PAPER 059

GRASS CARP (*Ctenopharyngodon idella*), BIGHEAD CARP (*Hypophthalmichthys nobilis*) AND EUROPEAN CATFISH (*Silurus glanis*) PRODUCTION IN CYPRINID FISH FARMS IN PELAGONIA (BITOLA, MACEDONIA)

Dijana Blažeković Dimovska[1], Aleksandar Cvetković[2], Stojmir Stojanovski[3]

[1]University "St. Kliment Ohridski", Faculty of Biotechnical Sciences, Bitola, Macedonia;
[2]University "St. Cyril and Methodius", Faculty of Veterinary Medicine, Skopje, Macedonia;
[3]Hydrobiological Institute, Ohrid, Macedonia;

E-mail: dijanablazekovic@yahoo.com ; acvetkovikj@gmail.com ; stojstoi@gmail.com;

ABSTRACT

Cyprinid fish farming in Pelagonia (Bitola, Macedonia) takes place in two largest fish farms in this region: Bel Kamen – Žabeni with an area of 170 ha and Bukri with an area of 55 ha. The most common fish that are grown here are those from the family Cyprinidae, such as common carp, grass carp, bighead carp, silver carp etc. Beside them, one of the fish that is also grown in these farms is european catfish. The aim of this study was to determine the production of grass carp (*Ctenopharyngodon idella*), bighead carp (*Hypophthalmichthys nobilis*) and european catfish (*Silurus glanis*) in cyprinid fish farms in Pelagonia (Bitola, Macedonia) in a period of three years. In order to investigate it, analyses of fish production were made in the two largest cyprinid fish farms in Pelagonia that are located in its south-eastern part. Investigations were carried out in a period of three years, from 2011 to 2013. Grass carp, bighead carp and european catfish production in fish farm Bel Kamen - Žabeni is more than double (46826 kg) compared with the fish farm Bukri (17404 kg). This situation is normal because of different ambient conditions and difference in fish farm capacity (ha).

Key words: grass carp (*Ctenopharyngodon idella*), bighead carp (*Hypophthalmichthys nobilis*), european catfish (*Silurus glanis*), cyprinid fish farms

INTRODUCTION

According FAO (2014), global fish production growth continues to outpace world population growth. Aquaculture remains one of the fastest growing food producing sectors and is set to play a key role in meeting the rising demand for fishery products. Fish remains an ever – important source of energy, protein and a range of essential nutrients, accounting for almost 17 percent of the global population`s intake of animal protein. The fisheries and aquaculture sector are vital source of livelihoods, nutritious food and economic opportunities.
Cyprinid fish farming in Pelagonia (Bitola, Macedonia) takes place in two largest fish farms in this region: Bel Kamen – Žabeni with an area of 170 ha and Bukri with an area of 55 ha. The most common fish that are grown here are those from the family Cyprinidae, such as common carp, grass carp, bighead carp, silver carp etc. Beside them, one of the fish that is also grown in these farms is european catfish.
Cyprinid fish farms usually have an area of 10-100 ha, with water depth of 1-2 m. The optimal water temperature is 25°C, the amount of dissolved oxygen is 7-9 mg/l and the pH range from 7 - 8.

MATERIAL AND METHODS

The aim of this study was to determine the production of grass carp (*Ctenopharyngodon idella*), bighead carp (*Hypophthalmichthys nobilis*) and european catfish (*Silurus glanis*) in cyprinid fish farms in Pelagonia (Bitola, Macedonia) in a period of three years.

In order to investigate it, analysis of grass carp, bighead carp and european catfish production were made in the two largest fish farms in Pelagonia: Bel Kamen - Žabeni and Bukri. Investigations were carried out in a period of three years, from 2011 to 2013.
Fish farms Bel Kamen - Žabeni and Bukri are located in the southeastern part of Pelagonia (Bitola, Macedonia) and working within ZK "Pelagonija" - Bitola. They were built in 1960/61, with the enclosure of part of the Black River old bed with two embankments. Fish farm Bel Kamen - Žabeni occupies an area of 170 ha, while Bukri an area of 55 ha.

RESULTS

Cyprinid fish farming in Pelagonia (Bitola, Macedonia) takes place in two largest fish farms in this region: Bel Kamen – Žabeni with an area of 170 ha and Bukri with an area of 55 ha. D. Blaževković Dimovska et al. (2015) considered that the stocking in these fish farms is planned according to their condition and the quantity of available offspring. These two fish farms are very rich in algae and dense herbage. Therefore, it is necessary to enter herbivorous fish species which will control the herbage within normal limits and will provide better conditions for carp breeding as the most abundant species in these ponds. Best results are achieved with polyculture fish breeding that provides breeding of more fish species which do not competitive eating, using different foods and occupies different living space. The best way for stocking is represented by 70% carp, 10 % grass carp and 20% bighead carp, although this relationship may change.
The grass carp (*Ctenopharyngodon idella*) (Figure 1) is one of the largest members of the family Cyprinidae, and is the only member of the genus Ctenopharyngodon (E. W. Chilton & M. I. Muoneke 1992). After silver carp, grass carp currently has the largest production in freshwater aquaculture globally. This species is characterized by a wide, scale head, sub- terminal or terminal mouth with simple lips, no barbells, slightly protracted upper jaw and very short snout. Its length is less than or equal to its eye diameter and its postorbital length is more than half its head length. The color of adult grass carp is dark gray on the dorsal surface with lighter sides (white to yellow) that have a slightly golden shine. Fins are clear to gray-brown (L. M. Page & B. M. Burr 1991; K. Opuszynski & J. V. Shireman 1995). Its weight is 30-50 kg (E. W. Chilton and M. I. Muoneke 1992) and length can reach more than 1 m (L. Nico & P. Fuller 2001).
According Fish Base (2004), grass carp have been extensively introduced (mainly for macrophyte control) to many parts of the world. Grass carp have been widely introduced in North, Central and South America, the South Pacific Islands, Asia, the Indian subcontinent, Europe, Scandinavia and Africa. For polyculture in ponds or pens, grass carp can be stocked either as the major species or a secondary species together with other carp species. Grass carp not only grow quickly but have a low requirement for dietary protein. They can be produced at low cost by feeding them with aquatic weeds, terrestrial grasses and by-products from grain processing and vegetable oil extraction.

Figure 1. Grass carp (***Ctenopharyngodon idella***) from fish farms in Pelagonia (Bitola, Macedonia) (original)

Table 1 shown grass carp production in cyprinid fish farms in Pelagonia (Bitola, Macedonia) in a period of three years.
In 2011, there was 9.300 kg grass carp production in fish farm Bel Kamen - Žabeni, while 2.003 kg in fish farm Bukri.
In 2012, there was 3.340 kg grass carp production in fish farm Bel Kamen - Žabeni, while 388 kg in fish farm Bukri.
In 2013, there was 420 kg grass carp production in fish farm Bel Kamen - Žabeni, while 2.971 kg in fish farm Bukri.

In a period of these three years, total amount of grass carp production in fish farm Bel Kamen - Žabeni was 13060 kg, while in Bukri 5362 kg.

Table 1. Grass carp (***Ctenopharyngodon idella***) production in cyprinid fish farms in Pelagonia (Bitola, Macedonia)

Year / Fish farm	FISH FARM "BEL KAMEN – ŽABENI"	FISH FARM "BUKRI"
	Grass carp (***Ctenopharyngodon idella***) production (kg)	
2011	9300	2003
2012	3340	388
2013	420	2971
TOTAL	13060	5362

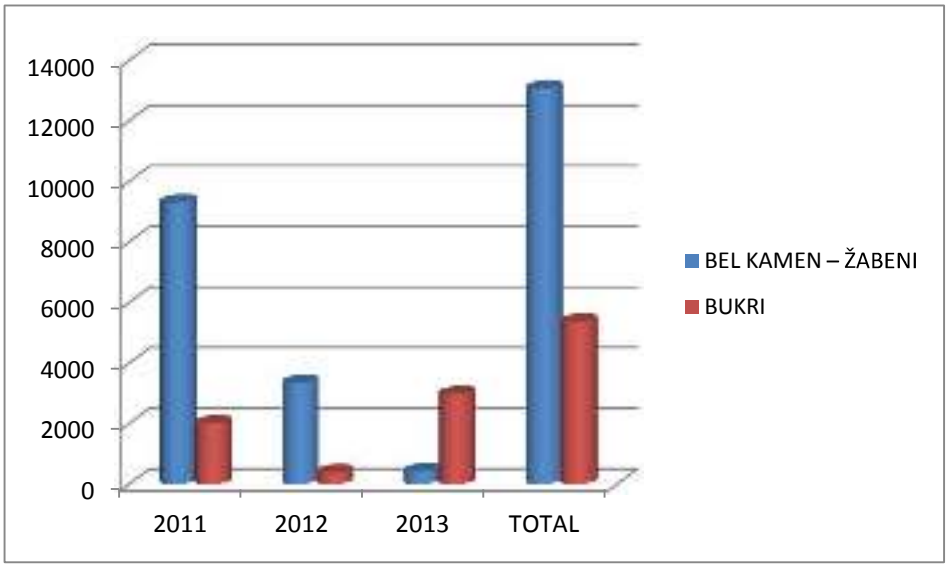


Figure 2. Grass carp (***Ctenopharyngodon idella***) production in cyprinid fish farms in Pelagonia (Bitola, Macedonia)

Figure 3. Main producer countries of *Ctenopharyngodon idella* (FAO Fishery Statistics, 2006)

Bighead carp (*Hypophthalmichthys nobilis*) (Figure 4) is a eurythermic fish, being able to tolerate water temperatures of 0.5-38 °C. This species is basically a zooplankton feeder throughout its life under natural conditions. In culture, bighead carp will also accept artificial feed, such as the by-products from grain processing and organic detritus, in addition to natural food. Bighead carp are fast growing and become very large, reaching a maximum weight of 40 kg. The body of a bighead carp is laterally compressed with the top being a dark gray color which grades down to off white on its belly. It has many dark blotches on its sides. Its head is comparatively large with no scales and a large terminal mouth. The bighead has no teeth and its lower jaw protrudes out farther than its upper jaw. The eyes are situated low on its head and are positioned downward. Due to the natural features of bighead carp, the systems used for its culture are rather limited. Extensive culture in open-waters and pond-based polyculture are the major systems used. The most important factor involved in the production of bighead is to ensure a sufficient supply of quality seed (FAO, 2006).

Figure 4. Bighead carp (***Hypophthalmichthys nobilis*)** from fish farms in Pelagonia (Bitola, Macedonia) (original)

Table 2 shown bighead carp production in cyprinid fish farms in Pelagonia (Bitola, Macedonia) in a period of three years.
In 2011, there was 10.485 kg bighead carp production in fish farm Bel Kamen - Žabeni, while 4.393 kg in fish farm Bukri.
In 2012, there was 8.952 kg bighead carp production in fish farm Bel Kamen - Žabeni, while 3.200 kg in fish farm Bukri.
In 2013, there was 8.538 kg bighead carp production in fish farm Bel Kamen - Žabeni, while 2.853 kg in fish farm Bukri.
In a period of these three years, total amount of bighead carp production in fish farm Bel Kamen - Žabeni was 27.975 kg, while in Bukri 10.446 kg.

