>Slag’s name</th>
<th>Franc. Designations</th>
<th>Dedicated to products:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Granular slag</td>
<td>The crud</td>
<td>Aggregator 0 - 8</td>
<td>Traditional additives, porcelain, silicates materials</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cement like material for slag, cement like addition in slag, vitreous wool, porous concrete, lacquers for masonry and plastering, prefabricate concrete elements.</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>The coarse grinding sand</td>
<td>0.2 - 6</td>
<td>Natural sand</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Strainer sand</td>
<td>0 - 2.5</td>
<td>Natural sand</td>
</tr>
<tr>
<td>4</td>
<td>The shallow ground</td>
<td>Filler 0.09-2.0</td>
<td>Filler</td>
<td>Asphalt of qualities (4-5,6 AC4, AC8, AC16)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>Bit und. 0-0.09</td>
<td>Tradit. addition silicates mater.</td>
<td>Cement like addition, and wool production of hyaline</td>
</tr>
<tr>
<td>6</td>
<td>Crystal slag</td>
<td>Thick stone</td>
<td>60 - 80</td>
<td>Concrete and holder side of the road</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>40 - 60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>The crushed</td>
<td>Gravel 31.5-63</td>
<td>Sand or gravel, natural sand</td>
<td>Concrete for road construction, quarry</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>The crushed</td>
<td>Aggregator 0-63</td>
<td>Concrete for road construction, quarry</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>Particular 2.5-31.5</td>
<td>Concrete for construction of roads, the thick asphalt concrete, asphalt concrete layers with fine fractions the, all types of asphalts and tampons for roads, streets pavement</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>Sand 0.09-8</td>
<td>2 - 25</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Effervescent slag.</td>
<td>Filler 0-0.09</td>
<td>Filler</td>
<td>Asphalt</td>
</tr>
<tr>
<td>14</td>
<td>The crushed</td>
<td>Bit 31.5</td>
<td>Tradit. additi. silicates mater.</td>
<td>Raw materials for clinker and vitreous wool, light concrete, road construction and porous concrete</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>Aggregator 0-315</td>
<td>Expan. aggre.</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>Particular 2-25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>Filler 0-0.09</td>
<td>Filler</td>
<td>asphalt, tiles of all kinds</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Research of Quality and Possibility of Ferronickel Slag Application**

Slag of Ferronickel, in this group also the Drenas slag, by analysis of their chemical composition Fig. 2 present special group of raw silicate materials. Ratio between SiO₂ and CaO is definition of the strength, connecting skills of the slag relations between crystal and amorphous phases.

Increasing the concentration of MgO, up to 7% will be expressing the maximum strength effects. Iron is mainly in the form of FeO and the concentration that does not exceed the extreme limit. The risk of oxidation of Fe²⁺ to Fe³⁺ is minimal, a fact that favours connecting activity of the connecting materials. Connecting skills of the slag reduced to a minimum during granulation with water and crystal growth phase. Macro grinding of slag fractions separately or together with additional materials increase in sufficient scale connecting character of the mixture.
Figure 2. The average main components composition of the electric furnace slag

![Graph showing chemical composition of slag over time](image)

**Table 3.** Research properties of Ferronickel slag

<table>
<thead>
<tr>
<th>Research</th>
<th>Research method by SK-EN</th>
<th>Research results</th>
<th>Condition for quality under stand. SK-EN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific measures in fresh condition (g/cm³)</td>
<td>12697-6</td>
<td>2,77</td>
<td>2000-3000</td>
</tr>
<tr>
<td>Specific measures in dry condition (g/cm³)</td>
<td>12697-6</td>
<td>2,69</td>
<td>2000-3000</td>
</tr>
<tr>
<td>Receiving water(%) for φ = (0/2 mm)</td>
<td>12697-8</td>
<td>1,07</td>
<td>Is not described</td>
</tr>
<tr>
<td>Volume measures in friable condition(g/m³)</td>
<td>12697-6</td>
<td>1,4932</td>
<td>Is not described</td>
</tr>
<tr>
<td>Volume measures in compressed condition(g/m³) in dry condition</td>
<td>12697-6</td>
<td>1,5871</td>
<td>Is not described</td>
</tr>
<tr>
<td>Pressure solidity (Mpa) in fresh condition</td>
<td>224</td>
<td>min.128,64</td>
<td>&lt; 4 mm 0,5</td>
</tr>
<tr>
<td>Pellet of clay (%)</td>
<td>0</td>
<td>&gt; 4 mm 0,25</td>
<td></td>
</tr>
<tr>
<td>Composition of organic matter (%)</td>
<td>Does not contain</td>
<td>Is not described</td>
<td></td>
</tr>
<tr>
<td>Equivalent fractions</td>
<td>12697-1</td>
<td>82,5</td>
<td>min. 60 the crushed</td>
</tr>
<tr>
<td>Equivalent fractions &lt;0.063 mm</td>
<td>12697-1</td>
<td>0,7</td>
<td>&lt; 5% natural</td>
</tr>
<tr>
<td>Equivalent fractions &lt;0.09 mm</td>
<td>12697-1</td>
<td>1,8</td>
<td>&lt; 10 % the crushed</td>
</tr>
</tbody>
</table>

*Source: Laboratory for asphalt "B & A & M" Maribor, Tomasicevo 36*

From the results of the granular analysis slag granulated with water, has very homogeneous structure, but the concentrations of fine fractions "dust flying" are high, (Fig.3.). Participation of poor corn and pellet of clay is minimal, thus increasing the quality and rates of equivalent slag fractions.
Results and Discussion

Slag dump of the "Ferronickel" foundry in Drenas, with this level of pollutant generation components, represents very high environmental concerns. High concentrations of the “dust flying” granular slag have expanded polluting effects the whole ecosystem, exceeding local pollution level. Judging by the results of chemical-physical analysis, from technological aspect is possible that these slag from permanent pollutants, with partial processing to return to the subject available to industry. The main components of the slag: SiO$_2$, CaO, MgO and FeO, are with related concentrations and standard qualities subject for silicate.

CaO presence and other basic oxides play a crucial role in promoting the connecting activities, constrained and continuity progress of slag hydrating process.

Results of tests of strength, have resulted, that the increased strength of the products is dependent exclusively to reports, SiO$_2$: CaO. Judged according to chemical-physical characteristics, slag are related with eruptive raw materials and may find application to all types of concrete and asphalt with high stability against degradation, light concrete, and other products with silicate originating.

High concentration of small factions (0-0,71 mm, and "dust flying" Fig.3.), to these slag, has minimized its use to large grain asphalt layers, but also in favour of its application to porous concrete and light concrete in general. Slag granulating with water dilutes the binding properties and favours the presence of "flying dust".

Granulometrik high homogeneity, as well as the appropriate structure of refraction of particles makes these products of slag be distinguished by the fine porous structure, thus favouring the basic characteristics of cementing products and volume weights.

Research in the field of production of slag, confirm that there are safe opportunity to influence the slag production technology. Effervescent clinker production would increase the possibilities of slag characteristics.

Conclusion

During this research work are examined chemical and physical-mechanical characteristics and application possibilities of Ferronickel slag in Drenas, to construction materials and chemical industry. So far research results terms of slag qualities, prove that they are approximated with the standard requirements for silicate raw materials and some parameters are very advanced that in traditional subjects. Reuse / recycling of the Ferronickel slag will express significant effects in relation to:
- Rational use of raw materials,
- Improvement of the physical-mechanical products, by increasing the mechanical strength, fire sustainability energy conservation, climate Resistance, etc.
Increasing the production base and encourage the other programs in the context of use of waste as raw materials for the recycling industry in Kosovo.

Reuse/recycling of this slag would express significant contributions to environment through:
- Reducing dump volume and its pollutants components,
- Increase the value of slag,
- Creating of conditions to manage slag dump in Drenas,
- Improve the environment, etc.

Increased application of Ferronickel slag of Drenas, unless strong economic and financial incentives, would be simultaneously contributing to the development of an industry aware toward environment.

References


Haziraj N, (1988) Moznost pridobivanje gradbenga materila iz zlindre pri proizvodnji ferronikla-a”; Magistaro delo; Ljubljana,

Ibrahim I, (2005) Desulfurimi i ferronikelit jashtë furre–mundësi për intensifikimin dhe optimalizimin e procesit të përfitimit të ferroniklet, Punimi i magjistraturës, Mitrovicë,

Murati N, Rizaj M, Beqiri E, Ibrahim I, (2008) “Research on possible use of the ferronickel electrical furnaces’ slag for production of construction materials”. Istambul-


Experimental Ground of Application of Extract from Saffron Inoculun under Heart Ischemia

Rena A. Sadykhzadeh∗

Institute of Physiology n.a. A.I.Karayev, NAS, Baku, Azerbaijan

Received January 29, 2010; Accepted April 21, 2010

Abstract: According to studies the extract of saffron (Crocus sativus L) introduced per of prior to pituitary spasm, realizes anti-ischemic effect, levelling deviations in ECG indicators. In order to evaluate the mechanism of therapeutic action we studied the saffron’s influence towards the intensity of lipid peroxidation, the condition of antioxidant system of the organism itself and the system of blood coagulation in rats during experimental cardiac ischemia. Our experimental data indicate that saffron delays the production of free radicals during ischemia increases the activity of antioxidant systems therefore presenting the destabilization of cell membrane of cardiomyocytes. At the same time saffron positively effects on blood coagulation of rats with experimental ischemia. So, the antioxidant functions are one of the most important components in realization of medical action of saffron in heart ischemic disorders, what prognoses the possibility of its application an effective medical preparation for prophylaxis and the treatment of CHD.

Key words: Saffron, spasm, anti-ischemic effect, ECG indicators, cardiomyocytes.

Introduction

High death incidence from cardiovascular diseases and, moreover, dramatic process of their rejuvenation are negative life satellites in human civilization. This explains the urgency of elaborating new effective medicine derived from the vegetable sources in prophylaxis and treatment of CHD. Last decade the antihypoxants – the medical preparations, increasing the tissue stability (including cardiac tissue) to hypoxia, drew attention of the researchers, dealing with the elaboration of medical preparations for people sick with CHD. Their pharmacological action is due to their ability to binding free radicals and decreasing the rate of oxidation process.

Nowadays failure in control of lipid peroxidation level is considered to be a pathogenic marker of quite a number of cell damaging, including the damages occurring during atherogenesis, after ischemia, herbicide and tetrachlorcarbon poisoning, impact of ionizing irradiation, radioactive damaging, in cancerogenesis, aging, inflammation, disturbances of reproduction system, neuro-psychological, autoimmune diseases (Vladimirov, et all 1991).

From this standpoint a big attention is paid to the study of biological role of bioantioxidants as the factors capable of regulating the intensity of lipid peroxidation, which is shown to be a non-specific response of the organism to the disease. The use of the natural compounds is particularly perspective, because they, being biotics, easily and organically get into the human metabolic processes and practically do not have any side effects typical for synthetic preparations (Sgapoval G.S, 2003).

Saffron is one of the most valuable ingredients of folk medicine, the curable characteristics of which are known from the famous book “Canon” by doctor, scientist-encyclopedist Ibn-Sina. The best is considered to be Khorasan saffron, which is cultivated widely in Azerbaijan.