Table 2. Bighead carp (***Hypophthalmichthys nobilis*)** production in cyprinid fish farms in Pelagonia (Bitola, Macedonia)

Year / Fish farm	FISH FARM "BEL KAMEN – ŽABENI"	FISH FARM "BUKRI"
	Bighead carp (***Hypophthalmichthys nobilis*)** production (kg)	
2011	10485	4393
2012	8952	3200
2013	8538	2853
TOTAL	27975	10446

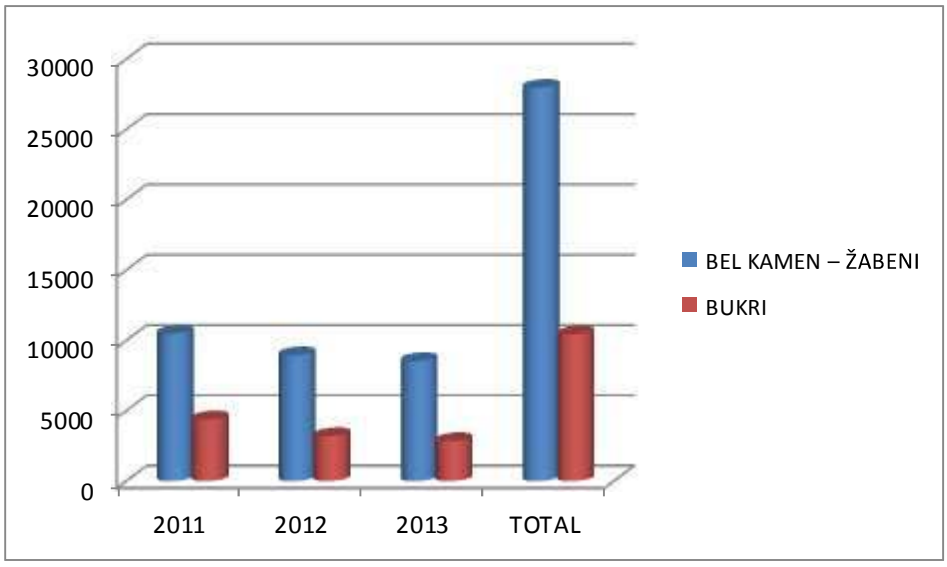


Figure 5. Bighead carp (***Hypophthalmichthys nobilis*) production** from fish farms in Pelagonia (Bitola, Macedonia)

Figure 6. Main producer countries of *Hypophthalmichthys nobilis* (FAO Fishery Statistics, 2006)

The European catfish (*Silurus glanis*) (Figure 7) is one of the largest freshwater fish worldwide. Although it originally inhabited rivers of Eastern Europe and Western Asia, this species is spreading within Europe, due to its popularity among anglers and interest in it as a potential species for aquaculture (A. M. Cunico & J. R. S. Vitule, 2014). It is also known as wels or sheatfish with recorded individuals of 5 m in length and 306 kg in weight (G. H. Copp et al. 2009; Z. S. Hogan 2011). According (G. H. Copp et al. 2009) this species is used for recreational and commercial fishing, as well as for aquaculture, because they show rapid growth and are hardy and physiologically robust. This species is native to rivers of Eastern Europe and Western Asia, but is currently spreading throughout Europe and the world due to its popularity among anglers and interest in it as a potential species for aquaculture (A. Alp et al. 2011). The FAO Database of Introduced Aquatic Species – DIAS (FAO 2013) notes that *Silurus glanis* has been introduced into the UK, Denmark, The Netherlands, Cyprus, Italy, Spain, Algeria, Tunisia, Belgium, Germany, France, Kazakhstan, Croatia, Turkey, Syria and China, mainly by anglers and aquaculture activities, with records of self-sustainable populations in more than 80% of the countries to which it has been introduced.

Figure 7. European catfish (***Silurus glanis***) from fish farms in Pelagonia (Bitola, Macedonia) (original)

Table 3 shown european catfish production in cyprinid fish farms in Pelagonia (Bitola, Macedonia) in a period of three years.
In 2011, there was not european catfish production in fish farm Bel Kamen - Žabeni, while 406 kg in fish farm Bukri.
In 2012, there was 2.195 kg european catfish production in fish farm Bel Kamen - Žabeni, while 1.080 kg in fish farm Bukri.
In 2013, there was 3.596 kg european catfish production in fish farm Bel Kamen - Žabeni, while 110 kg in fish farm Bukri.
In a period of these three years, total amount of European catfish production in fish farm Bel Kamen - Žabeni was 5791 kg, while in Bukri 1596 kg.

Table 3. European catfish (***Silurus glanis***) production in cyprinid fish farms in Pelagonia (Bitola, Macedonia)

Year / Fish farm	FISH FARM "BEL KAMEN – ŽABENI"	FISH FARM "BUKRI"
	European catfish (***Silurus glanis***) production (kg)	
2011	/	406
2012	2195	1080
2013	3596	110
TOTAL	5791	1596

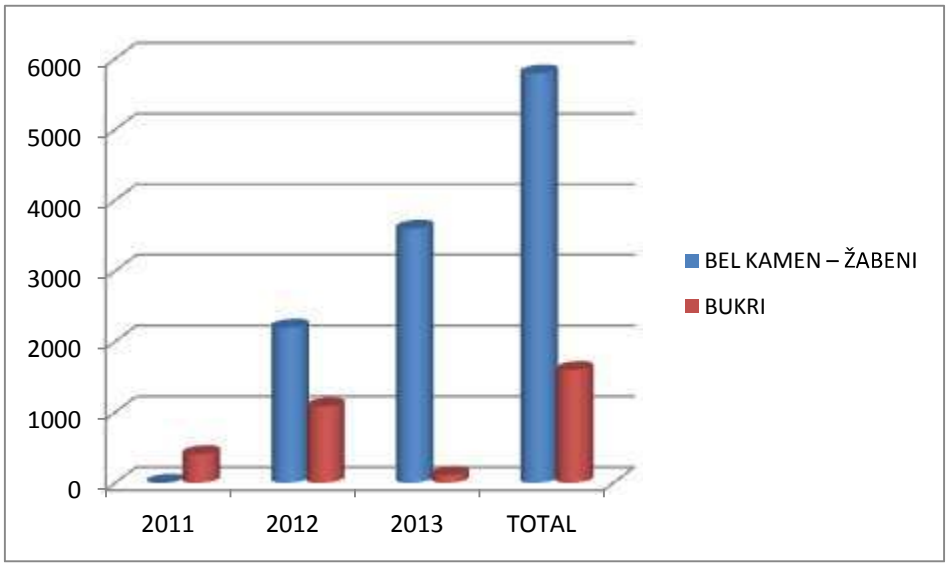


Figure 8. European catfish (***Silurus glanis***) production in cyprinid fish farms in Pelagonia (Bitola, Macedonia)

D. Blaževković Dimovska (2015) considered that spawning in these fish ponds is natural and uncontrolled and it is necessary to put a greater number of female fish in order to provide a sufficient number of offspring for stocking. In practice, there is ratio of 1: 3 (one female and three males) in area of 1 ha. Spawning begins when the water temperature reaches 20°C, usually in late April and early May. Fish hunting begins in early November and lasts 10-12 days.

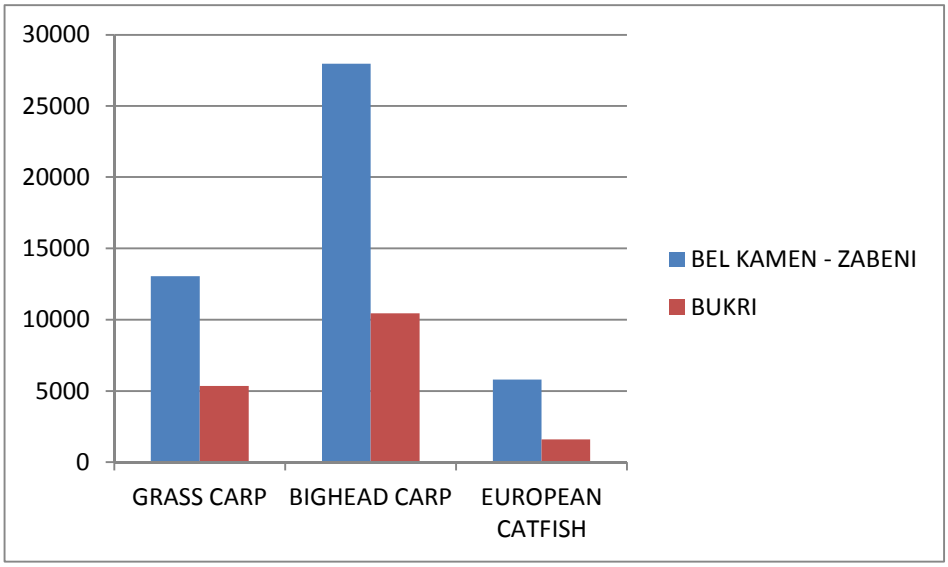


Figure 9. Comparison in fish production (kg) between fish farms Bel Kamen – Žabeni and Bukri

Taking into account the quantities of fish (kg) of a period of three years respectively (2011, 2012 and 2013), it can be notes that the fish production in fish farm Bel Kamen - Žabeni is more than double (46826 kg) compared with the fish farm Bukri (17404 kg). This situation is normal because of different ambient conditions and difference in fish farm capacity (ha).

Figure 10, 11, 12. Fish hunting in cyprinid fish farms in Pelagonia (Bitola, Macedonia)

CONCLUSIONS

Cyprinid fish farming in Pelagonia (Bitola, Macedonia) takes place in two largest fish farms in this region: Bel Kamen – Žabeni with an area of 170 ha and Bukri with an area of 55 ha. The most common fish that are grown here are those from the family Cyprinidae, such as carp, grass carp, bighead carp, silver carp etc. Beside them, one of the fish that is also grown in these farms is european catfish.

In a period of 2011, 2012 and 2013, total amount of grass carp production in fish farm Bel Kamen - Žabeni was 13060 kg, while in Bukri 5362 kg.

In a period of 2011, 2012 and 2013, total amount of bighead carp production in fish farm Bel Kamen - Žabeni was 27.975 kg, while in Bukri 10.446 kg.

In a period of 2011, 2012 and 2013, total amount of European catfish production in fish farm Bel Kamen - Žabeni was 5791 kg, while in Bukri 1596 kg

Taking into account the quantities of fish (kg) of a period of three years respectively (2011, 2012 and 2013), it can be notes that the fish production in fish farm Bel Kamen - Žabeni is more than double (46826 kg) compared with the fish farm Bukri (17404 kg). This situation is normal because of different ambient conditions and difference in fish farm capacity (ha).

REFERENCES

Cunico, A. M., Vitule, J. R. S. (2014): First records of the European catfish,Silurus glanis Linnaeus, 1758 in the Americas (Brazil), BioInvasions Records (2014) Volume 3, Issue 2: 117–122.

Alp, A., Kara, C., Uçkardes, F., Carol, J., Garcia-Berthou, E. (2011): Age and growth of the European catfish (Silurus glanis) in a Turkish Reservoir and comparison with introduced populations. Reviews in Fish Biology and Fisheries 21: 283–294.

Blaželković-Dimovska, D., Cvetković, A., Stojanovski, S. (2015): „Common carp (*Cyprinus carpio* L.) production in cyprinid fish breeding facilities in Pelagonia (Bitola, Macedonia)“, *Int. journal ecosyst. ecol. sci.*, Vol. 5 (1): 139-144.

Chilton, E. W., and M. I. Muoneke (1992): Biology and management of grass carp (Ctenopharyngodon idella, Cyprinidae) for vegetation control: a North American perspective. Rev. Fish Bio. Fish. 2:283-320.

Copp, G.H, Britton, J.R, Cucherousset, J., Garcia-Berthou, E., Kirk, R., Peeler, E., Stakenas, S. (2009): Voracious invader or benign feline? A review of the environmental biology of European catfish Silurus glanis in its native and introduced ranges. Fish and Fisheries, 10: 252–282

FAO, 2013. Database of Introduced Aquatic Species (DIAS). http://www.fao.org/fishery/introsp/search/en (Accessed 10

FAO, 2006. Food and Agriculture Organization of the United Nations. Fisheries and Aquaculture Department.http:// www.fao.org/fishery/culturedspecies/Cyprinus_carpio/en.

Fish Base (2004) World Wide Web electronic publication. Froese, R. and D. Pauly. Editors. www.fishbase.org, version (10/2004).

FAO, 2014. The state of world fisheries and aquaculture.

Hogan, Z.S. (2011): Ecology and Conservation of Large-Bodied Freshwater Catfish: A Global Perspective. American Fisheries Society Symposium 77: 39–53

Nico, L. and Fuller, P. (2001): Ctenopharyngodon idella (Valenciennes 1984) nonindigenous aquatic species. Non-indigenous species. Florida Caribbean Science Center. Biological Resources Division. Web Site http://nas.er.usgs.gov/queries/

Opuszynski, K. and Shireman J.V. (1995): Herbivorous fishes: culture and use for weed management. In cooperation with James E. Weaver, Director of the United States Fish and Wildlife Service's National Fisheries Research Center. CRC Press, Boca Raton, Florida.

Page, L. M., and Burr, B. M. (1991): A fieeld guide to freshwater fishes. Houghton Mifflin Company, Boston.

PAPER 061

THE EFFECT OF EARTHQUAKES ON MARINE ECOSYSTEMS IN ADRIATIC SEA

Adisa Daberdini[1], Elton Rogozi[2], Rrapo Ormëni[3]

[1]Polytechnic University of Tirana, Sheshi Nene Tereza, Tirana, Albania;
[2]Institute of Public Health, Str. Aleksander Moisiu, Nr. 80, Tirana, Albania;
[3]Institute of Geosciences, Energy, Water and Environment, UPT, Tirana, Albania;

E-mail: adisadaberdini@hotmail.com, adisa.daberdini@gmail.com.