The unique chemical composition of saffron is rich with carotinoids, flavonoids, many vitamins, quite a number of amino acids (including the essential ones), microelements and others provides a wide spectrum of its biological effect, including antioxidizing, directed to different structural, metabolic and regulatory systems of organism (Kasumov, 2002; Abdullaev, 2002). In prevention of formation and detoxication of free radicals, excessively formed in cells, the endogen antioxidant protective system plays the primary role, and in the case of its deficiency the introduction of antioxidants from outside plays therapeutic role. There are 2 components in the organization of antioxidant system .The main antioxidants are the enzymes of a group of superoxide dismutase, whose

∗ Corresponding: E-Mail: veфа-quliyeva@rambler.ru; Tel: +9912 4502314
function consists in catalytical transformation of peroxide anion in hydrogen peroxide and molecular oxygen.

The low molecular components, complementing and completing the enzyme activity is introduced by a wide group of fat- and water-soluble compounds, which include almost all vitamins, numerous vegetable phenols and polyphenols, bioflavonoids, catechines, carotinoids and others.

According to our earlier studies, the extract of saffron (Crocus Sativus L) in dosage of 150-250 mg/kg to rabbit’s and rat’s mass, introduced per os an hour prior to pituitary spasm, realizes anti-ischemic effect, levelling deviations in ECG indicators with the prevalence of minimal changes.

In this work in order to evaluate the mechanism of therapeutic action we studied the saffron’s influence towards the intensity of lipid peroxidation, the condition of antioxidant system of the organism itself and the system of blood coagulation in rats during experimental cardiac ischemia.

Material and Methods

The experiments were conducted on 54 Wistar white male rats culled into 3 groups: I group – control group; II group – the animals with pituitary coronarospam; III group – animals, exposed to pituitary coronarospam during the administration of the studied extract.

The pituitary coronarospam served as a model of cardiac pathology. The myocardial ischemia during the i.v. injection of pituitrin in dosage of 2.5 units/kg in the rats’ tail vein causes a profound electrical instability of myocardium. This method provides a stable experimental model of stenocardia (Khadjay, 1961). The decapitation of animals was conducted 15 min after the injection of pituitrine (in period of maximal morpho-functional changes in myocardium) and after 2 hours (in period of normalization of myocardial processes). The processes of lipid peroxidation were evaluated by the presence of molecular products of lipid peroxidation - lipid hydroperoxides and malondialdehyde in the cardiac tissue and blood (Asakawa & Matsushita, 1980). The activity of catalase was defined spectrophotometrically, the protein level was measured by Lowry method. For estimation of the condition of coagulant system the following indicators were utilized: the coagulant activity of the whole blood, time of plasma recalcification (by Bergerof technique), protrombin index (Kvik method), the concentration of fibrinogen, plasma toleration to heparin (Siga method). Anticoagulant mechanism was evaluated by measuring fibrinolitic activity. The received data was processed via methods of variation statistics.

Results and Discussion

The conducted research showed that during modeling the coronary spasm along with the contractile myocardial deficiency, high intensity of lipid peroxidation took place. In cardiac tissue and in blood a significant raise of lipid hydroperoxide and final product of lipid peroxidation process - malon dialdehyde is observed (Table 1).

In 2 h of post-ischemic period the content of products of lipid peroxidation practically did not differ in intact animals from their content. We consider this fact appropriate, as by this time the acute morphological and functional changes in myocardium already pass.

The cardio-toxic effect of the produced free radicals, leading to structural and functional deficiency in cell biomembranes of cardiomyocytes and the aggravation of loading myocardial cells with calcium, underlies intracellular damages of myocardium during ischemia. Moreover, the activation of lipid peroxidation depresses the synthesis of one of the mighty vasodepressing factors - prostacyclin, activates the synthesis of tromboxan and leads to hypercoagulation (Kurashvili, 2001;, Meyyerson, 1984; Ishiharajima, et all, 1986).

The lack of positive correlative bond between lipid peroxidation activity and reaction of antioxidant system is noteworthy. So, our results indicate that during the increase of lipid peroxidation products in cardial muscle and blood the levels of sulfhydryl groups, being non-enzyme components of antioxidation system, decreased simultaneously the decrease of activity of catalase – the enzyme of antioxidant system (Table 2) – was observed. The results of studies of blood coagulant system during experimental rat ischemia treated by saffron extract are presented in the Table 3. According to the
experimental data the most sensible to ischemia was general coagulation of the whole blood, which decreased significantly.

The consequence of ischemia to the 15th minute was also a slight increase in fibrinogen, the decrease of toleration to heparin and fibrinolytic activity. Therefore, during the pituitary coronarospasm in rats the ischemia is primary and the decrease of general coagulation of blood is secondary.

As it is seen from the presented table, during the recovery of bioelectrical activity of myocardium by the saffron extract the excessive activation of lipids peroxidation decreases.

Table 1. The effect of saffron extract on the intensity of lipids peroxidation in the heart and blood of rats during the experimental coronarospasm (M±m)

<table>
<thead>
<tr>
<th>Observable indicators</th>
<th>Control</th>
<th>Coronarospasm (15 min)</th>
<th>Saffron+ Coronarospasm (15 min)</th>
<th>Coronarospasm (120 min)</th>
<th>Saffron+ Coronarospasm (120 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroperoxide (relative unit)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In heart</td>
<td>6.1±0.5</td>
<td>12.4±0.52</td>
<td>9.1±0.4**</td>
<td>8.9±0.35*</td>
<td>7.11±0.4**</td>
</tr>
<tr>
<td>Hydroperoxide (relative unit)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In blood</td>
<td>0.79±0.088</td>
<td>1.12±0.08</td>
<td>1.0±0.04*</td>
<td>0.98±0.068</td>
<td>0.9±0.05*</td>
</tr>
<tr>
<td>Malon dialdehyde (n mol/mg protein)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In heart</td>
<td>4.61±0.2</td>
<td>7.52±0.4</td>
<td>5.6±0.3**</td>
<td>6.0±0.5*</td>
<td>4.92±0.3**</td>
</tr>
<tr>
<td>Malon dialdehyde (n mol/mg protein)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In blood</td>
<td>0.73±0.06</td>
<td>1.2±0.08</td>
<td>0.87±0.04*</td>
<td>0.88±0.1*</td>
<td>0.76±0.07**</td>
</tr>
</tbody>
</table>

* - p<0.05; ** - p<0.001 relatively to the control group.

Table 2. The effect of saffron on the content of thiol groups (n mol/mg protein) and catalase activity (unit/mg protein) in the heart and blood of rats during experimental coronarospasm (M±m)

<table>
<thead>
<tr>
<th>Observable indicators</th>
<th>LD-SH</th>
<th>C3-SH</th>
<th>G-SH</th>
<th>Catalase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (heart)</td>
<td>42.2±1.0</td>
<td>24.7±0.9</td>
<td>17.4±0.4</td>
<td>282±4.3</td>
</tr>
<tr>
<td>Control (blood)</td>
<td>33.2±1.1</td>
<td>18.6±0.3</td>
<td>15.8±0.5</td>
<td>298±5.3</td>
</tr>
<tr>
<td>Coronarospasm (15 min. heart)</td>
<td>26.8±0.9**</td>
<td>18.5±0.1**</td>
<td>12.8±0.3**</td>
<td>196±3.1*</td>
</tr>
<tr>
<td>Coronarospasm (15 min. blood)</td>
<td>22.2±0.9*</td>
<td>13.5±0.37</td>
<td>12.3±0.1</td>
<td>214±4.2</td>
</tr>
<tr>
<td>Saffron+Coronarospasm (15 min. heart)</td>
<td>38.6±1.1**</td>
<td>21.6±0.9**</td>
<td>15.5±0.5*</td>
<td>254±2.1**</td>
</tr>
<tr>
<td>Saffron+Coronarospasm (15 min. blood)</td>
<td>27.5±1.1**</td>
<td>15.3±0.5*</td>
<td>14.3±0.2**</td>
<td>264±3.2*</td>
</tr>
<tr>
<td>Coronarospasm (120 min. heart)</td>
<td>39.4±2.1*</td>
<td>21.3±1.2*</td>
<td>16.2±0.9</td>
<td>252±3.9</td>
</tr>
<tr>
<td>Coronarospasm (120 min. blood)</td>
<td>30.2±0.9</td>
<td>15.8±0.4*</td>
<td>13.1±0.2**</td>
<td>241±5.6*</td>
</tr>
<tr>
<td>Saffron+Coronarospasm (120 min. heart)</td>
<td>40.7±2.6</td>
<td>2.1±1.3</td>
<td>17.0±0.7</td>
<td>275±3.8</td>
</tr>
<tr>
<td>Saffron+Coronarospasm (120 min. blood)</td>
<td>33.2±1.2</td>
<td>17.2±0.4*</td>
<td>15.2±0.4</td>
<td>277±4.8</td>
</tr>
</tbody>
</table>

Footnote: * p<0.05; ** - p<0.001 relatively to the control group.
**Table 3.** The effect of saffron on the system of coagulation in rats during the experimental heart ischemia (M±m)

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Observables</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>General blood coagulation, sec</td>
</tr>
<tr>
<td></td>
<td>Beginning</td>
</tr>
<tr>
<td>Control</td>
<td>76.6±6.5</td>
</tr>
<tr>
<td>Ischemia (15 min)</td>
<td>52.1±4.5*</td>
</tr>
<tr>
<td>Saffron extract +ischemia (15 min)</td>
<td>78.2±7.1</td>
</tr>
<tr>
<td>Ischemia (120 min)</td>
<td>71.5±6.9</td>
</tr>
<tr>
<td>Saffron extract +ischemia (120 min)</td>
<td>78.9±7.3</td>
</tr>
</tbody>
</table>

Footnote: * - p<0.05 relatively to controls

So, the levels of hydroperoxides significantly go down from 12.4 ±0.52 relative units to 9.1±0.6 relative units. And malon dialdehyde accordingly decreases from 7.52±0.4 mol/mg to 5.6±0.3 nmol/mg (Table 1). The pattern of changes of content of hydroperoxide and malon dialdehyde in the blood is equivalent to the changes in myocardium, but is noticeably less (Table 1). During the stabilization of lipid peroxidation in prophylactic administration of saffron extract the oxidation of different types of endogenous sulfhydryl groups is inhibited and the decrease of catalase activity is observed (Table 2), this way preserving the protein-lipid component of cardiomycocytes membrane from ischemic damage. The prophylactic administration of saffron extract provides a positive effect on the system of coagulation: the steadfast retardation of general whole blood coagulation in animals takes place from 52.1±4.5 to 78.2±7.1 on the 15 minute of ischemia, which indicates to the decrease of ischemia, which, perhaps, is related to the improvement of myocardium microcirculation. Multiple clinical and experimental researches shows that antioxidants are highly effective agents, preventing the formation and progression of atherosclerosis, as they block the formation of thrombus and atherosclerotic plaques on the vessel walls.

Bearing anti-platelets features and inhibiting pathological vessel growth, antioxidants are the best “cleaners” of blood vessels. It is evident, that their application leads to decrease several times the risk of onset and successful treatment of such diseases as hypertension, stenocardia, myocardial infarction, stroke and thrombophlebitis (Simonenko, 1998; Axford Gately. & Wilson, 1993; Birnbaun et al., 1996).

It is much more perspective the application of natural phenol compounds belonging to the group of vegetable flavonoids. According to the research held in our Republic and abroad, the saffron is enriched with these compounds (Table 4). The high antioxidant activity of vegetable flavonoids is well-known and it defines prominent anti-allergic, anti-cancerogenous, anti-inflammatory and anti-viral properties (Andersen & Markham, 2005).

Our experimental data indicate that saffron delays the production of free radicals during ischemia, increases the activity of antioxidant systems, therefore preventing the destabilization of cell membrane of cardiomycocytes, which is one of the leading factors of heart failure. At the same time, saffron positively effects on blood coagulation, delays the general whole blood coagulation of rats with experimental ischemia. So, the antioxidant functions are one of the most important components in realization of medical action of saffron in heart ischemic disorders, what prognoses the possibility of its application as an effective medical preparation for prophylaxis and the treatment of CHD.
Table 4. Chemical composition of saffron

<table>
<thead>
<tr>
<th>Composition</th>
<th>Dry weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>10.3-14.03</td>
</tr>
<tr>
<td>Wax</td>
<td>18.6-20.1</td>
</tr>
<tr>
<td>Volatile oil</td>
<td>1.0-1.5</td>
</tr>
<tr>
<td>Bonded oil</td>
<td>2.0-2.8</td>
</tr>
<tr>
<td>Sugar</td>
<td>40.3-41.2</td>
</tr>
<tr>
<td>Carotinoids:</td>
<td>7.9-8.1</td>
</tr>
<tr>
<td>crosin</td>
<td>3.49-3.52</td>
</tr>
<tr>
<td>pikocrosin</td>
<td>3.69-3.72</td>
</tr>
<tr>
<td>crocetin</td>
<td>0.31-0.33</td>
</tr>
<tr>
<td>carotin (α, β, γ)</td>
<td>0.68-0.75</td>
</tr>
<tr>
<td>Alcaloides</td>
<td>0.08-0.1</td>
</tr>
<tr>
<td>Aminoacids</td>
<td>12.93-13.24</td>
</tr>
<tr>
<td>Vitamin A, B, B1, C</td>
<td>1.20-1.52</td>
</tr>
</tbody>
</table>

References
Asakawa T, Matsushita S, (1980), Colorium condition of thiobarb, acid test for detecting lipid hydroperoxides, Lipids, 15, 137-140.
Gross Alpha/Beta Measurements in Drinking Water Samples Using Different Methods

Florinda Cfarku*, Elida Bylyku, Brunilda Daci

Centre of Applied Nuclear Physics, Faculty of Natural Sciences, Tirana University, P. O. Box. 85 “Qesarak” Street, Tirana, Albania

Received May 09, 2010; Accepted May 13, 2010

Abstract: Natural radionuclides generally represent the main source of radiation exposure to the public. In the environment, they either arise from the direct release of Radon from ground into ambient air or through dissolution of U-and Th-series members into water. As a consequence the control of natural radionuclides in water for human consumption has become a major goal worldwide during the recent decade. Limitations were set and the need for simple and rapid procedures for their implementation becomes necessary. Liquid scintillation techniques provide the detection and quantification of alpha and beta emitters in aqueous sample. Liquid Scintillation Counter (LSC) techniques using Pulse Shape Discrimination (PSD) allow counting of alpha and beta radiation in the same sample simultaneously. In this study, Packard Tricarb 3170 TR-SL LSC has been used. Ultima Gold LLT produced by Packard Instrument Company was used as the liquid scintillator. The optimum counting parameters and Pulse Shape Discrimination (PSD) settings were provided for the best alpha and beta separation. PSD was verified by counting a pure alpha Am²⁴¹ and a pure beta Cl³⁶. Spill of beta in alpha and alpha in beta was found around 0.1% at the optimum discriminator setting of 128. The counting efficiencies were 100% and 95% for alpha and beta counting respectively. Water samples were pre-concentrated before the measurements. Albanian maximum permissible level for gross alpha radioactivity is 0.1 BqL⁻¹ and 1 BqL⁻¹ for gross beta radioactivity in drinking water. LSC method results were compared with the Gas Flow Proportional Counter.

Key Words: Liquid scintillation counting, Calibration, Water sample, Alpha activity, Beta activity.

Introduction

Liquid Scintillation Spectrometry has become of widespread interest during the recent years [Anonymous, (1993), Anonymous, (1998)]. Natural waters contain a number of both alpha and beta radionuclides in widely varying concentrations. Some of the difficulties that arise when measuring low-energy beta and alpha particles using conventional methods are completely avoided. Sample is counted directly in a homogeneous solution of an appropriate organic scintillator. Under these conditions, problems relating to sample self-absorption, attenuation of particles by detector windows, and beta backscattering from detector are solved. Alpha and Beta emitting radionuclides may be counted simultaneously in the same liquid scintillation sample. A scintillation pulse consists of an initial component and delayed component (Knoll, 1979). These components occur in different proportions in alpha and beta pulses, with the result that alpha pulses are longer than beta pulses. LSC uses special pulse decay discriminator to discriminate the pulses as either alpha events or beta events and stores the events appropriately in separate multichannel analyzers (MCA) (Sanchez-Cabeza & Pujol, 1995). A time-based Pulse Decay Discriminator may be adjusted by the operator, or the system, to determine the optimum setting for specific sample conditions. PSD is affected by the sample chemistry, vial type, geometry and degree of quenching (Moebius, 1997).

Materials and Methods

The Liquid Scintillation Counter used for the measurements was Packard Tricarb 3170 TR-SL. Standard 20 mL plastic vials were used. Packard Ultima Gold LLT was used as the cocktail (Passo CJ and Cook, 1996)

*Corresponding: E-Mail: fcfarku@yahoo.com; Tel: +355 042222969; Fax: +355 042257813
Sample Preparation for LSC

Water samples were pre-concentrated; 500 mL sample was evaporated slowly to dryness on a hot plate and then reconstituted in 1 M HCl to 4 mL. The sample solution was transferred into a 20 mL plastic vial and added Ultima Gold LLT (14 mL). The vial was shaken until aqueous and organic phases were mixed completely (Dazhu, Y. Yongjun, Z. and Mobius, S. 1991). The vials were placed in the counter and liquid scintillation counting was performed using the defined an alpha/beta sample counting protocol for 600 minute each. Distilled water was used to prepare blank sample. The measured count rates were corrected for background and the spillover.

The optimum sample/scintillant ratio was determined using the total available volume of 20 mL. For the best alpha/beta separation minimal sample volume was required. The optimum sample/scintillant ratio was found as 4-mL water in 14-mL scintillant. Background was minimum level and Figure of Merit (FOM) was maximum level at this ratio for this ratio.

α/β PSD Optimization

PSD is optimized to accurately separate the pulse types and store the events in separate MCA’s. Only a pure beta and a pure alpha standard are required to establish this optimum setting (Anonymous, 1978). A plot of percent spillover of alpha events into the beta MCA and beta events into the alpha MCA is automatically generated by the instrument. The optimum discriminator setting is automatically calculated from the intersection of the two curves. The optimum pulse shape discriminator value was determined using pure alpha Am241 and a pure beta Cl36 standard. For the most accurate results, standards were prepared as identical as possible to the samples and counted individually at defined alpha/beta standards counting protocol to establish the PSD value (Dazhu, Y, at al, 1991). PSD was found as 128 setting the alpha channel to 100-600 keV and the beta channel to 0-900 keV. Spillover of alphas into beta MCA (as a fraction) was 0.0148; spillover of betas into alphas MCA (as a fraction) was 0.0139 (Figure 1).

Counting Efficiency and Quench

The prepared standard samples were measured and the corresponding efficiency was calculated from the count rate of the known activity. The alpha counting efficiency was found as 100%, the beta efficiency was 95%. Increasing amounts of quenching agent to the prepared standard samples searched the effect of quenching on the PSD (Moebius, 1997). From the count rate in the whole energy channel and the known standard activity the appropriate counting efficiency is calculated and plotted versus the quenching parameter (Figure 2). Calibration curves were prepared and used finding the efficiency of the unknown quenched sample.
Spillover Calculations
The spillover calculations are made to determine the actual cpm. The equations for true count rate due to alpha ($A_T$) and beta disintegrations ($B_T$) are given below respectively:

$$A_T = \frac{A_0 - A_0 X_\beta - B_0 X_\beta}{1 - X_\beta - X_\alpha} \text{ and } B_T = \frac{B_0 - B_0 X_\alpha - A_0 X_\alpha}{1 - X_\alpha - X_\beta}$$

$A_0= \text{ observed net count rate in alpha MCA}$
$B_0= \text{ observed net count rate in beta MCA}$
$X_\alpha= \text{ alpha counted as beta}$
$X_\beta= \text{ beta counted as alpha}$

In this experiment, $X_\alpha = 0.0148$ and $X_\beta = 0.0139$ for PSD=128.

Corrected cpm values both alpha and betas were used to calculate alpha and beta radioactivity (Passo & Cook, 1996).

Table 1. Gross Alpha and Beta Activity in samples measured by two methods

<table>
<thead>
<tr>
<th>Drinking Water Sample</th>
<th>Liquid Scintillation Counter</th>
<th>Gas Flow Proportional Counter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gross Alpha Bq/L</td>
<td>Gross Beta Bq/L</td>
</tr>
<tr>
<td>Shkoder</td>
<td>0.036 ± 0.009</td>
<td>0.132 ± 0.012</td>
</tr>
<tr>
<td>Puke</td>
<td>0.041 ± 0.012</td>
<td>0.068 ± 0.030</td>
</tr>
<tr>
<td>Kukes</td>
<td>0.044 ± 0.007</td>
<td>0.151 ± 0.007</td>
</tr>
<tr>
<td>Peshkopi</td>
<td>0.048 ± 0.020</td>
<td>0.289 ± 0.020</td>
</tr>
<tr>
<td>Kruje</td>
<td>0.053 ± 0.009</td>
<td>0.135 ± 0.011</td>
</tr>
<tr>
<td>Durres F, Kuqe</td>
<td>0.043 ± 0.012</td>
<td>0.402 ± 0.020</td>
</tr>
<tr>
<td>Tirane Bovile</td>
<td>0.026 ± 0.010</td>
<td>0.216 ± 0.009</td>
</tr>
<tr>
<td>Tirane Selite</td>
<td>0.022 ± 0.007</td>
<td>0.278 ± 0.020</td>
</tr>
<tr>
<td>Pogradec</td>
<td>0.031 ± 0.003</td>
<td>0.261 ± 0.013</td>
</tr>
<tr>
<td>Berat</td>
<td>0.042 ± 0.012</td>
<td>0.386 ± 0.030</td>
</tr>
<tr>
<td>Vlore</td>
<td>0.055 ± 0.006</td>
<td>0.264 ± 0.012</td>
</tr>
<tr>
<td>Korce</td>
<td>0.068 ± 0.020</td>
<td>0.461 ± 0.30</td>
</tr>
<tr>
<td>Tepelene</td>
<td>0.019 ± 0.007</td>
<td>0.063 ± 0.009</td>
</tr>
<tr>
<td>Gjirokaster</td>
<td>0.045 ± 0.012</td>
<td>0.339 ± 0.019</td>
</tr>
</tbody>
</table>
Results and Discussion

For all samples are measured gross alpha and beta activity with two methods: by Liquid Scintillation Counter with alpha/beta discrimination and compared with the results of Gas Flow Proportional Counter (Ultra Low Level $\alpha/\beta$ Counter MPC 9604). Results were given in Table 1. It has been demonstrated that liquid scintillation counter is applicable for gross alpha and beta analysis. The results for water samples counted by LSC and GFPC agree within ± 2σ for different mixtures of alpha and beta. The use of LSC with PSD for routine is advantageous because of the counting of alpha and beta radiation in the same sample simultaneously. In terms of sample preparation and counting time, LSC provides the best means of ensuring that the time and steps required are minimal. In addition, Tri-Carb alpha/beta LSC’s can count up to 400 large vials (20 mL) automatically. GFPC has some disadvantages when compared to LSC. Counting efficiency for alphas is 30%, or less, compared to 100% for LSC and for betas are 65%, compared to 95 % for LSC. The LSC PSD method will provide good sensitivity. The result of Table 1 has shown that all measurements were statistically acceptable from known activities and, therefore, it was concluded that the method is suitable for the determination of gross alpha and beta activities in water samples in routine work for a high range of activity ratios.