ABSTRACT

Tsunamis are one of the most destructive natural hazards that affect the coastal areas. Its waves are capable of destroying the objects on the coast and re-shaping the coastal geography, geomorphology and ecosystem. These waves have unusually long-wavelength in excess of 100kms, generated in the open sea and transformed into a train catastrophic oscillations on the sea surface close to coastal zones. This study represents a simple model for the changes calculation that coastal structure of the Adriatic Sea may undergoes by a tsunami impact in the maritime dimension. The study has been carried out based on the coastal structure of Adriatic Sea, in the subsequent studies, that how this structure will affect on the tsunami wave. After the tsunami wave, the coastal structure undergoes some changes, and these changes will directly affect in the marine ecosystem. The sediment structure of Adriatic Sea is formulated based on a previous approaching model built by Bruce E. Jaffe and Guy Gelfenbuam, 2007. This calculation model is approached based on the Adriatic Sea structure. The difference on the deposit granule size has more impact on the tsunami wave speed, rather than its thickness. The result of this study shows how to built an approximate model for the structuring that the Adriatic Sea coast may undergoes by the seismic activity, which in some cases may develop tsunami with marine dimension. The Physical structure may damaged by the force of the wave itself, physical removal of flora and fauna and increased sediment load which could kill sediment sensitive species and sea grasses by smothering. Chemical changes may included saltwater intrusion, eutrophication (enrichment) of the water resulting from increased runoff, raw sewage and decomposition of flora and fauna. Non biodegradable waste such as plastics may contribute to a buildup in marine debris.

Key words: Tsunami, Sedimentation, Deposits, Effect, Marine Ecosystem, Adriatic Sea.

INTRODUCTION

In the frame of the geophysical knowledge of the Mediterranean region the geodynamic evolution of the Adriatic microplate, very complex and still debated, plays a key role. Many international studies have been carried out with the aim of better assessing the seismicity of this region. Albania is situated in Alpine-Mediterranean seismic belt comprising the zone of contact between lithosphere plates of Africa and Eurasia. The Albanian orogen and its surroundings are divided into two active tectonic domains: an external compressional domain, constituting the Adriatic collision zone (Outer Albanides), and an internal extensional domain (Inner Albanides) (Aliaj et al, 2001).. The typology of the earthquakes in Albania comprises all four primary and well-known types of earthquakes: earthquakes with main-shock followed by aftershocks, earthquakes with foreshocks and aftershocks, swarms and compound earthquakes (Ormeni et al, 2012). We present here the results of the analysis in parameters of events and some features of Seismicity that have occurred in the Albania and surrounding area.

Table 1. Historical data of tsunami event in Adriatic Sea

No.	Year	Month	Day	Region
1	1833	01	19	Albania
2	1851	10	12	Vlore, Albania
3	1866	01	02	Albania

4	1866	03	02	Vlore, Albania
5	1866	03	06	Albania
6	1866	03	13	Albania
7	1869	12	28	Vlore, Albania
8	1893	06	14	Vlore, Albania
9	1920	11	26	Sazan, Albania

MATERIAL AND METHOD

A tsunami occurs after a huge mass of water is displaced by some force from its equilibrium configuration. Gravity acts as a restoring force, tending to bring the displaced mass of water back to its original equilibrium state. Most tsunamis are generated by submarine earthquakes, but possible sources are also inland/coastal earthquakes, landslides and meteoric impacts. Due to their generation mechanism, periods and wavelengths associated with tsunamis are longer than those associated with ordinary wind-driven sea waves and for largeOn Albania and its surrounding territory, between 39°00'-43°00' N and 18°30'-21°30'E, 458 earthquakes was located with ML=1.5-4.7 (Richter). Figure 1 shows the Seismicity located for the period of time 2014. Seismic phases recorded by the Albanian network, integrated with data of INGV (Italy) Montenegro, Thessaloniki (Greece) and Kosovo networks, are used to prepare the database for this study (Ormeni et al, 2013). The standard procedure uses the program Hypoinvers (Fred.W.Klein, 2002) of the Atlas packet, and velocity model Vel-Albanid (Ormeni, 2007) for earthquake locations. Some formula for determination of the magnitude according to the time duration of the seismic signal is also used.

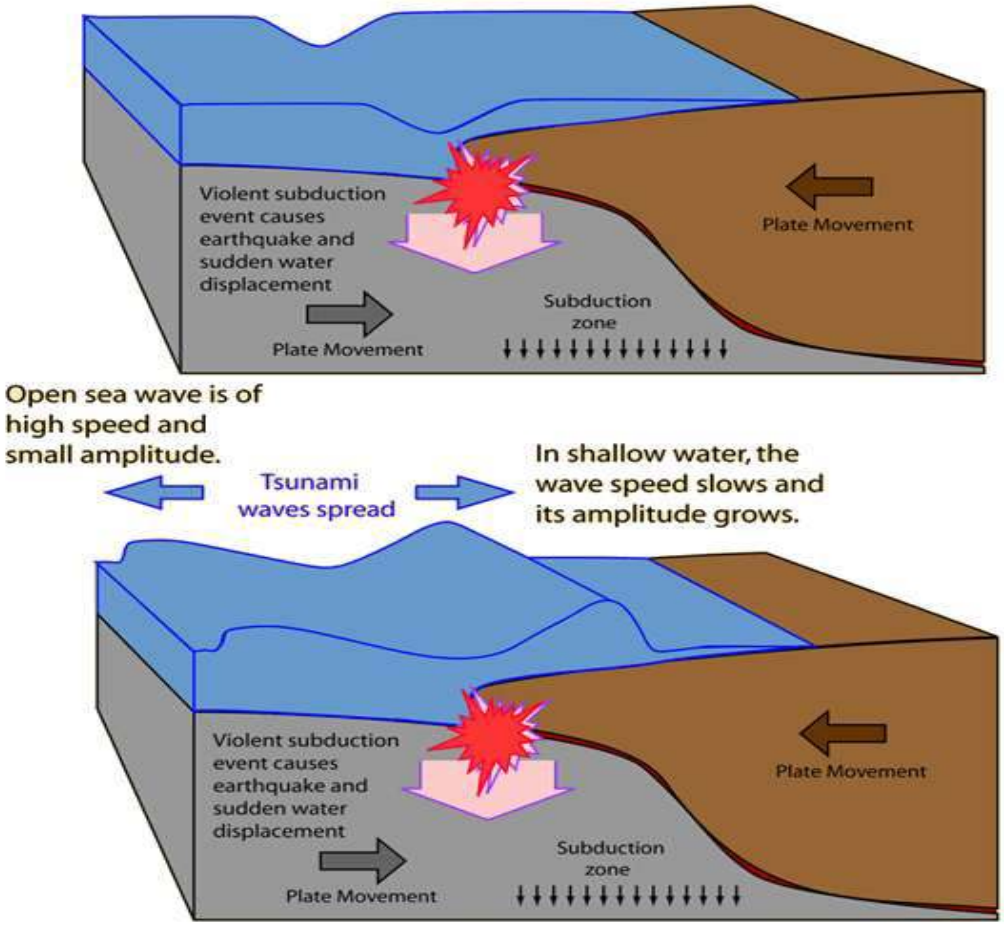


Fig.2 Ilustration of how happen the tsunami event.

Table 2. The wave speed depends upon wavelength and the depth of the water for tsunamis at sea. Characteristic data is shown in the table at right. As they enter shallower water, their wavelength and wave speed diminishes, causing their amplitudes to greatly increase.

Depth (meters)	Velocity (km/h)	Wavelength (km)
7000	943	282
4000	713	213
2000	504	151
200	159	48
50	79	23
10	36	10.6

RESULTS

1.Direct impacts of the tsunami on coastal ecosystems

Ecosystems weakened by a catastrophe such as a tsunami are likely to be more vulnerable to a subsequent catastrophe, provided there was no time for sufficient recovery. Investments in environmental restoration may, therefore, be a sensible strategy to fasten regeneration processes, thereby enhancing overall robustness and decreasing the vulnerability to subsequent hazards.If impacts were minor and natural regeneration is fast, such investments may not improve the situation; rather they may represent a waste of resources that could be used for other more tangible efforts to reduce various risks.

2.Offshore ecosytems

In places of direct heavy wave impact there was only little evidence of recent coral mortality. Overall, direct tsunami impacts were highest in colonies on unconsolidated substratum on the reef slope; damage was mainly influenced by reef aspect, submarine topography and it was highest in bays. The most dramatic destruction of coral reefs was, however, due to the effects of the earthquake. The actual causes of reef decline are commonly difficult to trace back; reef degradation is normally caused by the interaction of several stressors. Other impacts may be due to chronic mechanical damage, such as trawling, dredging, push nets, anchoring and dynamite fishing; though less important in terms of scale, these impacts are normally unambiguous.

CONCLUSION

The result of this study shows how to built an approximate model for the structuring that the Adriatic Sea coast may undergoes by the seismic activity, which in some cases may develop tsunami with marine dimension.
The most seismic activity inside the Albanian territory, analyzed in this paper have been generated in an area with complex features from the nontectonic point of view.
The local earthquakes are distributed in depth between 0 and 25 km, with maximum concentration between 4 and 12 km.
The Physical structure may damaged by the force of the wave itself, physical removal of flora and fauna and increased sediment load which could kill sediment sensitive species and sea grasses by smothering.

REFERENCES

Aksornkoae S. & Tokrishna R. (2003). Overview of shrimp farming and mangrove loss in Thailand. In: *Shrimp Farming and Mangrove Loss in Thailand* (eds E.B. Barbier and S. Sathirathai). Edward Elgar Publishing Ltd., Northampton, USA.

Alongi, D.M. (2002). Present state and future of the world's mangrove forests. *Environmental Conservation* 29(3): 331-349.

Alongi, D.M. (2008). Mangrove forests: Resilience, protection from tsunamis, and responses to global climate change. *Estuarine, Coastal and Shelf Science* 76: 1-13.

Baird A.H., Campbell S.J., Anggoro A.W., Ardiwijaya R.L., Fadli N., Herdiana Y., Kartawijaya T., Mahyiddin D., Mukminin A., Pardede S.T., Pratchett M.S., Rudi E. & Siregar A.M. (2005). Acehnese reefs in the wake of the Asian Tsunami. *Current Biology* 15: 1926-1930.

Barbier E. & Cox M. (2002). Economic and demographic factors affecting mangrove loss in the coastal Provinces of Thailand, 1979-1996. *Ambio* 31(4): 351-357.

Mazda, Y., Wolanski, E. & Ridd, P.V. (Eds.), 2007. *The Role of Physical Processes in Mangrove Environments. Manual for the Preservation and Utilization of Mangrove Ecosystems.* Terrapub, Tokyo.

McAdoo, B.G., Goff, J.R., Fritz, H.M., Cochard, R. & Kong, L.S. (2009). *The tsunami project: Integrating engineering, natural and social sciences into post-tsunami surveys.* American Geophysical Union, Fall Meeting 2009, abstract #NH34B-01.

Papadopoulos, G.A. (2005). "Tsunamis in the Mediterranean Sea" in "The Physical Geography of the Mediterranean Sea", Oxford University Press (under preparation).

Papadopoulos, G.A. and Plessa, A. (2001). "Historical Earthquakes and Tsunamis of the South Ionian Sea Occurring from 1591 to 1837", Bulletin of the Geological Society of Greece, Vol. XXXIV, No. 4, pp. 1547-1554.

Soloviev, S.L., Solovieva, O.N., Go, C.N., Kim, K.S. and Shchetnikov, N.A. (2000). "Tsunamis in the Mediterranean Sea 2000 B.C.-2000 A.D.", Kluwer Academic Publishers, Dordrecht, The Netherlands.

Tinti, S. and Maramai, A. (1996). "Catalogue of Tsunamis Generated in Italy and in Côte d' Azur, France: A Step towards a Unified Catalogue of Tsunamis in Europe", Annali di Geofisica, Vol. 39, pp. 1253-1299.

Thampanya U., Vermaat J.E., Sinsakul S. & Panapitukkul N. (2006). Coastal erosion and mangrove progradation of Southern Thailand. *Estuarine, Coastal and Shelf Science* 68: 75-85.

Thanawood C., Yongchalermchai C. & Densrisereekul O. (2006). Effects of the December 2004 tsunami and disaster management in Southern Thailand. *Science of Tsunami Hazards* 24(3): 206-217.

PAPER 062

IDENTIFICATION OF THE REPRODUCTION SEASON OF OTTERS (LUTRA LUTRA) IN THE DRINOS RIVER

Etleva Hysaj[1*], Gligor Paspali[1], Ferdinand Bego[2]

[1] Department of Biology and Chemistry, University "Eqrem Çabej", Gjirokastra, Albania
[2] Department of Biology, Faculty of Natural Sciences, University of Tirana, Albania

E-mail: hysaj_etleva@yahoo.com

ABSTRACT

Identification of the reproduction season of the otter (*Lutra lutra*) along the Drinos river has been the objective of our study in the two years period (October 2010-October 2012). The Drinos river section Virua-Andon Poçi (10km) was selected as study area, as it provides the optimal combination of the environmental factors relevant to the reproduction of otters. For the identification of the reproduction season of otters we used the following indicators or parameters: changes in the territorial marking intensity (measured as number of sprainting points/200m, number of spraints/200m, and number of jelly secretions/200m), changes in the activity along the river banks, and first sight of the cub's footprints following its mother while hunting. The highest values of the marking intensity were identified in April-May (in average, number of sprainting points/200m =1.62, number of spraints/200m = 4.48 and number of secretions/200m = 0.72), indicating so an increase of the otter's marking intensity in this period in comparison with other months or seasons. In addition, in the same period (April-May) a high territorial marking activity along the river banks were observed (scratching, rolling, scent marking, male and female tracks and footprints at the same spots). First sight of cub's footprints in the middle of October 2011, is another key indicator for the identification of the start of reproduction season of otters. Based on these indications we conclude that the start of reproduction season for otters in the Drinos river coincides with the bimonthly period April-May, as the most typical characteristics the otter's reproduction behaviour are observed only during this period of time. Our results confirm that in the Drinos river the otter reproduction is characterised by a single reproduction season, and this reproduction seasonality reflects the seasonality of the environmental conditions in the Drinos as a typical Mediterranean river.