Acknowledgement: The authors gratefully acknowledge the Risø National Laboratory, University of Copenhagen, Kingdom of Denmark, for its technical and financial support of the work undertaken here (Project 2007-2009).

References


Optimization of Operational Parameters of the Photocatalytic Degradation of Reactive Red 120 Dye under UV Irradiation

S. K. Kavitha1*, P. N. Palanisamy2

1Department of Chemistry, Velalar College of Engineering and Technology, Erode-638 012, Tamilnadu, India; 2Department of Chemistry, Kongu Engineering College, Perundurai, Erode-638 052, Tamilnadu, India

Received February 9, 2010; Accepted June 14, 2010

Abstract: The photocatalytic degradation of a reactive azo dye (C.I. Reactive Red 120) has been investigated in aqueous suspension using different photocatalysts under UV irradiation. TiO2-P25 was found to be more suitable for the degradation of the dye. Adsorption studies of the TiO2 suspension in dark showed that adsorption has a strong dependence on pH and follows a Langmuir adsorption model. An attempt has been made to optimize the process parameters viz., substrate concentration, pH of the solution and catalyst loading for the degradation of the dye using TiO2-P25. The degradation of the dye was found as maximum in acidic medium and it follows approximately a pseudo-first kinetic order according to the Langmuir-Hinshelwood model. The effect of addition of the electron acceptors H2O2 and K2S2O8 and the influence of additives such as Na2CO3 and NaCl on the degradation were also studied.

Keywords: Photocatalytic degradation, TiO2, UV irradiation, Reactive Red 120

Introduction

Advanced oxidation processes have been previously described as a promising option to remove persistent pollutants from contaminated water when conventional water treatment processes are not efficient enough. Among these heterogeneous photocatalysis (Prevot et al., 2001) in the presence of irradiated semiconductor oxides has been successfully used to decolorize and mineralize many organic pollutants including dyes and their intermediates present in aqueous systems using both artificial light and under sunlight (Vinodgopal & Kamat, 1994; Hachem et al., 2001).

Over the past several years heterogeneous semiconductor photocatalysis using TiO2 as the photocatalyst has received considerable attention for water and wastewater treatment. The photocatalysed degradation of various organic systems employing irradiation in presence of TiO2 can result in complete oxidation to carbon-dioxide, water or mineral acids.

The key advantages of this technology include lack of mass transfer limitations, operation at ambient conditions and the possible use of solar irradiation. The catalyst itself is inexpensive, non-toxic, commercially available and photochemically stable (Konstantinou & Albanis 2004). It has a wide band gap of 3.2 eV and hence can be successfully used as a photocatalyst for the treatment of dye pollutants (Poulios & Aetopoulou, 1999; Epling & Lin, 2002; Tang et al., 1997).

In the present study an attempt has been made to study the photocatalytic degradation of textile dye Reactive Red 120 using TiO2 in the form of slurries employing UV irradiation. Optimized conditions for maximum degradation were determined by varying the experimental parameters like catalyst loading, initial concentration of the dye and initial pH of the solution. The influence of addition oxidants H2O2 and K2S2O8 and the presence of inorganic salts Na2CO3 and NaCl on degradation rate were also studied.

* Corresponding: E mail: skkavitha@yahoo.com Phone: +91424 2430333; Fax: +91424 2431725
Materials and Methods

Materials
The commercial dye Reactive Red 120 was obtained as gift sample from Sivasakthi Dyeing unit, SIPCOT Industrial Estate, Perundurai, India and used as such without any purification. Titania P-25 (surface area 50 m$^2$/g) was obtained from Degussa. The titania particles are mixture of both anatase and rutile forms. All the other catalysts and chemicals used were of AR grade. They were obtained from S.D Fine chemicals and were used as received. Required concentrations of dye solutions were prepared by dissolving the dye in distilled water. pH of the solutions were adjusted by adding 1M HNO$_3$ or 1M NaOH.

Experimental and analytical methods

Adsorption Experiments
The adsorption tests were performed using 200 ml aqueous solution of dye at different initial concentrations and pH of the solution put in contact with 1 gm/l of TiO$_2$ for two hrs and kept in dark at 25°C. The solution was centrifuged and the concentration of the unadsorbed dye was measured to determine the extent of adsorption as a function of initial concentration at different pH.

UV Irradiation Experiments
The study was carried out in a batch reactor. The reaction vessel was an immersion well photoreactor consisting of double walled cylinder of 750ml capacity, made of pyrex glass, with ports at the top for air sparger. Water was circulated in between the two walls of the reactor to arrest the heat produced during the reaction and to eliminate the IR radiation and short wavelength radiation. Irradiations were carried out using a 125 W medium pressure mercury lamp. The slurry composed of dye solution and catalyst was placed in the reactor and stirred magnetically. The samples were withdrawn from the reactor vessel periodically for the analysis of decolourisation and degradation. The concentration of the dye was determined at $\lambda_{max}$ 515 nm measuring the absorbance using spectrophotometer (Model: Hitachi U-2001) and the degradation of the dye was measured by COD test. pH adjustments for the solution were carried out by measuring the pH using ELICO, India LI 120-pH meter.

Results and Discussion

Adsorption of the dye in dark
Adsorption tests were carried out in dark to study the adsorption of the dye on the surface of TiO$_2$ at different initial concentrations and different pH. The equilibrium constants for adsorption were determined by fitting the experimental data to the Langmuir Eq. [1] to describe the adsorption of the dye on the surface of TiO$_2$.

$$q_e = \frac{q_m bC_e}{1 + bC_e}$$  \[1\]

where $q_m$ is the maximum amount of dye adsorbed forming a complete monolayer, $b$ is the equilibrium parameter, $C_e$ is the concentration of the dye in aqueous solution and $q_e$ is the concentration of the dye on the solid. The Langmuir equilibrium constants ($K_a=q_mb$) are given in Table 1 and the isotherms are shown in Figure 1. The L – shaped isotherms obtained in all the cases show that there is no strong competition between the solvent and the adsorbate for the adsorbent sites (Giles, 1974).
It is observed that the dye adsorbs in acidic media and negligible adsorption is observed in alkaline media. This can be explained as the point of zero charge of the TiO$_2$ is 6.25 and TiO$_2$ surface is positively charged in acidic media whereas it is negatively charged in alkaline media (Sauer 2002). Hence at pH greater than 7 the anionic dye is repelled and therefore the extent of the adsorption decreases. Similar results have been reported in literature (Hoffmann et al., 1995; Kiriakidou et al., 1999).

**Decolourisation of the dye using different photocatalysts**

The photocatalytic activity of various commercial photocatalysts was investigated under UV irradiation. TiO$_2$-P25 and ZnO were found to be more efficient as shown in Figure 2 and the order of activities of the photocatalysts is TiO$_2$-P25>Hombikat>ZnS>CdS. In general, semiconductors with large band gap have strong photocatalytic activity. TiO$_2$-P25 and ZnO have a band gap of 3.2eV and hence show strong activity. TiO$_2$ is the most promising photocatalyst as it is chemically inert and stable with respect to photocorrosion and chemical corrosion (Nishimoto et al. 1985; Matthews 1989). The high photoreactivity of TiO$_2$-P25 compared to Hombikat (TiO$_2$ anatase) is due to the slow recombination of the electron-hole pair and large surface area. The surface area of TiO$_2$-P25 is six times as high as that of TiO$_2$ anatase(Weller 1993). ZnO is unstable due to incongruous dissolution to yield Zn(OH)$_2$ on the ZnO particle surfaces and thus leading to catalyst inactivation (Bahnemann et al., 1987). Moreover, ZnO and CdS suffer from photocorrosion induced by self-oxidation and they can react with the photogenerated holes giving the following reactions:
These competing reactions lead to decrease in photocatalytic activity (Neppolian et al., 2002a). The occasional release of Cd$^{2+}$ metal ions into the aqueous medium may cause heavy metal pollution (Kakuta et al., 1985). Hence TiO$_2$ proves to be more a suitable bench mark catalyst for photodegradation of textile dyes due to its high photoactivity, high surface area and resistance to photocorrosion and was used in this present study for the degradation of the dye Reactive Red 120 UV irradiation.

**Photodegradation of the dye using TiO$_2$ and kinetics of photodegradation**

As the photocatalytic mechanism suggests, both TiO$_2$ and a light source are necessary for the degradation reaction to occur. Experiment was conducted on the irradiation of the dye under only UV light, in the presence of TiO$_2$ without UV irradiation and in the presence of TiO$_2$ with UV irradiation. No degradation was observed in the presence of UV light only. In the presence of TiO$_2$ without irradiation slight loss was observed due to the adsorption of the dye on the surface of TiO$_2$. However, as shown in Figure 3 when dye was irradiated with TiO$_2$ about 98% of the dye was degraded within two hours of irradiation.
The photocatalytic degradation of the dye Reactive Red 120 containing TiO$_2$ obeys pseudo-first-order kinetics. At low initial concentration the rate expression is given by

$$\frac{-d[C]}{dt} = k'[C]$$

where $k'$ is the pseudo-first-order rate constant. The dye is adsorbed on the TiO$_2$ surface and the adsorption–desorption equilibrium is reached in 45 minutes. After adsorption the equilibrium concentration of the dye solution is determined and it is taken as the initial dye concentration for kinetic analysis. Integrating Eq. [4] with the limit of $C = C_0$ at $t=0$ with $C_0$ being the equilibrium concentration of the bulk solution

$$\ln \left( \frac{C_0}{C} \right) = k't$$

where $C_0$ is the equilibrium concentration of the dye and $C$ is the concentration at time $t$.

The linear fit between $\ln(C_0/C)$ and irradiation time, as shown in Figure 4 supports the conclusion that the degradation of Reactive Red 120 follows first-order kinetics. The correlation constant for the fitted line was calculated to be $R^2 = 0.9981$ and the rate constant was calculated to be $0.0646$ min$^{-1}$. 

**Figure 3.** Photocatalytic degradation of Reactive Red 120
Effect of catalyst loading

Experiments were conducted to study the variations in the rate of degradation at different catalyst concentrations ranging from 0.5 gm/l to 4 gm/l. It is observed that the rate increases with increase in catalyst concentration, becomes maximum and remains almost constant thereafter as shown in Table 2. The optimum catalyst concentration for the degradation of the dye Reactive Red 120 is 2.5 gm/l. The results are in good agreement with those reported in literature (Mills and Morris 1993; Chen & Ray 1998). The photocatalytic destruction of other organic pollutants has also exhibited the same dependency on catalyst dose (Akyol et al., 2004). This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration, because with the increase of catalyst dose total active surface increases and hence more active sites are available on catalyst surface (Gonclaves et al., 1999). At the same time, due to an increase in turbidity of the suspension with high dose of photocatalyst, there will be decrease in penetration of UV light and hence photoactivated volume of suspension decreases (Daneshvar et al., 2003). Thus it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due light scattering.

Table 2. Effect of TiO₂ loading on the degradation rate during the photocatalytic degradation of Reactive Red 120 (C₀ = 100 mg/l, pH 4.1)

<table>
<thead>
<tr>
<th>[TiO₂] g/L⁻¹</th>
<th>r₀ mgL⁻¹min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.0213</td>
</tr>
<tr>
<td>1.0</td>
<td>2.6971</td>
</tr>
<tr>
<td>1.5</td>
<td>2.9642</td>
</tr>
<tr>
<td>2.0</td>
<td>3.2721</td>
</tr>
<tr>
<td>2.5</td>
<td>3.7076</td>
</tr>
<tr>
<td>3.0</td>
<td>3.6637</td>
</tr>
<tr>
<td>3.5</td>
<td>3.5236</td>
</tr>
<tr>
<td>4.0</td>
<td>3.5239</td>
</tr>
</tbody>
</table>
Galindo et al. (2001) reported an empirical relationship between the initial decolourisation rate and TiO$_2$ concentration, $r_0 \propto [\text{TiO}_2]^n \ [\text{dye}]$, where $n$ is an exponent less than 1 for the dye studied. In the present work the dependence of TiO$_2$ concentration on the initial decolourizations rate, as calculated from Figure 5, follows a similar relationship $r_0 \propto [\text{TiO}_2]^{0.3556}$, when catalyst concentration is less than 2.5 gm/l.

![Graph showing relationship between ln r$_0$ and ln[TiO$_2$]](image)

**Figure 5.** Relationship between ln $r_0$ and the amount of TiO$_2$: C$_0$= 100 mg/l ,pH 4.1

**Effect of initial dye concentration**

The effect of initial concentration of the dye solution on the degradation rate of the dye was investigated by varying the dye concentrations from 50 to 250mg/l in the presence of 2.5 gm/l TiO$_2$ under UV light. The photodegradation rate, as shown in Figure 6 is observed to decrease with increase in initial concentration. The results are in agreement with those reported by Toor et al. (2006). The possible explanation for this behaviour is that as the initial concentration of the dye increases the path length of the photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photons absorbed by the catalyst in lower concentration as stated by Muneer et al. (1997) and the same effect was observed by Neppolian et al. (2002). Further as the concentration increases, the concentration of unadsorbed dye in the solution increases leading to lesser penetration of light through the solution onto the surface of TiO$_2$. This decreases the concentration of OH radical which is the most reactive species formed on the surface and hence the rate of degradation decreases.

The influence of initial concentration of the solute on the degradation rate of most of the organic compounds can be described by a pseudo-first-order kinetics in terms of Langmuir-Hinshelwood equation (Eq. 6) modified for heterogeneous catalytic reactions:

$$r_0 = -\frac{dC}{dt} = \frac{k \cdot K \cdot C}{1 + K \cdot C_0}$$

\[6\]
Figure 6. Kinetics of photodegradation of Reactive Red 120 at different initial concentrations

where $k_v$ reflects the limiting rate of the reaction at maximum coverage under the experimental conditions. $K_e$ represents the equilibrium constant for adsorption of the dye on to illuminated TiO$_2$. In Eq (4) $k_v$ represents the apparent rate constant because it is also dependent on the source of visible light and the radiation field inside the photocatalytic reactor.

A linear expression, as shown in Figure 7 can be obtained by plotting the reciprocal initial rate against the reciprocal initial concentration. The values of $K_e$ and $k_v$ at different pH values are shown in Table 3.

Figure 7. Representation of Langmuir - Hinshelwood equation: pH 4.1, [TiO$_2$] = 2.5 gm/l
Table 3. Langmuir – Hinshelwood constants for the photodegradation of Reactive Red 120 at different pH values.

<table>
<thead>
<tr>
<th>pH</th>
<th>Ke (Lmg⁻¹)</th>
<th>kₐ, min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.003823</td>
<td>13.6593</td>
</tr>
<tr>
<td>6</td>
<td>0.006112</td>
<td>7.1565</td>
</tr>
<tr>
<td>8</td>
<td>0.008375</td>
<td>3.7642</td>
</tr>
<tr>
<td>10</td>
<td>0.009469</td>
<td>1.2018</td>
</tr>
</tbody>
</table>

Effect of pH of the solution

An important parameter in the photocatalytic reactions taking place on the particulate surface is the pH of the solution, as it dictates the surface charge properties of the photocatalyst, size of the aggregates it forms and the positions of the conductance and valence bonds (Galindo et al., 2001; Mills et al., 1993). Further the generation of hydroxyl radicals is also a function of pH. Hence attempt was made to study the influence of the initial pH on the degradation of the dye Reactive Red 120 at different initial concentrations in the pH range of 4 to 10.

The results obtained from experiments with varying pH of the dye solution are shown in Figure 8. The rate of degradation is high in acidic medium and decreases as the pH of the solution is increased. These results are reflected by the kₐ and Ke values of the Langmuir-Hinshelwood equation at different pH values, as given in Table 3.

Figure 8. Effect of pH of the solution on the rate of degradation of the dye Reactive Red 120 at different initial concentrations

The interpretation of pH effect on the photocatalytic process is very difficult because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and the charged radicals formed during the reaction process. The ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively, as given in the following equations:

\[ TiOH + H^+ \rightarrow TiOH^+ \]  \[ TiOH + OH^- \rightarrow TiO^- + H_2O \]  \[ 7 \]

The point of zero charge of TiO₂ is 6.25 and TiO₂ surface is positively charged in acidic media whereas it is negatively charged in alkaline media (Sauer et al. 2002). This accounts for the higher
degradation rate of the dye in acidic medium. Similar results have been earlier reported in the photocatalytic degradation of a number of dyes (Guillard et al., 2003; Muneer et al., 1997).

**Influence of H$_2$O$_2$**

One possible way to increase the reaction rate would be to increase the concentration of OH\(^\cdot\) because these species are considered to be promoters of photocatalytic degradation. The addition of electron acceptors like hydrogen peroxide to the heterogeneous system increases the concentration of OH radical, since it inhibits the electron hole recombination, according to the following equation.

\[
\text{TiO}_2 (e^-) + H_2O_2 \rightarrow \text{TiO}_2 + OH^- + OH^\cdot
\]  

[9]

Hydrogen peroxide is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from a conduction band and thus promotes the charge separation and it also forms OH\(^\cdot\) radical according to Eq(9)

However at high concentration of H$_2$O$_2$ it also acts as scavenger as shown in Eqs [10] and [11]

\[
H_2O_2 + OH^\cdot \rightarrow HO_2^+ + H_2O
\]  

[10]

\[
HO_2^+ + OH^\cdot \rightarrow H_2O + O_2
\]  

[11]

The optimum concentration of H$_2$O$_2$ for the degradation of the dye with initial concentration of 100 mg/l at pH 4.1 was found to be 2 ml/l of the dye solution, as shown in Figure 9.

![Figure 9. Effect of H$_2$O$_2$ concentration on rate of degradation:C$_0$ = 100 mg/l, pH 4.1, [TiO$_2$]= 2.5 gm/l](image)

**Influence of persulphate**

The effect of another electron acceptor, persulphate ion, on the photocatalytic degradation of the dye was studied by adding varying amount of K$_2$S$_2$O$_8$ to the dye solution of concentration 100mg/l under optimized conditions. The percentage degradation of the dye increased with increasing amount of persulphate ion as shown in Figure 10. About 98 % degradation was achieved within two hours of irradiation time with 200mg persulphate ion concentration instead of 82 % degradation in the same duration in the absence of persulphate ion.
The sulphate anion ($SO_4^{-}\cdot$) is a strong oxidant ($E^0=2.6\text{eV}$) and engages in the following three possible modes of reactions with organic compounds. (i) by abstracting a hydrogen atom from saturated carbon. (ii) by adding to unsaturated or aromatic carbon and (iii) by removing one electron from the carboxylate anion and from certain neutral molecules. In addition, it can trap the photogenerated electrons and/or generated hydroxyl radical (Minero et al. 1993).

\[
SO_4^{-}\cdot + e^{-} \rightarrow SO_4^{1-} \tag{12}
\]

\[
SO_4^{-}\cdot + H_2O \rightarrow OH^{+} + SO_4^{2-} + H^{+} \tag{13}
\]

The hydroxyl radical and sulphate radical anion formed (eqs. 14, 15) are powerful oxidants that can degrade the dye molecules at faster rate. The $SO_4^{-}\cdot$ has the unique nature of attaching the dye molecule at various positions and hence the fragmentation of the dye molecule is rapid (Neppolian et al., 2002b).

\[
SO_4^{-}\cdot + \text{dye} \rightarrow SO_4^{2-} + \text{dye}^{\cdot}\tag{14}
\]

\[
SO_4^{-}\cdot + \text{dye}^{\cdot}\tag{\text{intermediate}} \rightarrow SO_4^{2-} + \text{CO}_2 + \text{HNO}_3 + \text{other inorganics} \tag{15}
\]

However at high dosage of S$_2$O$_8$ $^{2-}$ the inhibition of reaction occurs due to the increase in concentration of SO$_4^{2-}$ ion (Eq. 12).The excess of SO$_4^{2-}$ ion is adsorbed on the TiO$_2$ surface and it reduces the catalytic activity. The adsorbed SO$_4^{2-}$ ion also reacts with photogenerated holes (Eq. 17) and with hydroxyl radicals (Eq. 18).

\[
SO_4^{2-} + h^{+} \rightarrow SO_4^{\cdot}\tag{16}
\]

\[
SO_4^{2-} + \cdot OH \rightarrow SO_4^{\cdot} + OH^{-} \tag{17}
\]

Since SO$_4^{\cdot}$ is less reactive than 'OH radical and h$^+$ the excess SO$_4^{2-}$ does not increase the photodegradation of the dye beyond the optimum dosage.

**Figure 10.** Effect of K$_2$S$_2$O$_8$ on the degradation of Reactive Red 120: $C_0=100\text{mg/l}$, pH 4.1

The sulphate anion ($SO_4^{-}\cdot$) is a strong oxidant ($E^0=2.6\text{eV}$) and engages in the following three possible modes of reactions with organic compounds. (i) by abstracting a hydrogen atom from saturated carbon. (ii) by adding to unsaturated or aromatic carbon and (iii) by removing one electron from the carboxylate anion and from certain neutral molecules. In addition, it can trap the photogenerated electrons and/or generated hydroxyl radical (Minero et al. 1993).

\[
SO_4^{-}\cdot + e^{-} \rightarrow SO_4^{1-} \tag{12}
\]

\[
SO_4^{-}\cdot + H_2O \rightarrow OH^{+} + SO_4^{2-} + H^{+} \tag{13}
\]

The hydroxyl radical and sulphate radical anion formed (eqs. 14, 15) are powerful oxidants that can degrade the dye molecules at faster rate. The $SO_4^{-}\cdot$ has the unique nature of attaching the dye molecule at various positions and hence the fragmentation of the dye molecule is rapid (Neppolian et al., 2002b).

\[
SO_4^{-}\cdot + \text{dye} \rightarrow SO_4^{2-} + \text{dye}^{\cdot}\tag{14}
\]

\[
SO_4^{-}\cdot + \text{dye}^{\cdot}\tag{\text{intermediate}} \rightarrow SO_4^{2-} + \text{CO}_2 + \text{HNO}_3 + \text{other inorganics} \tag{15}
\]

However at high dosage of S$_2$O$_8$ $^{2-}$ the inhibition of reaction occurs due to the increase in concentration of SO$_4^{2-}$ ion (Eq. 12).The excess of SO$_4^{2-}$ ion is adsorbed on the TiO$_2$ surface and it reduces the catalytic activity. The adsorbed SO$_4^{2-}$ ion also reacts with photogenerated holes (Eq. 17) and with hydroxyl radicals (Eq. 18).

\[
SO_4^{2-} + h^{+} \rightarrow SO_4^{\cdot}\tag{16}
\]

\[
SO_4^{2-} + \cdot OH \rightarrow SO_4^{\cdot} + OH^{-} \tag{17}
\]

Since SO$_4^{\cdot}$ is less reactive than 'OH radical and h$^+$ the excess SO$_4^{2-}$ does not increase the photodegradation of the dye beyond the optimum dosage.
Influence of Na$_2$CO$_3$

The waste water from dyeing operations normally contains considerable amount of carbonate ions as sodium carbonate is the common auxiliary chemical used in textile processing operations. Therefore it is important to study the influence of carbonate ion on the treatment efficiency. As shown in Figure 11 the degradation percentage of the dye gradually decreased with increasing carbonate ion concentration. This is due to the hydroxyl scavenging property of carbonate ions, which can be accounted from the following eqs. 18 and 19.

\[
OH^* + CO_3^{2-} \rightarrow OH^- + CO_3^{*-} \quad [18]
\]

\[
OH^* + HCO_3^- \rightarrow H_2O + CO_3^{*-} \quad [19]
\]

![Figure 11. Effect of Na$_2$CO$_3$ on the degradation of Reactive Red 120: C$_0$=100 mg/l, pH 4.1](image)

Thus the free hydroxyl radical which is a primary source for the photocatalytic degradation decreases gradually with increase in the carbonate ion concentration resulting in the ultimate decrease in the percentage degradation of the dye significantly. Similar trend has been reported by Nansheng et al. (1993).