Key words: Otter, reproduction season, Drinos river, Albania

INTRODUCTION

The otter is a medium size carnivore species of the family Mustelidae closely related with aquatic ecosystems that is sensitive to changes or alterations of such ecosystems (Gasith and Resh, 1999; Magalhães et al., 2002). The combination of a set of environmental factors that provide favourable conditions in securing abundant food, safe places to breed and rear the cubs as well as available resting sites seems to play a determinant role in breeding strategy of otters and keeping their population healthy (Kruuk, 1995, Ruiz-Olmo, 1998; Ruiz-Olmo *et al*., 2001; Ruis-Olmo *et al.,* 2005).

The presence of a thick and dense riparian vegetation, with the presence of old growth trees along the river bank provides suitable temporary and permanent places to female otters for breeding and rearing their cubs (Liles, 2003). This vegetation may also help better protection of small cubs from human disturbance and predators, such as red foxes and shepherd dogs (Kruuk, 2006; Green *et al*., 1984). The presence of water and food, both in terms of food availability and diversity, are vital factors that greatly influence the reproduction season and reproduction strategy of otters (Ruiz-Olmo *et al*., 2001; Ruiz-Olmo *et al.* 2005).

Drinos river, as already mentioned in previous studies, provides suitable habitats for otters as already demonstrated by wide distribution and permanent presence of otters along the river and its tributaries and adjacent water bodies (Hysaj and Bego, 2008; Hysaj and Bego, 2011; Hysaj *et al.,* 2013; Bego and Hysaj, 2013; Hysaj *et al.,* 2014).

Drinos river, as a typical Mediterranean river is characterised by high seasonality and variability of water regime. Seasonal variations of environmental parameters, both abiotic and biotic ones, determine the seasonality of reproduction strategy of otters in the Mediterranean rivers (Ruiz-Olmo et al., 2012).

The aim of our study is to identify the start of the reproduction season of otters along the Drinos river, situated in the Southern Albania, and to find out the most important sectors of the river used by female otter to breed and rear the cub.

MATERIAL AND METHODS

The study area includes the river section Virua-Andon Poci (10 km long) of the Drinos river that was intensively surveyed during a two years period of time (October 2010-Octoberr 2012). (fig.1). This river sector was chosen as study area due to optimal environmental conditions it provides for otters; otter presence along this river section is permanent and marking intensity is highest ever observed along the entire Drinos river to date (Hysaj and Bego, 2008; Hysaj and Bego, 2011; Hysaj *et al*., 2013; Bego and Hysaj, 2013; Hysaj *et al*., 2014).

Figure 1. Study area where otter marking signs were surveyed.

For the identification of the breeding season in otters along the Drinos river we used the following parameters: changes in the territorial marking intensity (measured as number of sprainting points/200m, number of spraints/200m, and number of jelly secretions/200m), changes in the activity along the river banks, and first sight of the cub's footprints following its mother out of the den while hunting.

The mean values of territorial marking intensity were assessed on a bimonthly basis along the whole year. Changes in otter's activity along the river bank were detected through observation of typical activity signs (scratching, rolling, scent marking, male and female tracks and footprints at the same spots, fresh spraints and jelly secretions at the same spots, resting sites along the riverbanks). Identification of the small cub footprints was made through intensive observations along this river section along the whole year. Sighting of the first cub footprints and the period when they were observed for the first time are considered as key elements in defining the reproduction season of otters in Drinos river.

RESULTS

The mean values of the marking intensity on bimonthly basis for the whole year of intensive surveys along the river section Virua-A. Poçi show that the period April-May is characterised by the highest territorial marking intensity by otters (in average, number of sprainting points/200m =1.62, number of spraints/200m = 4.48 and number of secretions/200m = 0.72), (Figure 2). We think that such an increase of Otter's marking intensity coincides with the

beginning of the breeding season, time when both adult male and female demonstrate their readiness to copulate by increasing their territorial marking intensity with spraints and jelly secretions (Mason and Macdonald, 1986)

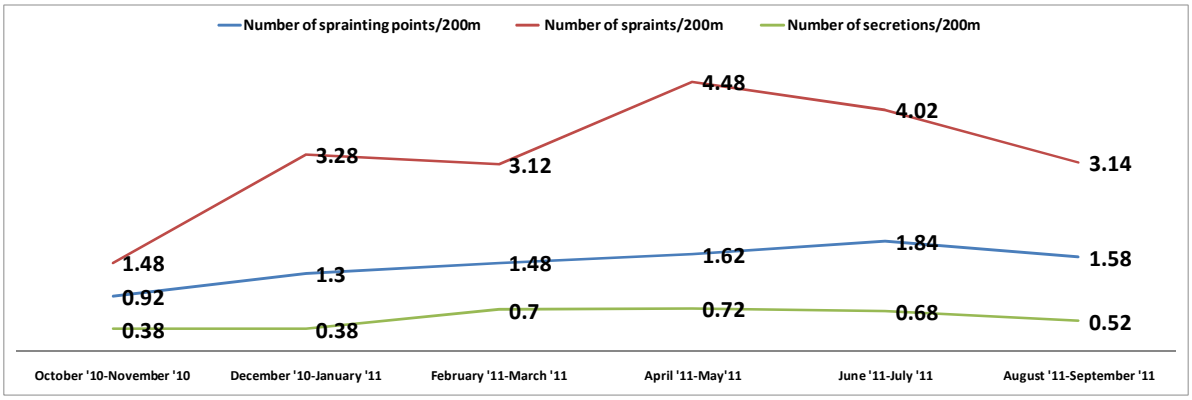


Figure 2. Mean bimonthly values of marking intensity by otters along the river section Virua-Andon Poci.

Figure 2 shows that the mean values of territorial marking intensity decreased in the subsequent period June-July (number of sprainting points/200m =1.84, number of spraints/200m = 4.02 and number of jelly secretions/200m = 0.68) and August-September (number of sprainting points/200m = 1.58, number of spraints/200m = 3.14 and number of jelly secretions /200m = 0.52). The decrease of marking intensity after the copulation is explained by the fact that the pregnant female tries to hide the location of the natal den from the potential predators. According to Green *et al.*,(1984), the pregnant female during this period of time starts preparation of the natal den; she is less frequently visible and hunts for short intervals, avoiding hunting very close to the den site. This feeding behaviour is also favoured by the presence of abundant and diverse food for otters in this river section during summer time (Hysaj *et al.,* 2014). Food abundance and diversity that characterise this river section are considered as main factors that determine the seasonality of reproduction strategy of otters, as already confirmed by other authors in the Mediterranean rivers (Ruiz-Olmo *et al.,* 2005; Ruiz-Olmo *et al.,* 2012).

During the period April-May, the increased marking intensity was accompanied with an increase of otters activity on the riverbank sides related with reproduction behaviour. Thus, during this period there was noticed an increase of scratches often associated with scent marking on the riverbank side and footprints of male and female at the same spot. In some river stretches, such as the Argjinatura, close to Nimisa tributary and in vicinity of Palokastra village, there were observed some resting sites for otters on the bank sides that were used by both male and female otters. These resting sites were also marked with fresh scents and jelly secretions (Figure 3/1). During the same period (April-May), in various places there were observed dozens of fresh spraints and jelly secretions in the same sprainting point (Figure 3/2), a clear indication of increased territorial marking activity of males competing for the female to copulate. Along the riverbed and river banks during this period there were also observed rolling and scent marking (Figure 3/3). According to Georgiev (2008), this phenomenon is more frequent during breeding season. Along this river section during April-May there were often observed footprints of male and female otters at the same spots, recognised by different size of the footprints (Figure 3/4). According to Prigioni *et al*., (1995) such phenomena (i.e. changes in territorial marking intensity and changes in marking activity along the river banks) are basic elements to identify the beginning of the reproduction season of otters in Mediterranean rivers.

Figure **Error! No text of specified style in document.**: Aspects of marking activity by otters during the reproduction season April-May along the river section Virua-Andon Poçi: 1) Resting sites on the bankside. 2) Scents and jelly secretions. 3) Rolling and scant marking. 4) Male and female footprints

First sighting of the small cub footprints leaving the natal den and following its mother out of the den is a hard fact to confirm the reproduction season of otters in Drinos river (Figure 4/1). In first two weeks of October 2011, we have often observed the footprints of the cub and its mother indicating the time when the small cub comes out of the natal den and follows the mother to hunt (Figure 4/2). These female-small cub footprints were observed along the riverbed and riverbanks covered with thick reeds. This fact indicates the careful and safety behaviour of the mother to protect her cub outside the den. Footprints of the small cub are also observed along the shallow water river stretches and in ponds of calm and slow water speed. Shallow and calm or slow speed water courses with abundant food are favoured places by otter females to rear their cubs (Ruiz-Olmo *et al*., 2005) and where small cubs can safely learn to swim during the first weeks after leaving the den (Kruuk 1995, 2006).

Figure 4: Fooprints 1) small cub footprints (⟶), 2) small cub footprints (⟶) associated with mother footprints (⟶).

Footprints of the small cub were observed parallel to water course, indicating that the cub was having its first experiences outside of the natal den.

Assuming that the pregnancy in otters takes some 9 weeks, while the small cub stays inside the natal den for about 12 weeks, then the first sight of small cub out of the den in first two weeks of October confirms the start of reproduction season or copulation back to April-May.

Intensive searching for the first footprints of the cubs were repeated during the first weeks of October 2012 , and the observation of the small cub footprints in the same places and in the same period of time confirmed our finding that otters have one reproduction season along the Drinos river and is using the same river sections to breed and rear the cubs. River sectors such as Argjinatura, river stretch close to Nimisa tributary, and river stretch in proximity of Palokastra village serve as safely breeding and rearing sites for otters along the Drinos. Ruiz-Olmo *et al* (2005) have noted that some river sections are reused as breeding and rearing sites for otters for many generations, confirming that the presence of safe dens for the cubs is also an important habitat selection factor of female otters.

The river section Virua-A. Poci surveyed under this study reassured the importance of preserving this section of the Drinos river for the long term survival of otters in the Drinos valley (Hysaj and Bego, 2008; Hysaj *et al*., 2013). At the same time we argue the need that this river section should be designated as Natura2000 Site in Albania.

CONCLUSIONS

The beginning of breeding season for otters in Drinos river coincides with the period April-May. Typical otter's behaviour signs related with reproduction are observed only during this period of time. Maximal values of territorial marking activity are observed in April-May. During this period an increase of otters activity on riverbanks is noticed. The small cub emerging from the natal den in first weeks of October in both years (2011 and 2012) confirms that the breeding season of otters along the Drinos river begins in April-May. Our study shows that there is only one reproduction season for otters in Drinos river, and this is determined by the high seasonality of the environmental conditions of the Drinos river, as a typical Mediterranean river. Food availability, current speed and the presence of safe dens are important habitat selection factors for otter females in selecting the breeding and rearing sectors along the river. As finding such favoured sectors by female otters to give birth and rear the cubs is not easy, it seems that the female otters reuse the same breeding and rearing sectors of the river as long as they provide abundant food and safe dens.

REFERENCES

Bego F., Hysaj E. 2013. Influence of the artificial water reservoirs in the feeding strategy and distribution of the otter (Lutra lutra) along the Drinos river valley, Albania. 3th International Conference of Ecosystems (ICE) Tirana, Albania. Proceeding Book, Paper 053: 156-163.

Gasith A. & Resh V.H. 1999. Streams in Mediterranean climate regions – abiotic influences and biotic responses to predictable seasonal events. Ann. Rev. Ecol. Syst. 30: 51–81.