Influence of NaCl

Sodium chloride usually comes out in the effluent from textile mills as the dyeing process often requires high concentrations, upto 100 gm/l of sodium chloride. The study of the influence of NaCl is important in photocatalysis, because the NaCl may reduce reaction rates by poisoning the TiO$_2$ active sites or by scavenging radicals via the chloride ion (Abdullah et al., 1990). Hence studies have been carried out with NaCl in the range 25 to 100 mg/100ml dye solution. The degradation percentage of the dye decreased with increase in the amount of chloride ion as shown in Figure 12.

Since the iso–electric point (IEP) of Degussa P25 TiO$_2$ is 6.6 (Abdullah et al., 1990) it is positively charged at pH below 6.6. In the presence of NaCl the Cl$^-$ ions migrate to the positively charged TiO$_2$ surface and scavenge for h$^+$ and $OH^*$. The h$^+/OH^*$ scavenging reactions of Cl$^-$ ions at pH < pH$_{IEP}$ of TiO$_2$ are as follows (Arslan et al., 2000)
The $\text{Cl}_2^*$ formed is capable of oxidising the organic compounds, but at a lower rate than $\text{OH}^*$ radicals (Minero et al., 1993). In the presence of $\text{O}_2$, dye$^{**}$ is further oxidized into lower molecular weight organics and carbon dioxide as shown in Eq (24). Thus at pH < 6.6 the degradation reaction should be less favourable in the presence of NaCl as already reported in previous studies (Tanaka et al., 1994).

**Conclusion**

The results of the present study show that heterogeneous photocatalytic degradation of the dye Reactive Red 120 can be efficiently carried out using TiO$_2$ catalyst under UV irradiation. It is observed that adsorption plays an important role in the photodegradation of the dye and the degradation kinetics follows the Langmuir–Hinshelwood model. Both adsorption and photodegradation is the maximum in acidic medium. The degradation rate depends upon the process parameters like catalyst concentration, dye concentration and pH. The optimum catalyst dose for the degradation of 100 mg/l solution of RR 120 is 2.5g/l of TiO$_2$ and the degradation takes place effectively in acidic medium. The addition of oxidants like H$_2$O$_2$ and K$_2$S$_2$O$_8$ increases the degradation rate whereas the presence of Na$_2$CO$_3$ and NaCl decreases the reaction rate.
References


Solar Energy Supported Desalination Processes for Desalting of Sea Water#

Mehmet Emin Argun∗
Selcuk University, Engineering & Architecture Faculty, Department of Environmental Engineering, 42003 Konya, TURKEY

Received February 25, 2010; Accepted June 5, 2010

Abstract: This study is a review of solar energy supported desalination processes. Although the sun light captured by earth excessively meets of world’s need, we can use a few amount of this source. Solar energy supported desalination is one of the method developed for desalination. Solar energy usage will also decrease CO2 emission which is responsible of global warming. A lot of studies to improve the efficiency of solar energy systems have been carried out during last years. Solar energy can be used both of direct or indirect methods. Direct methods have low efficiency and low cost. Indirect methods include sun collectors which heating water, heat exchanger, evaporation compartments, photo voltaic panels which may used to drive the pumps and valves and may be finally have membrane treatment. Productivity and economic conditions determine which method will choose.

Keywords: Solar energy; desalination; sea water; water scarcity.

Introduction

Desalination of sea water has an increasing importance because of global warming and increasing water scarcity. In a lot of regions of the world especially in the Middle East and Africa, drinking water availability per-capita has fallen sharply since 1950. Today it is the lowest in the world and will continue to fall with increasing population and industrialization. Increasing energy prices also required alternative energy source. In the some region of world which water scarcity is present and water treatment is needed, desalination is the most efficient method for providing fresh water from brackish and/or seawater (Hrayshat and Al-Rawajfeh, 2008; Mohsen and Al-Jayyousi, 2008). Today, renewable energy based desalination such as solar and wind energy has revealed as promising and cost-effective alternative to energy intensive desalination systems having high capital and operational cost because of scarce availability of indigenous energy resources such as crude oil and natural gas (Akash et al., 1997, Mohsen and Shobaki, 2002). However, the performance of the renewable based desalination systems may be negatively affected from daily and seasonal variations of ambient temperature, solar irradiance, wind velocity, and demand for potable water (Kershman et al., 2005). Solar energy supported desalination systems can be divided into three parts: direct solar radiation, indirect solar radiation and hybrid systems. These systems are described below.

Direct Solar Radiation for Heating of Water

Direct solar radiation has been generally used for a long time to desalination of sea or brackish water in solar still which is the simplest method. This single basin type of desalination may be especially hopeful and attractive for rural settlement far away from the electric grid. Some advantages of solar stills are as follow; they are easily constructed, operated and maintained. Solar stills may constructed by locally available materials and not need to unskilled personal. The disadvantages are mainly focused on the low water yield and large areas for installation.

In the view of literature, numerous studies have been made to increase the productivity of solar stills. External condenser and reflector have been used for increasing solar radiation on the glass cover in a basin type still by El-Bahi and Inan (1999). Al-Hayek and Badran (2004) found that internal reflector increased the productivity about 20% in a single-slope still. Aybar et al. (2005) studied on an inclined solar water distillation system under actual environmental conditions of northern Cyprus.

∗Corresponding: E-mail: argun@selcuk.edu.tr, Tel.: +90-3322-2232058 Fax: +90-332-2410635
#This study has been presented in Taibah International Chemistry Conference-Kingdom of Saudi Arabia and pressed only it’s abstract in the Abstracts book.
Covering of outer surface of the back glass wall with highly reflecting materials have also been found to be productive for single-slope still (El-Swify and Metias, 2002). There were also theoretic studies about the effect of external reflector (Ayav and Atagündüz, 2007) and both of internal and external reflectors (Tanaka and Nakatake, 2006) on the amount of solar radiation. Abdallah et al. (2008) found increasing thermal performance of a solar still up to 30% by assembling mirrors on all interior sides. Tanaka and Nakatake (2009) has theoretically analyzed the optimum tilt angle and the optimum orientation of one step azimuth tracking tilted-wick solar still with a vertical flat plate reflector and found that the increase in the daily output of a tilted-wick still averaged at about 41% for these days. Velmurugan et al. (2009) tested a stepped solar still and an effluent settling tank for desalting of the textile effluent. The settled effluents have been transferred to the stepped solar still as raw water. Some combinations of fin, sponge, pebble have been used to improve of the productivity. Maximum productivity has been found 98% when all of fin, sponge and pebbles were exist in the basin.

**Indirect Solar Radiation for Heating of Water**

All of desalination methods which consist of multi effect distillation (MED), flash distillation (FD), membrane distillation (MD) and membrane filtration (MF) can benefit from solar energy. Solar supported desalination systems consist of three main components: the water heating subunit with sun panels, the evaporation subunit which occur heat exchange between circulation liquid and sea water and finally condensation of evaporated sea water (Mohsen and Al-Jayyousi, 2008). The main disadvantages of distillation have been reported as low efficiency, accumulation of salt at the bottom of basin and weak heat transfer. Bouchekima et al. (2001) studied the capillary film distiller which had advantage of heat recovery to overcome these disadvantages. They reused the heat of vapour condensation to evaporate another quantity of water by using a very thin fabric comprised of single, finely woven layer. Banat et al. (2007) were used solar supported MD system which circulating fluid heated by solar collectors, then the heated fluid has passed through the sea water via a heat exchanger and finally the hot water has transferred to the membrane system. Thereafter, heated sea water has passed the evaporator channel from its inlet to its outlet while cooling down. The sea water has directly used as cooling water and transferred to the condenser channel in counter flow to the hot feed. Thus preheating of sea water by the latent heat of condensation has been made. In another study, desalination pipeline system has been worked and it has been reported as getting simultaneous desalination and efficient transport of distilled water (Inoue et al., 2006). The temperature differences between seawater and inland atmosphere have been used to meet the energy source for the operation of the desalination pipeline system. It has indicated that the desalination pipeline system could supply distilled water through one year for some inland area about 100 km apart from the coastal area at a distilled water production rate of 3.2-35.0 L/min (about 10,000 m³/y) for a pipe with a diameter of 2 m, 19-205 L/min (about 60,000 m³/y) for a pipe with a diameter of 4 m.

An experimental design of humidifier system consisting of a double-pass flat plate solar air heater with two glass covers has been studied by Yamalı and Solmuş (2008). The idea of closed water and open-air cycles had been the main principle of the set-up. In outdoor environment, some systematic tests had been performed in order to evaluate the effect some parameters such as mass flow rate of the feed water, process air and cooling water, double-pass flat plate solar air heater and initial water temperature. According to the results given by Yamalı and Solmuş (2008), working principle of the experimental system had been explained as follow; firstly, the process air at the ambient conditions has transferred to the double-pass flat plate solar air heater leading to humidification of saline water, which came from the water storage tank. Finally, the water vapour has condensed and turned into fresh water through the condenser.

In another study sea water had been desalinated the distillation chamber consisted of a humidifier and a dehumidifier units (Dayem, 2006). The unit has not separated with walk between the two enclosures. The circulation of air in the two units was maintained by natural convection. The preheating of cold salt water has made by passing it through the distillation unit and then further heating has performed with the solar collectors. Solar collectors have total flat-plate collector field area of 3.1m². Heating processes had been made by either solar collectors or electrical heater. The heated salt water temperature had been fixed to 70°C. The condensed water has fallen into the walls via 7° inclined roof of the unit. Two horizontal pipes with small holes (1mm diameter) have used to
inject the hot salt water in to the evaporator to improve of the evaporation rate. The distillation productivity of this multiple-effect distillation unit has found as 24 l/day. Today, the usage of energy towers (Omer et al., 2008), Fresnel concentrators (Trieb et al., 2002), parabolic trough concentrators (Bardi, 2008; Trieb et al., 2002) and parabolic dish collectors (Argun and Kulaksiz, 2010) for water heating have increasingly used and reached to hopeful achievement. Sun tracking increased efficiency of these systems (Abdallah et al. 2008).

Hybrid Systems

Hrayshat (2008) has been studied on a stand alone reverse osmosis (RO) desalination unit supported by photovoltaic (PV) solar energy and a computer code in C++. The computer program was used to simulate the process and to predict the water production by using the available solar radiation data, sunshine hours and salinity of the feed water. The highest annual water production had been observed as 1679m³/year for TDS of 7000 mg/L by the researcher.

Eltawil and Zhengming (2009) were developed a new hybrid desalination system that constitutes of wind turbine (WT) and inclined solar water distillation (ISWD) integrated with main solar still (MSS). A rotating shaft placed in the MSS to break boundary layer of the water surface and wind turbine has been used to supply energy needs. Effect of different water depths (0.01, 0.02 and 0.03 m), different water flow rates (25.0, 41.7 and 58.3 ml/min) and two modes of operation have also experimented. A hybrid solar desalination process of the multi-effect humidification dehumidification and the basin-type unit was used by Hou and Zhang (2008). The multi-effect humidification dehumidification desalination (HDD) process has been plotted via pinch technology, and then the withdrawn water from multi-effect HDD process was reused to further desalinate in a basin-type unit. The hybrid solar desalination system consisting of sequential conventional solar still following by a solar collector field and hot water storage tank has been investigated by Voropoulos et al. (2004). They obtained that hot water volume draw-off equal to 1/4, 1/2 or 1 tank volume reduces distilled water output by 36%, 57% or 75%, respectively, by simultaneous energy output of about 1900, 3300 and 5200 MJ.

Another study focused on the use of both wind energy conversion (WEC) and photovoltaic power generation (PV) for brackish water desalination (Kershman et al., 2005). The WEC and PV have been used to power supply for a Reverse Osmosis (RO) desalination plant. They aimed to reduce the annual grid power consumption more than 80% by the WEC configuration. Fath et al. (2008) have been studied on the PV and thermally-driven membrane distillation (MD) system. The unit performance for a sunny day had been observed as 7.25 kWh/d. The results indicated that the system produced about 11.2 l/d for every m² of the collector area. The system supported by both solar thermal and solar PV energies. The PV panels have been used as auxiliary energy supplier in the case of solar thermal collectors could not capable. The maximum solar intensity of 995 W/m² during a clear day and the evaporator inlet temperature above 60°C had been obtained by Fath et al. (2008). The electric conductivities for feed and distillate water have obtained as 526 and 3 μS/cm, respectively. Fath et al. (2008) also reported that the daily production was 64 l/d (11.2 l/m²d), while the accumulated solar energy was 41.6 kWh/d (7.25kWh/m²d).

Conclusions

This brief review has demonstrated that solar heating of sea water by direct, indirect radiation or hybrid systems could be effectively used for decreasing salinity of the sea water. This paper also presented the results of energy needs for desalination. The mentioned desalination processes have been found as effective for decreasing salinity to the acceptable level for drinking water. Although these systems could not compete with classical desalination system yet, it is necessary to emphasize that these alternative energy sources are real, economical, innovational, environmentalist and natural investment because of continuously increasing fuel prices. These systems can be used in arid and coastal settlement which is far away from fresh water source, in island settlement and in every place where usable water is not enough and so the waste water must be treated and recycled.

References


Microelement Exploration Water Flow of Rimnik River

Naser Bajraktari¹, Besnik Baraj²*, Tahir Arbneshi³, Selim Jusufi³

¹Ministry of Environment and Spatial Planning, Prishtina, Kosova; ²University of Tirana, Albania; ³University of Prishtina, Kosova

Received January 20, 2010; Accepted March 13, 2010

Abstract: Compared to the increasing need on qualitative water use, many water flows are subject to a rising pollution by urban and industrial untreated water discharge, and in some cases by incidental run-offs. Besides them, there is also a great impact made by disseminated agricultural pollution and air and soil rinsing after atmospheric rainfalls. The main purpose of this paper is the micro-element exploration in water and sediments, along the water flow of Rimnik River. Some of the heavy metals: Pb, Cu, Ni, Cd, Fe, Zn and Li have been analyzed from the samples obtained in the specific areas. Some of the physical-chemical parameters and macro-pollutants such as: biological oxygen demand (BOD₅), wasted oxygen (OT), ammonia (NH₄⁺), nitrites (NO₂⁻), nitrates (NO₃⁻), sulfates (SO₄²⁻), phosphates (PO₄³⁻), etc. have been also defined. Water and sediment samples have been obtained and treated by the envisaged method under the regulation on standard methods, the fifteenth edition on water and waste water control. Heavy metals in these samples have been assessed using the atomic absorption spectroscopic method (AAS).

Key Words: Rimniku, water quality, sediment, water quality indicators, pollution, monitoring, water protection

Introduction

Degradation of natural resources has had an extraordinary impact on the development of nations and societies through various eras. Without doubt, water is one of the essential life resources, being also at the same time the basic element of environmental security. According to Mayers, 450 cases of misunderstandings over water resources have been discussed only in the second half of the previous century, where 37 of them have ended up in wars or aggressive actions against each other. The reason for those disputes has often been accusations on water pollution, jeopardizing to turn it into non-used water. Today 1.1 billion people in the world are not provided with a safe source of drinking water (Steck & Baraj, 2007). In the last 40 years surface and underground water monitoring, including sea water has been the subject of a continuous monitoring and evaluation (Alan & Gwyneth, 2003).

In post-war Kosovo, there is obviously a lack of strict and professional water protection. However the source of water pollution comprise the tendency for the revival of economy, relying also on the activation of old inherited obsolete technologies, financial inability to introduce modern technology, old water infrastructure in urban areas, lack of waste water treatment, industrial and urban waste disposal in inappropriate places (Anonymous, 2003; Lee & Jones-Lee, 1999; Anonymous, 2000). Population growth and also the pace of industrial development usually lead to water demand increasing, both in quantity and quality. Besides urban and industrial water use, water demand is increasing in terms of personal hygiene, irrigation in agriculture, water used for livestock, energy for cooling in thermal-energy and industries, as well as for fishing, sailing etc. (Anonymous, 2003). All these affect the quality of surface and underground waters (Lee & Jones-Lee, 1999). In most of the above activities, if adequate measures are not taken, an exceptional impact on water pollution will occur (Anonymous, 2000).

The purpose of this paper has been to make researches on surface water quality along the flow of Rimnik River. Researches have also been conducted earlier in order to determine the level of pollution in Drini i Bardhë River Basin, where River Rimnik gravitates, too (Bajraktari, et al., 2008). In most cases, Rimnik River serves as a key supplier in the summer for field and agricultural land irrigation in the locality of Rahovec.

The river flows to Zatriqi Mountain (Rahovec), passes by the town of Rahovec, Winery and several villages, and the river is influenced by several other discharges, as well as drainage of...

* Corresponding: E-mail: naserbajraktari@hotmail.com; Tel: +381 38 200 32 235; Fax: +381 38 200 32 245
agricultural lands farmed with different crops. Recently, the river has become a collector of urban and industrial waste water of this area. The final flow of this river ends up in Drini i Bardhë River Basin.

Some heavy metals; Pb, Cu, Ni, CDs, Fe, Zn and Li taken from the samples in certain places alongside Rimnik River are have been analyzed. There have also been analyzed several physical-chemical parameters and macro-contaminants as biochemical oxygen demand (BOD$_5$), wasted oxygen (OT), and some other chemical indicators (ammoniac, nitrites, nitrates, etc.).

**Material and methods**

**Equipment and reagents**

For the measurement of heavy metals it has been used AAS is Pekin -Elmer analyst 400, Spectrophotometer UV & Vis secocam, tut-tut-11 photometer nanocolor – visocolor, conductivity meter type of conductivity / TDS Metler Toledo NC126, pH meter consort C830, C 410 Clinical epilepsy photometer corning , turbidity meter Aquatic NTU / FNU, mineralizes (microwave) Ethos D Milestone. All chemicals required for the determination of physical parameters - chemical, micro and macro pollutions during sample analysis of surface waters and agricultural lands have been "pro analysis" (p.a.) chemically pure. Sample filtering has been done with filters of the following types: (Millipore Millex-FH) Hydrophobic PTFE 0:45 μm.

**Methods**

Samples for water analysis are taken and conserved as required by water standard regulation. Parameters such as: water temperature, pH value, TDS, turbidity, electrical conductivity, have been defined simultaneously in the sampling spot. In order to determine the amount of dissolved oxygen, we used Winkler Method. Then the measurement of the following parameters was carried out in the laboratory with standard methods: BO5, ammoniac, nitrites, nitrates, etc. Heavy metals (Pb, Cd, Cu, Zn, Fe, Ni and Li), in water and sediment are defined by the spectroscopic atomic absorb method SAA (Anonymous, 1992).

**Samples**

Sampling was carried out based on preliminary study so that there was a certain and appropriate distance between water sampling spots, sediment and land by the river in order to see their impacts between them. The Sampling Period is Spring – Autumn, 2008.

Sampling points were as follows: Source A1, A2 after discharge of municipal and industrial water to the town of Rahovec, A3 after water discharge from the winery and other secondary discharges, A4 after water stream discharge Sopaniq, discharged waters from several villages and drainage of agricultural land (Map 1).

Map 1. Sampling points along the Rimnik River course.
Scope of study

Rivers maybe represent more harmonized aquatic systems, when it comes to transport and microelement inter – reactions, in particular heavy metals. Due to the torrent water flow of the river, inter - reactions with rocks, sedimentary surface of the river bed are very intense, therefore each part of the river flow brings few or many changes in the contents of the river (Polic & Jablanoviç, 1999). The sub-basin selected for study is covered by various types of soil and human activities. As these waters containing heavy metals are used for irrigation in agriculture that will bring about the accumulation of these metals in the lands where these plants are farmed and people and animals would be negatively affected.

Results and Discussion

The results of this study on sampling periods are presented in Table I and II, however we will only discuss values of other sampling period results. Since the pollution comprises physical-chemical and biological impacts, water quality can be determined by different physical-chemical and biological parameters. Assessment of aquatic environment quality is traditionally based on the measurements of inorganic and organic substance concentrations. The higher the quantity of organic substances in water, the lower the concentration of oxygen and the higher the concentration of ammonium. (Dalmacija, 2000). The main indicators of polluted water are biochemical oxygen consumption (BOD₅), dissolved oxygen (DO), TDS, several chemical indicators (ammoniac, nitrites, nitrates, heavy metals, etc.) (Polic & Jablanoviç, 1999). We have presented in this paper, the water quality of Rimnik River in 4 sampling spots. In sampling spots: ‘Ura e Drenovcit’ (Drenovc Bridge) (A1), a locality non-affected by anthropogenic factor, mineral area comprising mainly dominant soil types with ultramaphic rocks composition [Fejza, et all, 2000]. The locality in the upper Rahovec, along exit road Malisheva – Rahovec, Mulliri i Aliagës (Aliaga’s Mill) (A2), the location where there is a conflux of Rimnik River with Rahoveci stream (or industrial, atmospheric and sanitation waste water collect) in close report 1:4 for the river of Rahovec. After the conflux, there is an enormous pollution and this water from the first category found in the first sampling point, can now be classified in the fourth water quality category. Fortesë (A3), a locality with the same pollution as the previous one, affected also by the drainage of agricultural lands and the village Fortesë. Xerxe (A4), a locality which is also added the flow of Sopaniq Stream. The water classification of this sub-basin (river) was carried out based on several indicators of water quality, at different sampling periods, compared to the parameters given in Table 1, by UNECE (Anonymous, 2007).