Georgiev, D.G. 2008. Seasonality in marking activity of the eurasian otter (Lutra lutra) in Southern Bulgaria. Proceedings of the anniversary scientific conference of ecology. Plovdiv, November 1st 2008, p. 236-240.
Green J., Green R. E jefferies D.J. 1984. A radio-tracking survey of otters Lutra lutra on a Perthshire river system. Lutra 27: 85-145.
Hysaj E., Bego F. 2008. Përhapja, gjendja dhe dieta e lundërzës (Lutra lutra l.) përgjatë luginës së Drinos. Proceedings of the International Conference on Biological and Environment Sciences: 271-279.
Hysaj E., Bego F. 2011. Ndikimi i sezonit riprodhues dhe faktorëve ambientale në intensitetin e shënimit të lundërzës (Lutra lutra L.) përgjatë luginës së Drinos. Journal of Institute Alb-Shkenca. Aktet Vol IV, 1: 73-77.
Hysaj E., Bego F., Prigioni C., Balestieri A. 2013. Distribution and marking intensity of the Eurasian Otter, Lutra lutra, on the river Drinos (southern Albania). Folia Zoologica, Vol: 62, Issue: 2, Page 115-120.
Hysaj E., Paspali G., Qirjo M., Bego F. 2014. Seasonal variations of the otter's diet along the drinos river (southern Albania). 4th International Conference of Ecosystems (ICE) Tirana, Albania. Proceeding Book, Paper 084: 314-319.
Kruuk H. 1995. Wild otters. Predation and populations. Oxford University Press, Oxford.
Kruuk H. 2006. Otters ecology, behaviour and conservation. Oxford University Press, 280 pp.
Liles G. 2003. Otter Breeding Sites. Conservation and Management. Conserving Natura 2000 Sites Conservation Techniques Series, N° 5. English Nature, Peterborough.
Magalhäes M.F., Batalha D.C. & Collares-Pereira M.J. 2002. Gradients in stream fish assemblages across a Mediterranean landscape: contributions on environmental factors and spatial structure. Freshw. Biol. 47: 1015–1031.
Mason C. F. & Macdonald S. M. 1986. "Otters: Ecology and Conservation" Cambridge University Press, Cambridge, 236 pp.
Prigioni C, Fumagalli R, Chirru L, Rugati C. 1995. Sprainting activity of captive otters: its relationship with breeding cycle and number of animals. Hystrix, (n.s.) 7 (1-2) (1995): 297-301 Proc. I1 It. Symp. on Carnivores.
Ruiz-Olmo J. 1998. Influence of altitude on the distribution, abundance and ecology of the otter (*Lutra lutra*) In: Behaviour and ecology of riparian mammals. Dunstone N., Gorman M.L. (Eds), 59-176.
Ruiz-Olmo J., Batet A., Mañas F., Martínez-Vidal R. 2012. Factors affecting otter (*Lutra lutra*) abundance and breeding success in freshwater habitats of the northeastern Iberian Peninsula. European Journal of Wildlife Research. 04/2012; 57(4):827-842.
Ruiz-Olmo J., Batet A., Jiménez J., Martínez D. 2005. Habitat selection by female otters with small cubs in freshwater habitats in northeast Spain. Lutra 2005; 48 (1): 45-56.
Ruiz-Olmo J., Lopez-Martin J.M., Palazon S. 2001. The influence of fish abundance on the otter (*Lutra lutra*) populations in Iberian Mediterranean habitats. Journal of Zoology, 254: 325-336.

PAPER 064

STIMULTANIOUS DETERMINATION OF ORGANCHLORINATED PESTICIDES AND PCB IN VEGETABLE OIL SAMPLES OF ALBANIAN MARKET

Oljana Pine[1)], Aurel Nuro[1)], Elda Marku[1)], Vlora Gashi[2)]

[1)] Tirana University, Faculty of Natural Sciences, Chemistry Department
[2)] Institute of Agriculture and Food, Peja, Kosovo

E-mail: ola_pine@hotmail.com

ABSTRACT

This study examines the levels of organochlorinated pesticides and polychlorinated biphenyls in vegetable oil samples collected in Albanian markets, in January 2015. Organoclorine pesticides are the first class of compounds introduced in agricultural and civil uses to counteract noxious insects and insect-born disease. The modern history of pesticides dates back to World War II when for the first time the insecticidal properties of DDT were recognized. In general they are lipophilic compounds with noticeable chemical and environmental stability. PCBs were used widely as transformer oil because of their stability and physical-chemical properties. The same properties are the reason that PCBs were reported to found everywhere in environmental and food samples.Ultrasonic bath extraction assisted with n-Hexane mixture and two clean-up steps have been used for analytical treatment of samples. The quantitative analysis of organochlorinateds pesticids and PCBs were performed by the gas chromatography method with electron capture detector (GC-ECD). Cyclopentadiene chlorinated pesticides and less chlorinated PCB congeners were found in higher concentrations in all samples. The levels of contaminants observed for the vegetable oil samples could be because of their before use for agricultural purposes, industrialization data or don't management of waste repositories of pesticides for the corresponding regions.

Key words: Organochlorinated pesticides, PCBs, vegetable oil gas chromatography

INTRODUCTION

Oils extracted from plants have been used since ancient times and in many cultures. As an example, in a 4,000-year-old kitchen unearthed in Indiana's Charlestown State Park, archaeologist Bob McCullough of Indiana University-Purdue University Fort Wayne found evidence that natives used large slabs of rock to crush hickory nuts, then boiled them in water to extract the oil. The production process of vegetable oil involves the removal of oil from plant components, typically seeds. This can be done via mechanical extraction using an oil mill or chemical extraction using a solvent. The extracted oil can then be purified and, if required, refined or chemically altered. Oils can also be removed via mechanical extraction, termed "crushing" or "pressing." This method is typically used to produce the more traditional oils (e.g., olive, coconut etc.), and it is preferred by most "health-food" customers. The plants such as soybeans, maize, sunflowers, olives, etc could be affected from the pesticides and other pollutants because soil contaminations, agricultural processes, atmospheric factors, etc ().

Organoclorine pesticides are the first class of compounds introduced in agricultural and civil uses to counteract noxious insects and insect-born disease. The modern history of pesticides dates back to World War II when for the first time the insecticidal properties of DDT were recognized. In general they are lipophilic compounds with noticeable chemical and environmental stability. Although most OCP have been progressively restricted and then banned in the 1970s in most industrialized countries a widespread environmental pollution has resulted from their use in agriculture and civil uses. Before 90' organochlorinated pesticides were used widely in Albania for agricultural purposes. The main agricultural areas were in the western of the country (Shkodra, Durresi, Tirana, Fieri, Lushnja, Vlora) but almost every were in the country had been developed different directions of agricultural (fruits, corns, vegetables, etc.). The most used organochlorinated pesticides were DDT, Lindane, HCB, Aldrins and Heptachlors. The scale of pesticides use after 90' in agriculture generally has decreased. The former has generated the expired pesticides, which due to the inappropriate conditions of conservation and storage have been damaged.

Mismanagement of oddments pesticides, for some years after 90' was another source of pesticides contamination in many areas of Albania.

Commercial PCB mixtures were used in a wide variety of applications and mainly as dielectric fluids in capacitors and transformers, and as heat exchange fluids. They are chemically highly stable, lipophilic compounds and resist microbial, photochemical, chemical and thermal degradation. Unfortunately, the same properties which make PCBs interesting for industrial use cause them to accumulate in biota (Erickson, 2001). The PCB concentrations were shown to increase through the different trophic levels of the food chains. PCBs cause adverse effects on reproduction, development, and endocrine function including thyroid hormone homeostasis and estrogen-responsive tissues (Safe, 1994). PCBs were not used before 90' in Albania. They were used mainly as electric transformer oil after 90'(Koci, 1999).

MATERIALS AND METHODS

Sampling of vegetable oil samples

16 Vegetable oil samples were collected from different supermarkets of Albania in January 2015. The vegetable oil samples were with different plant origin such as soybeans, maize, sunflowers, and olives. Only olives oil was made in Albania, other oils were imported from different countries. Samples were frozen during transportation and storage at +4^{o}C before analysis.

Preparation of samples for pesticide residues analysis

The extraction method used was based on EN 1258 for determination of organchlorine pesticides in fatty matrices. About 10 ml of vegetable oil was taked into a flask and about 20 ml of hexane was added and the samples were extracted for 2 x 30 min in ultrasonic bath. The sample was spiked with recovery standard (TCB) before exctraction. 20 g of silicagel with 45% acid sulphuric (m/m) were added for lipids hydrolyze. For a second clean-up procedure were used a florisil 5% water column. Extracts were concentrated under a kuderna Danish to approximately 1 ml and analyzed using gas chromatography-ECD (Kalantzi et al 2002; Santillo et al, 2004). The following organchlorine pesticides: hexachlorobenzene (HCB), dieldrin, endrin, hexachlorocyclohexane (HCH and isomers), heptachlor, heptachlor epoxide, methoxychlor, mirex and the DDT-related chemicals (*o*,*p*-DDE, *p*,*p*-DDE, *p*,*p*-DDD, *p*,*p*-DDT) were detected. PCB markers were the studied chlorinated biphenyls.

Apparatus and chromatography

Gas chromatographic analyses were performed with an HP 6890 Series II gas chromatograph equipped with a ^{63}Ni electron-capture detector and a split/splitless injector. The column used was a Rtx-5[low/mid polarity, 5% (phenyl methyl siloxane)] (30 m x 33 mm I.D., x 25mm film). The split/splitless injector and detector temperatures were set at 280^{0}C and 300^{0}C, respectively. Carrier gas was He at 1 ml/min and make-up gas were azot 24 ml/min. The initial oven temperature was kept at 60^{0}C for 4 min, which was increased, to 200^{0}C at 20^{0}C/min, held for 7 min, and then increased to 280^{0}C at 4^{0}C/min for 20 min. The temperature was finally increased to 300^{0}C, at 10^{0}C/min, held for 7 min. The total run time was 38 min. Injection volume was 2 µl, when splitless injections were made. Pesticide quantification was performed by internal standard method (Penttila and Siivinen, 1996; Skibniewska and Smoczynski, 2000; Santillo, 2004).

RESULTS

Levels of organochlorinated pesticides, their metabolites and polychlorinated biphenyls were analyzed in vegetable oil samples of Albanian markets, January 2015. EN 1528/1/2/3/4 protocols were used for determination of chlorinated compounds in oil samples. The following organchlorine pesticides: hexachlorobenzene (HCB), dieldrin, endrin, hexachlorocyclohexane (HCH and isomers), heptachlor, heptachlor epoxide, methoxychlor, mirex , *o*,*p*-DDE, *p*,*p*-DDE, *p*,*p*-DDD, *p*,*p*-DDT and PCB markers were detected using capillary gas chromatography with ECD technique. Total of organochlorinated pesticides in vegetable oil samples were shown in Figure 1. Total of organochlorinated pesticides in analyzed oil samples were between 4.2-21.27 ng/L. The average of pesticides in oil samples were 6.7 ng/L. The minimum was for M5 and the maximum for M8, both samples were with sunflowers origin. The role of pesticides in respective agricultural areas could do the difference. The level of pesticides fo all analyzed samples were lower than the accepted dairy intake (Wilhelm et al, 2002; Lazaro et al 1996; Nuro et al 2007). Distribution of organochlorinated pesticides in vegetable oil samples was shown in Figure 2. The distribution of pesticides depends from country or region origin and also from metabolism of pesticides in different plants. The most frequently detected pesticides were *p*,*p*-DDE, Endosulphanes, Aldrines and Methoxychlor (Figure 3). The concentrations and profile of organochlorinated pesticides could be because of their previous use for agricultural processes, pesticide degradation rate, metabolism of pesticides in different plants, etc. Total of PCB markers in

vegetable oil samples was shown in Figure 4. The average of PCB in oil samples were 2.6 ng/L. The minimum (M3, M13, M14) was 1.9 ng/L and the maximum (M4) 9 ng/L. The PCB levels were lower than accepted limit for all samples (Wilhelm et al, 2002; Lazaro et al 1996; Nuro et al 2007). The presence of PCB in oil samples could be because of industrial process for oil production or other factors such as soil contaminations, atmospheric factors, etc. Distribution of PCB markers in vegetable oil samples (Figure 5) were almost the same for all oil samples. This could be connected with their same origin of pollution for oil samples with PCBs. Profile of PCB markers in vegetable oil samples was shown if Figure 6. PCB 28, the volatile PCB marker was the main congener for all analyzed samples. PCB 153 and PCB 138 that are more soluble in lipids were shown to be the second pollutants in oil samples. The presence of PCB, their distribution and profile in oil samples could be because of industrial process for oil production, soil contaminations, atmospheric factors, etc.

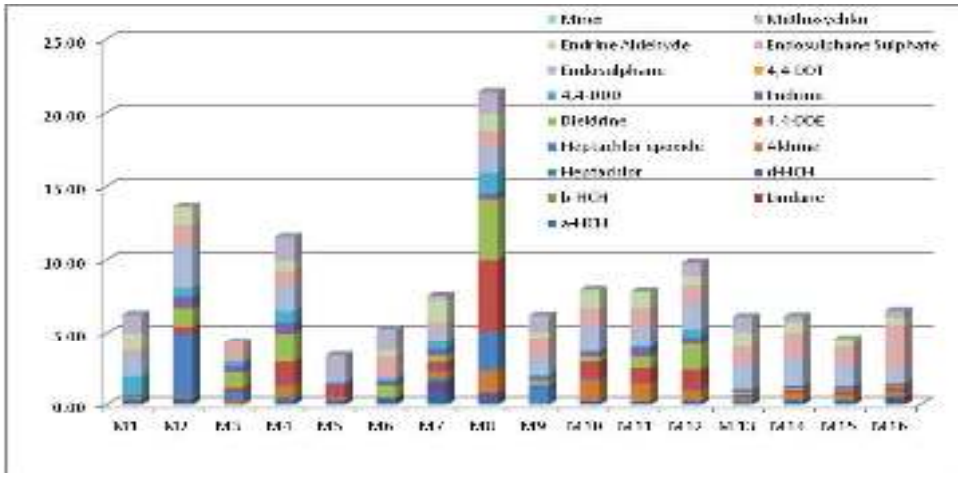


Figure 1. Total of organochlorinated pesticides in vegetable oil samples, January 2015

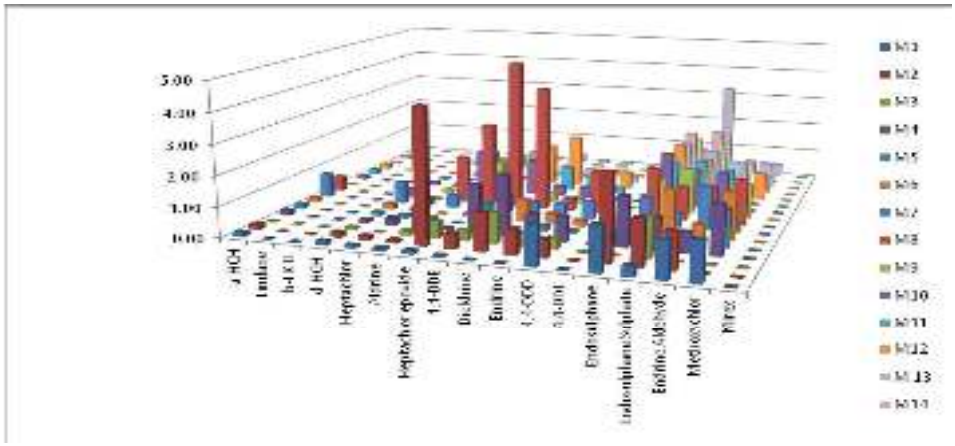


Figure 2. Distribution of organochlorinated pesticides in vegetable oil samples, January 2015

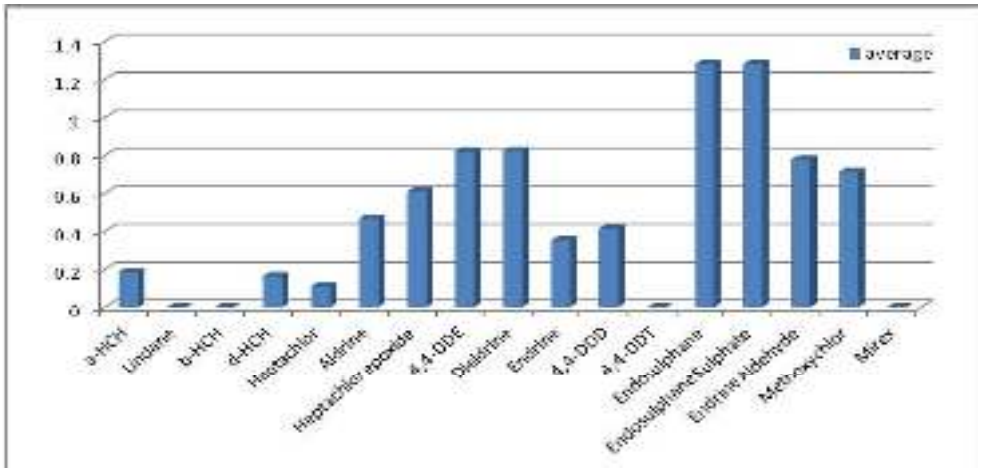


Figure 3. Profile of organochlorinated pesticides in vegetable oil samples, January 2015

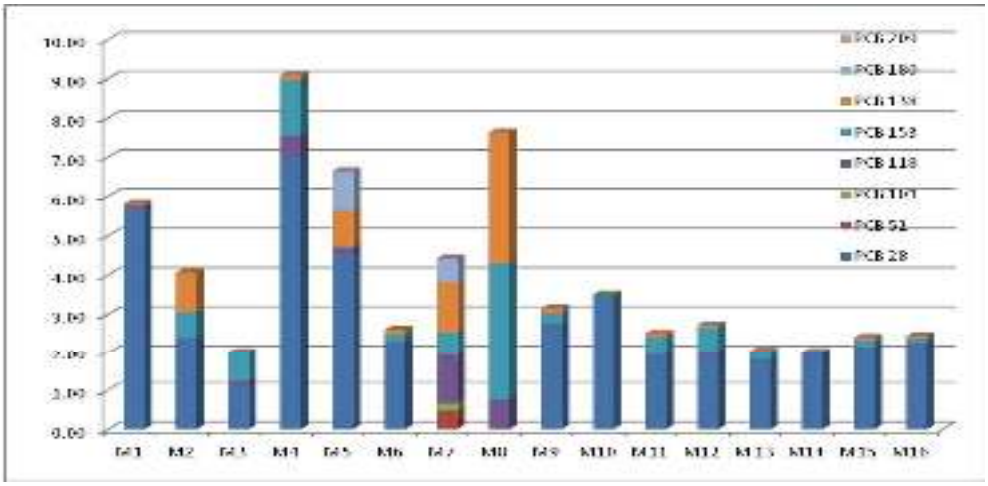


Figure 4. Total of PCB markers in vegetable oil samples, January 2015

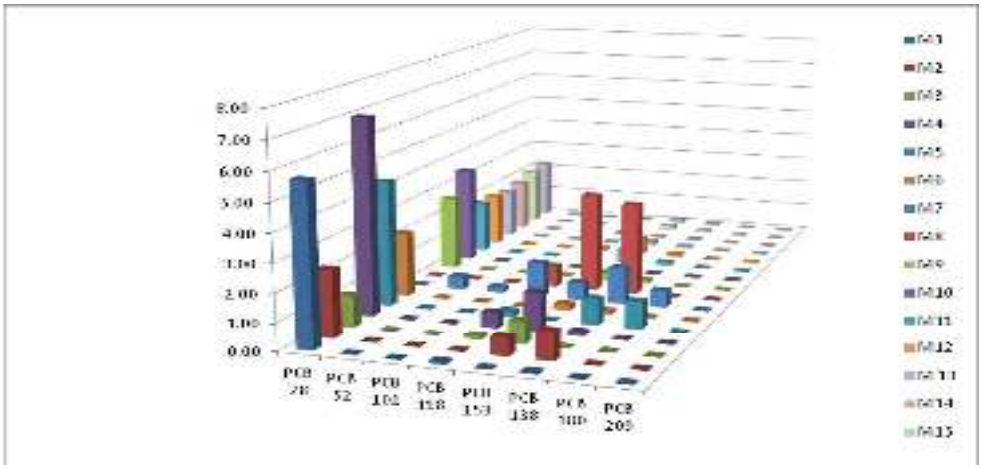


Figure 5. Distribution of PCB markers in vegetable oil samples, January 2015

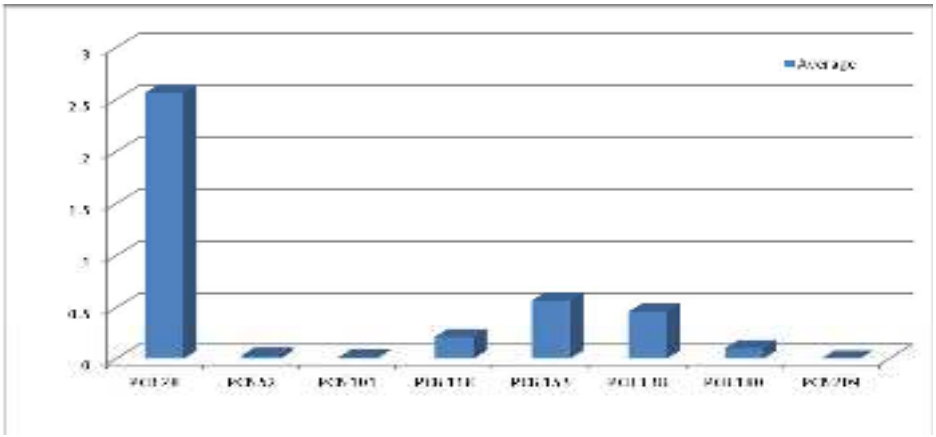


Figure 6. Profile of PCB markers in vegetable oil samples, January 2015

CONCLUSIONS

Levels of organochlorinated pesticides, their metabolites and polychlorinated biphenyls were analyzed in vegetable oil samples of Albanian markets, January 2015. EN 1528/1/2/3/4 protocols were used for determination of chlorinated compounds in oil samples. Almost in all analyzed vegetable oil samples from Albania markets were found organochlorinated pollutants concentrations. Found levels for organochlorinated pesticides and PCBs in oil samples were lower than accepted level. The presented data about concentrations of organochlorinated pesticides and PCB are the first reported data. The distribution of pesticides depends from country or region origin and also from metabolism of pesticides in different plants. The most frequently detected pesticides were *p*,*p*-DDE, Endosulphanes, Aldrines and Methoxychlor. The concentrations and profile of organochlorinated pesticides could be because of their previous use for agricultural processes, pesticide degradation rate, metabolism of pesticides in different plants, etc. The PCB 28, the volatile PCB marker was the main congener for all analyzed samples. PCB 153 and PCB 138 that are more soluble in lipids were shown to be the second pollutants in oil samples. The presence of PCB, their distribution and profile in oil samples could be because of industrial process for oil production, soil contaminations, atmospheric factors, etc.

REFERENCES

Di Muccio, 1996. Organoclorine, Pyrethrin and Pyrethroid Insecticides: Single Class, Multiresidue Analysis of. Pesticides. Pesticides. 6384-6411

Erickson, M.D. (2001). Introduction: PCB properties, uses, occurrence, and regulatory history. In: Robertson, L.W., Hansen, L.G. (Eds.), PCBs: Recent Advances in Environmental Toxicology and Health Effects. The University Press of Kentucky, Lexington, Kentucky, pp. 131–152.

EN 1528-1. (2000); Part 1: Fatty Food-Determination of Pesticides and polychlorinated biphenyls [PCBs]

EN 1528-2. (2000); Part 2: Extraction of fat, Pesticides and polychlorinated biphenyls [PCBs and -Determination of Fat Content

EN 1528-3. (2000); Part 3: Clean-up methods

EN 1528-4. (2000); Part 4: Determination, Confirmatory tests, miscellaneous

Lazaro R., Herrera A., Arino A., Pilar Conchello M., Bayrri S. (1996) Organochlorine pesticide residues in total diet samples from Aragon (Northeastern Spain). J.Agric.Food Chem. Vol. 44. P. 2742-2747.

Nuro A., Koci K., Marku E. (2007) Occurrence of Persistent Chlorinated Contaminants using Butter as an Integrative Matrix., Journal of Environmental Protection and Ecology 8,No 3, 544-555.

Penttila P.L., Siivinen K.,. (1996) Control and intake of pesticide residues during 1981-1993 in Finland Food Additives & Contaminants: Part A, Volume 13, Issue 6, pages 609 – 621

Skibniewska K., Smoczynski S. (2000) Modern looks on the residues chloroorganic insecticide in food. Żyw. Czlow. Metab. Vol. 27 (supl). P. 279-281.

Wilhelm M., Schrey P., Wittsiepe J., Heinzow B. (2002) Dietary intake of persistent organic pollutants (POPs) by German children using duplicate portion sampling. Int. J. Hyg. Environ. Health. Vol. 204. P. 359-362.

Kalantzi, O.I., Thomas, G.O., Alcock, R.E., Stephenson, A. & Jones, K.C. (2000) A global survey of PCBs and organochlorine pesticides in butter. Organohalogen Compounds 47: 357-360

Safe, S., (1994) Polychlorinated biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implications for risk assessment. Crit. Rev. Toxicol. 24(2):87–149.