Figure 1. Graphic view of the results for Cd, Li and Zn, in water samples
Table 1. Criteria of surface water quality, UNECE

<table>
<thead>
<tr>
<th>Category</th>
<th>$P_{int}$</th>
<th>NO$_3^-$</th>
<th>O$_2$ dissolved</th>
<th>BOD$_5$</th>
<th>COD</th>
<th>NH$_4^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class I</td>
<td>&lt;10</td>
<td>&lt;5</td>
<td>&gt;7</td>
<td>&lt;3</td>
<td>&lt;3</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Class II</td>
<td>10-25</td>
<td>5-25</td>
<td>7-6</td>
<td>3-5</td>
<td>3-10</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>Class III</td>
<td>25-50</td>
<td>25-50</td>
<td>6-4</td>
<td>5-9</td>
<td>10-20</td>
<td>0.5-2</td>
</tr>
<tr>
<td>Class IV</td>
<td>50-125</td>
<td>50-80</td>
<td>4-3</td>
<td>9-15</td>
<td>20-30</td>
<td>2-8</td>
</tr>
<tr>
<td>Class V</td>
<td>&gt;125</td>
<td>&gt;80</td>
<td>&lt;3</td>
<td>&gt;15</td>
<td>&gt;30</td>
<td>&gt;8</td>
</tr>
</tbody>
</table>

Table 2. Concentrations found in water samples (Sampling Period is September 2008)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>A1 Ura Drenocit</th>
<th>A2 Mulliri Aliagës</th>
<th>A3 Fortesë</th>
<th>A4 Xërxe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{H2O}$</td>
<td>ºC</td>
<td>22.3</td>
<td>22.1</td>
<td>23.4</td>
<td>23.3</td>
</tr>
<tr>
<td>$T_{Air}$</td>
<td>ºC</td>
<td>30</td>
<td>29.5</td>
<td>29</td>
<td>28.5</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>8.49</td>
<td>7.84</td>
<td>8.03</td>
<td>8.09</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>0.0</td>
<td>23.13</td>
<td>16.38</td>
<td>9.66</td>
</tr>
<tr>
<td>TDS</td>
<td>mg/l</td>
<td>409</td>
<td>425</td>
<td>483</td>
<td>211</td>
</tr>
<tr>
<td>Conductivity</td>
<td>µS/cm</td>
<td>818</td>
<td>851</td>
<td>963</td>
<td>423</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>mg/l</td>
<td>0.905</td>
<td>17.93</td>
<td>13.885</td>
<td>7.11</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>mg/l</td>
<td>20.2</td>
<td>54</td>
<td>52</td>
<td>22</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>mg/l</td>
<td>0.172</td>
<td>0.404</td>
<td>0.468</td>
<td>0.19</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>mg/l</td>
<td>0.089</td>
<td>4.385</td>
<td>4.461</td>
<td>1.08</td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>mg/l</td>
<td>3.33</td>
<td>19.9</td>
<td>14.25</td>
<td>6.65</td>
</tr>
<tr>
<td>O$_2$</td>
<td>%</td>
<td>69.9</td>
<td>5.7</td>
<td>25.6</td>
<td>55.2</td>
</tr>
<tr>
<td>O$_2$ wasted</td>
<td>mg/l</td>
<td>5.63</td>
<td>0.53</td>
<td>2.07</td>
<td>4.45</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>mg/l</td>
<td>7.042</td>
<td>64.67</td>
<td>60.21</td>
<td>14.20</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/l</td>
<td>0.087</td>
<td>0.045</td>
<td>0.036</td>
<td>0.038</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/l</td>
<td>0.005</td>
<td>0.004</td>
<td>0.004</td>
<td>0.005</td>
</tr>
<tr>
<td>Ni</td>
<td>mg/l</td>
<td>0.232</td>
<td>0.068</td>
<td>0.089</td>
<td>0.091</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/l</td>
<td>0.096</td>
<td>0.056</td>
<td>0.066</td>
<td>0.078</td>
</tr>
<tr>
<td>Li</td>
<td>mg/l</td>
<td>0.103</td>
<td>0.128</td>
<td>0.152</td>
<td>0.156</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/l</td>
<td>4.508</td>
<td>1.824</td>
<td>0.616</td>
<td>1.618</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/l</td>
<td>0.063</td>
<td>0.051</td>
<td>0.022</td>
<td>0.041</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/l</td>
<td>0.039</td>
<td>0.041</td>
<td>0.044</td>
<td>0.049</td>
</tr>
</tbody>
</table>
Table 3. Concentration found in sediment samples (Sampling Period is September 2008)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{H}_{2}\text{O}}$</td>
<td>°C</td>
<td>22.3</td>
<td>22.1</td>
<td>23.4</td>
<td>23.3</td>
</tr>
<tr>
<td>$T_{\text{Air}}$</td>
<td>°C</td>
<td>30</td>
<td>29.5</td>
<td>29</td>
<td>28.5</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>8.49</td>
<td>7.84</td>
<td>8.03</td>
<td>8.09</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/kg</td>
<td>4</td>
<td>28.4</td>
<td>30.3</td>
<td>37.3</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/kg</td>
<td>0.3</td>
<td>0.8</td>
<td>0.9</td>
<td>0.85</td>
</tr>
<tr>
<td>Ni</td>
<td>mg/kg</td>
<td>228.75</td>
<td>142.5</td>
<td>135</td>
<td>121.25</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/kg</td>
<td>6.15</td>
<td>16.6</td>
<td>17.8</td>
<td>9.05</td>
</tr>
<tr>
<td>Li</td>
<td>mg/kg</td>
<td>80</td>
<td>17</td>
<td>19</td>
<td>37</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/kg</td>
<td>1142.5</td>
<td>2062.5</td>
<td>2397.5</td>
<td>3115</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/kg</td>
<td>81.05</td>
<td>131.4</td>
<td>85</td>
<td>190</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/l</td>
<td>17.8</td>
<td>16.4</td>
<td>69.3</td>
<td>60.8</td>
</tr>
</tbody>
</table>

The research results along the course of Rimnik River are presented in a tabular form in Table II and III, and also some of the heavy metals in the graphic form. Figure 1. show that the results of our measurements indicate a certain determined parameter variability of water quality of the River. The dissolved oxygen (DO) is consumed in reactions during which new microbial cells develop from organic substances present in water. Over time, older cells die and organic substances linked to them get consumed in further reactions. This synthesis and dissolution of cells continues until the number of live cells considerably reduces and only organic substances, relatively stable, and very similar to humus remain in water (Manahan, 1991). The interval of concentrations for this relevant water quality indicator in our samples ranges from 0.015 - 13.7 mg / L (Table 2).

Biochemical oxygen consumption (BOD$_5$) is a measure of the presence in water of organic substances which can support the growth of microbial organisms. BOD$_5$ is the most known test on water pollution control (Manahan, 1991). It is clear that BOD$_5$ is measured with the dissolved oxygen quantity during aerobic microbial oxidation of a water sample, within a given time and temperature. The usual time is 5 days, the temperature 20 °C, and the result is recognized as five day biochemical oxygen consumption usually recorded as BOD$_5$ (Anonymous, 1992). Concentration of organic substances, expressed by BOD$_5$ in our samples was 3:33 - 19.9 mg / L, which indicates that these waters are loaded with organic substance (Table 2).
Water in natural state (unaffected) has a relatively low content of nitrogen and phosphorus; we have had several times such results in A1 sampling point. In these cases the water appearance is clean, with little or no vegetation and the water at the bottom is clean (Rozhaja & Jablanović, 1983]. Concentrations of nutrient salts of nitrogen in water, such as ammoniac, nitrates and nitrates cause the process of eutrophication. Ammonium is the first product of organic substance disintegration, it may be also toxic to fish and other aquatic organisms. Nitrates, as final products in the process of nitrification, highly concentrated, are toxic to new age organisms. Concentrations of ammonium in our measurements range from 0.905 - 17.93 mg / L. Concentration of nitrates, ranges from 0.028 to 0.468 mg / L, while the nitrate measurements carried out have shown the following concentrations: 6.8 - 54 mg / L. Phosphates show the value in A1 from 0.027, until 5.75 in the A4. (Tabela 2 dhe 3).

By waste water discharge and drainage of agricultural lands, the river also intakes a considerable amount of heavy metals (Pb, Ni, Zn, Cu, Fe, Cd, Cr and Li). In some cases the concentration exceeds the maximum amount allowed, for the determined class of the River (Balvay, 1991; Table 1 and 2). Table 1 indicates that pH value does not pose an obvious issue on the quality of river water and this value ranges mostly within usual values for natural ecosystems (from 7.84 - 8.49), while conductivity and turbidity, indicating that these waters are highly charged with different components. as për ujarët e kategorisë së II. Based on the chemical indicators, water quality of Rinnik River, in comparison with the European Union Directives on natural surface water classification; in some localities water of these rivers does not meet conditions even for water of category II. However at some points, especially after sewage water discharge of the Town of Rahovec, these waters go up to class IV and V, which means that these waters in the current state can not be used for recreation and bathing, for water sports and fish farming (excluding the source of the river). Due to the rapid water flow of the river, rock interactions, sedimentary surface of the river bed are very intense therefore each part of the river flow brings few or many changes in the contents of the River.

Urban and industrial waste disposal into the waters of rivers also causes significant increase of pollution with heavy metals (Miho et al, 2005). This is clearly pointed out by the value comparison in areas where there was technological discharge, with respective values in natural rocks, salts or clean area sediments. The concentration of heavy metals in sediment samples in some cases shows very high values (Rugova et al, 1989). I will stop here to discuss the indicated copper values from 0.038 to 0.087 mg / l and in sediment up to 37.3 mg / l. Specific value, indicated in the source by lithium, from 0.013 to 0.152 mg / l and in sediment up to 80 mg / l, whereas iron from 0.616 to 4.508 mg / l. and in sediment up to 3115 mg / l. The accuracy of analytical results is verified by the Association of General Environmental Analyses Laboratory AGLAE. Code test 08M1A3, dated 4/11/2008, in which 136 laboratories took part, conducted in the same sampling period during our researches on Rinnik River. According to this association, the given results from the reference samples have been acceptable.

Conclusions and Recommendations

Industrial waste water discharge and untreated urban water in Rinnik River are facing serious consequences both water fauna and irrigation water supply of the population, and in some cases its effect can be observed in wells nearby the flow. Long and uncontrolled discharge and without any prior treatment of urban, industrial and agricultural polluted waters into Rinnik River flows have resulted in changing of water quality of this river. Based on the measurement results and analyzed parameters appears that these waters mainly belong to category I and II, in the first sampling area (A1), considered unaffected by anthropogenic factor, sampling points (A2 and A3) belong to category IV and sampling point (A4) category III, of surface water quality, under the criteria of UNECE. Therefore, it is particularly important to separate waste water treatment prior to the discharge into Rinnik River bed, and further to Drini Bardhë River Basin. Even despite obvious omissions, it is still possible to reduce or prevent the negative tendency of these occurrences. Heavy metal assessment or researching in sediment or living organisms (algae, plants and other living organisms) is also relevant in determining the environmental water status. The collection of metals from water living organisms is a very important chain in determining the medium-term pollution. It concerns the assertion that its sediments and pollutants are continuously interacting with water organisms living in it. This means that even the sediment itself or water return to the pollution source. Therefore, we must first stop further pollution of Rinnik River and improve and preserve its natural wealth.
References
Polić P, Blagoević S, Teski metali u vodama, Prirodn. - matematički fakultet, Novi Sad 1999, f. 74