Santillo, D., Stringer R.L., and Johnston, P.A. (2004) The global distribution of PCBs, organochlorine pesticides, PCDDs and PCDFs using butter as an integrative matrix. Chemosphere. 40 1033-1040

PAPER 065

MICROBIOLOGICAL PARAMETERS IN ISHMI RIVER

Hajrije Dibra[1], Margarita Hysko[2]

[12]Tirana University, Faculty of Natural Sciences, Tirana, Albania;

Email: rinadibra@hotmail.com

ABSTRACT

Tirana and Lana Rivers are both emissary of Ishim River, so the accumulation is more evident in the water of Ishim river. Also a lot of private industrial economies are discharging industrial wastes in the rivers "Ishim", " Gjola" and " Zeza". It is made a specific and detailed study with the focus of microbiological monitoring, in order to evaluate the real conditions of Ishim River. There are assessed *Fecal Choliphormes* that are the most fundamental indicators for the fecal pollution by waste waters. For the determination of *Total Choliphormes* we used MPN method. We took samples in 5 (five) stations that are presented in the map. All data are elaborated in a statistical way and pressented by graphics and tables. Dates describe the microbiological situation o f Ishim River .Ishim River is one of the most polluted in Albania. The article gives a contribute in the assessment of water rivers pollution by the anthropogenic factor and in the microbiological quality of waters in Ishim River with two branches "Gjola" and "Zeza" in Fushe-Kruja Region.

Key words: indicators, pollution, waste waters, MPN, microbiological quality.

INTRODUCTION

Ishmi River is long about 74 kilometer and its water surface about 673 km square belongs to waters from Tirana river, Terkuza and Zeza stream. Being as a hole water created from the waters from Tirana and Zeza both this bodies brings also their pollution. Together the waters are going in Adriatik river.
The water quality of Ishmi River is actually under different factors, but the main factor remain the antropogen one.
The polluton is comming by waste waters, industrial water discharge, the pollution from pesticides and insecticides used in agriculture. Also the lack of management of urban wastes and the mismanagement of waters are created a degradation of surface waters and the siol around.
In the paper is given the microbiological situation in Ishmi River, and two branches Zeza and Gjola.
Fecal coliforms are studied, is made the matematical and statistical calculation and the datas are given also through grafics and tabs.

MATERIALS AND METHODS

For sampling were used glass bottles sterilized in a sterilizer at 180°C for 90 minutes . The top of the bottle was directed toward deep at the time of sampling. Each sample is associated with the label and identification: the station where the sample is taken, the date and time of sampling and water temperature. (Hysko M.2006) Samples are transported to the laboratory within 24 hours, so that doesn't changes parameters. The samples were placed in thermal boxes during the transportation.

Table 1 microbiological methods and nutritive terrain (APHA. 1992)

Test	Methods	Temp.and time of incubiation	Nutritive terrain
Total Coliforms	MPN	37°C for 24 h	Lactoze Broth(LB)
Dilution	1/10	Room temp.	Pepton diluents

Fecal Coloforms are studied with MPN methods.

For rivers Ishmi, with both Gjola and Zeza are defined water sampling points which are considered as most important to the level of these rivers pollution.

- station 1- Zeza river the place is located 500 -600 meters afert the river cross the city of Fusha –Kruja. The zone is known for the discharge of waste waters
- station 2- Gjola River the place for taking samples is Gjola bridge. Is evident in the area the depositation of urban wastes in the shores of the river. In this segment the rivers has aboundant waters.
- station 3 – Rinas bridge

In this station is the point where the vaters coming from Tirana rives (supossed the most polluted) and the waters from Lana and Limuthi stream.
The station is located 500 meters afer the bridge, are evident urban wastes in the shores but also in the water of the river. The water is aboundant mainly during the periods with rains.

- station 4 –Salmer bridge

In this station there are not a lot of buildings, so is not so populated zone. It is a agricultural activity in the area and the discharge of drenage waters brings to the river also pollution mainly during rain periods.
In the water are seen also plastic wastes that are going till its estuary.

- station 5- Teli bridge

it is also not a populated area. The surface is flat so the agriculture is the main activity. Is evident the polluation from animals and plants remains. The discharge of drenage waters brings to the river also pollution mainly during rain periods.
In the water are seen also plastic wastes that are going till its estuary.

RESULTS

For the five stations we took samples for identifying *Fecal Coliforms*. Data are showed in tables and graphics for each station.

Table 3-1 Microbiological data for station 1

Month	Fecal Coliforms
September	432000
November	520000
January	530000
March	695000

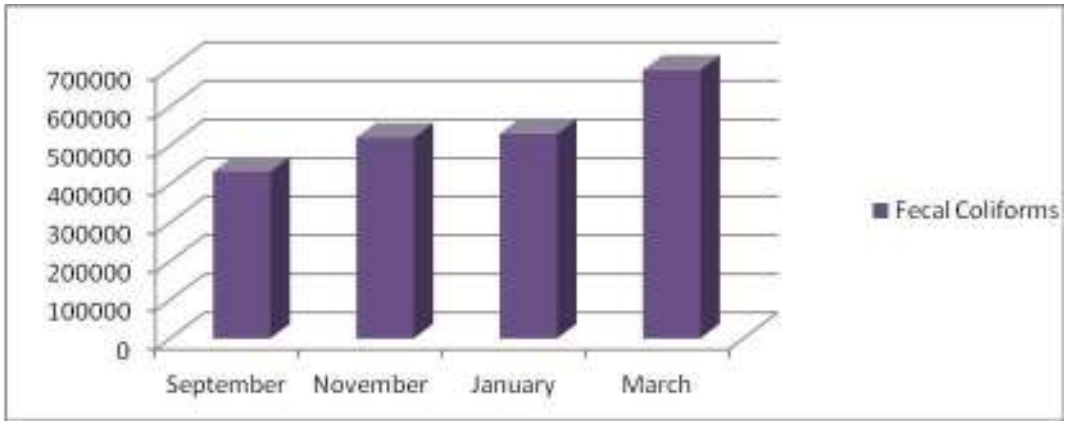


Figure 3-1 Values of fecal coliforms station 1

In the figure 3.1 are shown the average of Fecal Coliforms which are present in the station 1 of monitoring. As seen from the table and figure, the minimal values of 432000 Cfu/100ml water, of Fecal Coliforms is in September and the maximal value is in March with 695000 Cfu/100ml water. (Table 3.1 and figure 3.1)

Table 3-2 Microbiological data for station 2

Month	Fecal Coliforms
September	320000
November	380000
January	376000
March	287000

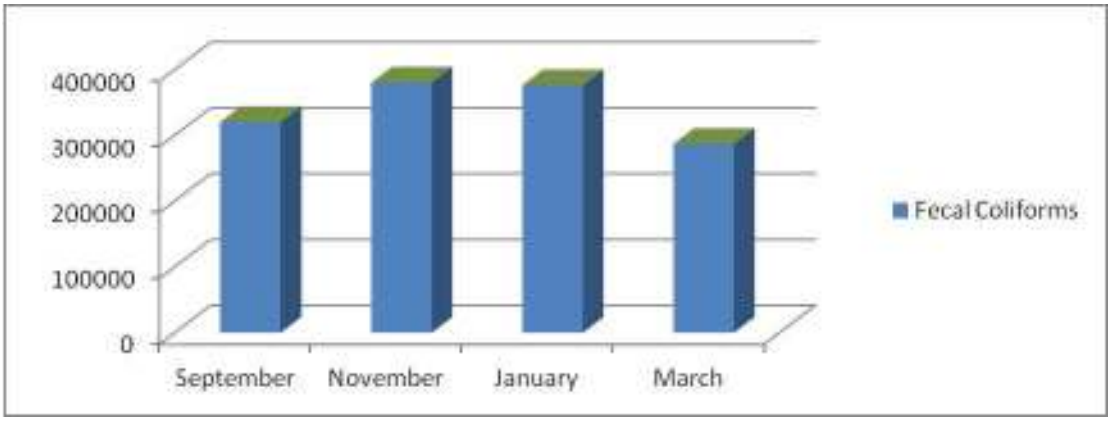


Figure 3-2 Values of fecal coliforms station 2

In the figure 3.2 are shown the average of Fecal Coliforms which are present in the station 1 of monitoring. As seen from the table and figure, the minimal values of 287000 Cfu/100ml water, of Fecal Coliforms is in March and the maximal value is in November with 380000 Cfu/100ml water. (Table 3.2 and figure 3.2)

Table 3-3 Microbiological data for station 3

Month	Fecal Coliforms
September	90000
November	93000
January	113000
March	850000

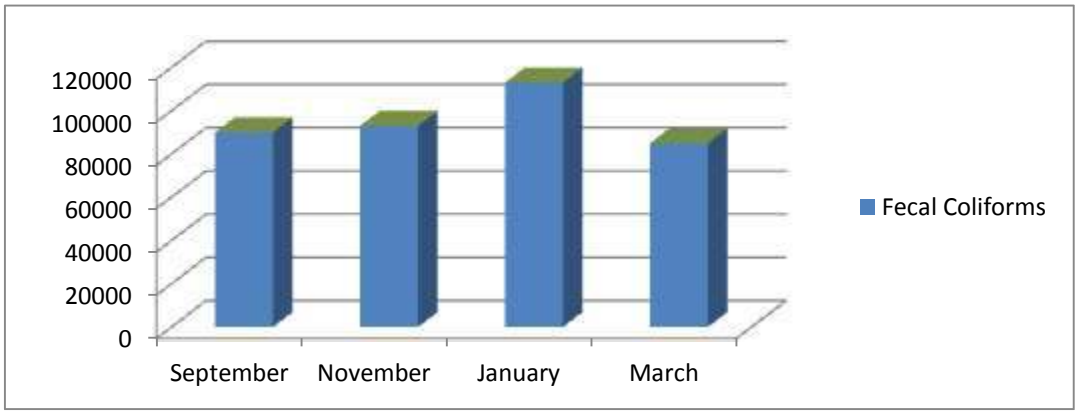


Figure 3-3 Values of fecal coliforms station3

In the figure 3.3 are shown the average of Fecal Coliforms which are present in the station 3 of monitoring. As seen from the table and figure, the minimal values of 850000 Cfu/100ml water, of Fecal Coliforms is in March and the maximal value is in January with 113000 Cfu/100ml water. (Table 3.3 and figure 3.3)

Table 3-4 Microbiological data for station 4

Month	Fecal Coliforms
September	210000
November	190000
January	195000
March	290000

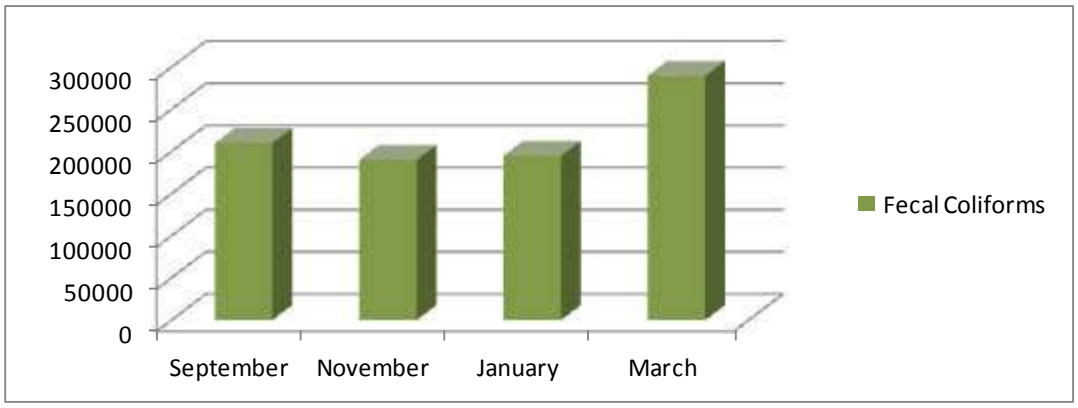


Figure 3-4 Values of fecal coliforms station 4

In the figure 3.4 are shown the average of Fecal Coliforms which are present in the station 4 of monitoring. As seen from the table and figure, the minimal values of 190000 Cfu/100ml water, of Fecal Coliforms is in November and the maximal value is inMarch with 290000 Cfu/100ml water. (Table 3.4 and figure 3.4)

Table 3-5 Microbiological data for station 5

Month	Fecal Coliforms
September	540000
November	520000
January	360000
March	500000

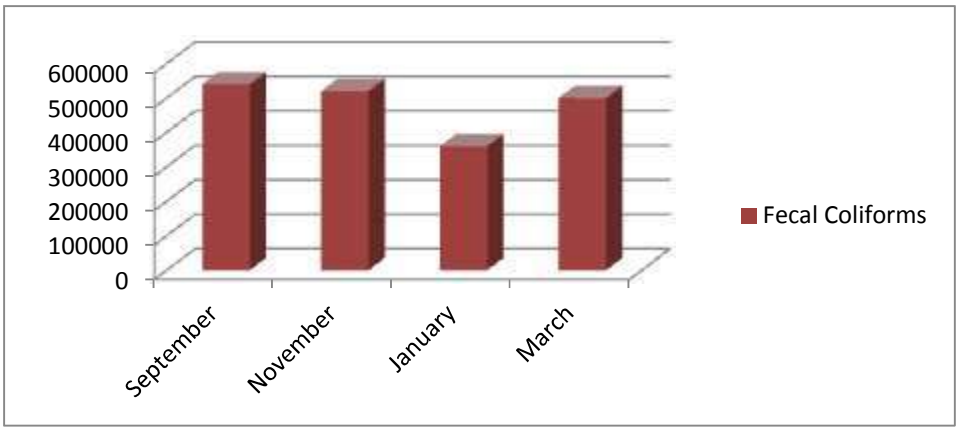


Figure 3-5 Values of fecal coliforms station 5

In the figure 3.5 are shown the average of Fecal Coliforms which are present in the station 5 of monitoring. As seen from the table and figure, the minimal values of 360000 Cfu/100ml water, of Fecal Coliforms is in January and the maximal value is in September with 540000 Cfu/100ml water. (Table 3.5 and figure 3.5)
The figures below show the comparison between the five stations

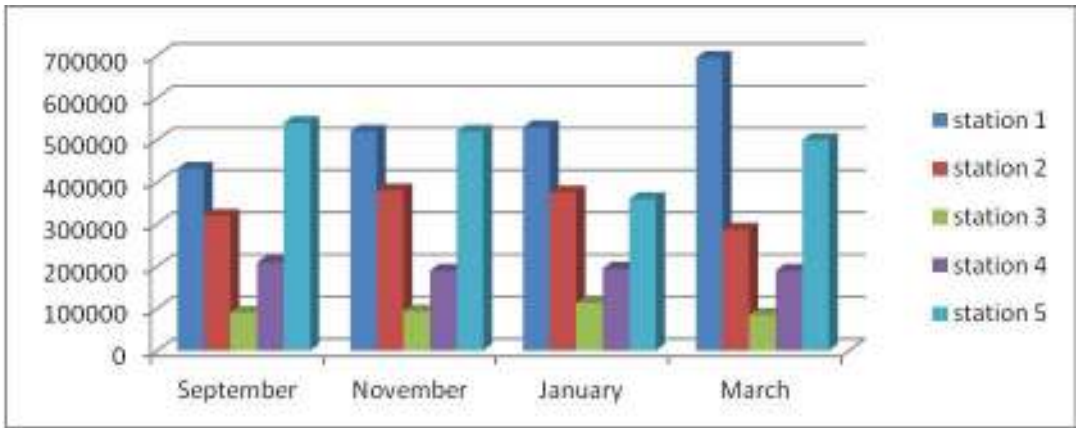


Figure 3-6 Dispersion of Fecal Coliformes for the five stations

The figure 3-6 shows that the first and the second station have the biggest pollution. The station nr 3 has the lowest values for Fecal Coliformes during the four months.

Standarts of total coloformes for the water rivers quality (ISO 6222:1999)

Total Coliformes	Very good quality	Good quality	Bad quality	Very bad quality
Cfu/100ml	1250	2500	5000	10000

The figure below shows the means of Fecal Coliforms in the five stations of monitoring.

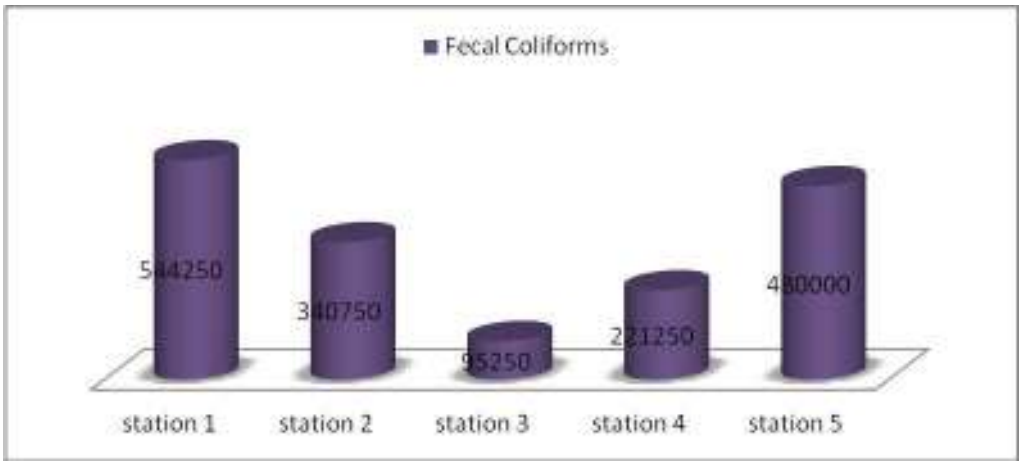


Figure 3-7 Means of Fecal Coliformes in the five stations of monitoring

See in the mean values of Fecal Coliformes as showed in the figure 3-7 the first station is the most polluted with 544250 Cfu/100ml water, meanwhile the less polluted is the station number three located in Rinas. In this station is the point where the river passes the town of Fushe-Kruja. The solid waste thrown in the river shore, dashing his bed and turning the riverbank in a garbage collection site.

CONCLUSIONS

Are tested and elaborated samples from the water of five stations in Ishmi River Zeza for the presence of Fecal Coliformes. The means of Fecal Coliformes is highest in the first station, which is the most polluted with the value 544250 Cfu/100 ml water, meanwhile the less polluted is the third station in Rinas station. The values of coliformes for the five stations are up the standards values. Based on the study the Ishmi River is considered with a high values of pollution. Tirana and Lana Rivers are both emissary of Ishmi River, so the accumulation is more evident in the water of Ishim.

REFERENCE

Hysko M.(2007):Manual I Mikrobiologjise.SHBLU.Tirane;
ISO 6222:1999: Wate quality - Enumeration of cultivable micro-organisms -Colony count by inoculation in a nutrient agar culture medium;
FISH, H. 1992: Freshwaters. In: Harrison. R. M. (Eds), Understanding our environment: an introduction to environmental chemistry and pollution. - *The Royal Society of Chemistry,* Cambridge, pp: 53-68;
Madigan, Martinko and Parker 2005, Brock Biology of Microorganisms Southern Illinois University, Carbondale
APHA.1992. *Standart Methods for the examination of water and wastewater.*18th. ed.American Public Health Association, Washington, DC;
KAVKA, G. G., B ., HOCH, B. M., HERNDL, G. J. (1996): Assesment of microbiological water quality in the Austrian section of river Danube, Arch, Hydrobiol, Suppl, 113, Large Rivers 10, 79-86;
Waldemar A; Kolwazan B.; Kazimierz G.; Adam P., 2006, Introduction to Environmental Microbiology. Wroclaw;

PAPER 066

POLLUTION AND DETERMINATION OF HEAVY METALS IN SOME POTATO SAMPLES IN KOSOVO

Kaltrina Jusufi[1], Majlinda Vasjari[2], Bardha Korça[1*], Eralda Dano[2]

[1]University of Prishtina "Hasan Prishtina", Faculty of Natural Sciences and Mathematics, Department of Chemistry, str. "Nëna Tereze" nr. 5, 10000 Prishtina, Kosovo;
[2]University of Tirana, Department of Chemistry, Faculty of Natural Sciences, Tirana, Albania;

E-mail: kaltrinajusufi@gmail.com; bardhakorca@gmail.com

ABSTRACT

Heavy metals are potential environment contaminants with the ability of triggering human health complications. A form of manifestation of this occurs when they are found in large amounts in foods which are commonly consumed by humans. The concentration of heavy metals in foods is of enormous interest to study, because of their toxic nature and the consequences of their entering the food chain. The reason behind this study was the determination of heavy metals in food, particularly in potatoes cultivated in areas around the coal-fueled power plants in Kosovo. The presence of heavy metals in the potato samples collected was analyzed using the inductively coupled plasma-atomic emission spectrometry (ICP-OES) after the microwave digestion of samples with HNO_3 and H_2O_2. Thirty potato samples were taken throughout the studied zones, in locations scattered around the area affected by coal pollution. The results in this study clearly indicated that heavy metals are dispersed in the surrounding areas of Kosovo's only two power plants and were transported by wind into the proximity of the agricultural lands. The obtained outcomes led to the conclusion that the agricultural soils which were used for potato cultivation around the power plants areas are slightly polluted due to the coal-fired plants.
Keywords: heavy metals, potatoes, ICP/OES

INTRODUCTION

Heavy metals today have become the main abiotic factors that have negative effects in living organisms. Plants play an important role in the cycle (mobility) of heavy metals in nature, because the consumption of plants allows heavy metals to enter the food chain and have a negative impact on health.
Potatoes (Solanum tuberosum L.) belong to the family Solanaceae, genus Solanum. They are considered to be some of the most intensively grown and most profitable crops and are recognized as very important agricultural and food products (M.B.Rajković, et al., 2002). The potato is the world's fourth largest food crop and is a staple in many diets around the world (E. Öztürk, et. al, 2011). In recent years, increasing attention has focused on heavy metal concentrations of vegetables all over the world. Metals such as lead, mercury, cadmium, and copper are cumulative poisons, which cause environmental hazards and are reported to be exceptionally toxic. (Ellen et al., 1990).
However, the contamination of vegetables with heavy metals which are natural constituents of the Earth's crust and atmosphere are of major concern from contamination and toxicity point of view. (Al-Chaarani B, et al, 2009, Samara C, et al;, 1992).
For these reasons, this paper includes an investigation of potato quality and pollution with heavy metals due to the power plants of Kosovo that are surrounding these agricultural lands with potato growth. In order to determine the heavy metal content we used ICP/AES technique to find the content of 21 elements in potato samples.

MATERIALS AND METHOD

Area of study

The area in which Kosovo's power plants are located is 10 km far from its capital, Pristina. We randomly made a selection of potatoes samples at a distance of 4-7 km around the KEK (Kosovo Energy Corporation). In the following chart is presented map of Kosovo, with the study area where we focused in this research study.

Fig. 1 Map of Kosovo with the zone of study encircled in red

Sample preparation

Potatoes samples were taken in sampled of two to three kilograms. They were initially cleaned with tap water and then with distilled water. Potatoes were picked in a selective way, were chopped and dried to constant weight at an initial temperature of 65^{o}C for 24 hours and then at 105^{o} C for two to three hours. Potatoes were milled and 250 mg of each sample were digested in microwave system in Teflon vessels (Berghof 12 vessels) with HNO_3 and H_2O_2 for 1 h according to (Berghof application report).

After this stage was completed, the digested samples were leveled with distilled water to 50 ml and then the determination of 21 elements was measured with inductively coupled plasma atomic emission spectroscopy (ICP / OES).

RESULTS

The data from the elements analysis (mg kg^{-1}) in the potato samples for 11 analyzed samples are presented in Table 1.

The appropriation of elements from plants depends on the physiological properties of plants, growing conditions, soil properties, meteorological conditions and especially the purines of fertilizer use. Mobility of pollutants depends on their type and soil pH values. For example, As and Se are mobile in alkaline soil reaction, while Hg , Pb , Cd and Zn are mobile in acidic soil.

From our research on potato samples cultivated in agricultural lands contaminated by the operation of electric power plants in Kosovo, it was possible to conclude that the samples contain Pb , Zn , Cu , Cr , Ni and Cd in substantial quantities. For comparison of results we used Standard of the Republic of Slovenia, 1996 for the maximum permitted quantities of heavy metals in fruits and vegetables.

The maximum amount of lead allowed in fruits and vegetables is from 0.10 mg kg^{-1} to 0.30 mg kg^{-1} (Slovenia Standards, 1996). By comparing the results of our samples, it is inferred that it ranges from 3.01 to 4.24 mg kg^{-1} (Table 1), where we can conclude that our samples are contaminated because they exceed more than ten times the limit of lead in vegetables.

Zinc is an element with average mobility in plants. If the concentration of zinc is high, it precipitates to the root of the plant. The concentration of zinc in the dry plant ranges from 15-150 mg kg^{-1}, usually from 20 to 50 mg kg^{-1}. Based on the legislation of Slovenia, as well as in the literature (Bergmann 1976), normal amount of zinc in the plant ranges from 15-150 mg kg^{-1} of dry matter. Critical values for zinc are twenty over 150 mg kg^{-1}. By comparing the results of our samples for zinc which range from 3.6 to 334.4 mg kg^{-1} (Table 1) we can conclude that three of our samples exceed the limit of zinc in vegetables.

The toxic action of copper is present when the total concentration in soil ranges from 25-40 mg kg^{-1} and if the pH value of the soil is 5.5 (which is not the case in our samples). Slovenian standards of normal values of copper in plants range from 3-15 mg kg^{-1} of dry matter. Critical values are concentrations that are higher than 15 mg kg^{-1}. In our research, none of the potato samples exceed critical values.

Table 1. The content of the analyzed elements in potatoes samples (in mg kg^{-1})

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Elements											
Ag	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Al	19,8	56,51	10,6	41,59	10,70	58,22	20,58	46,66	48,87	14,85	17,20
As	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ba	0,57	0,28	0,41	0,38	0,49	0,41	0,35	0,57	0,32	0,30	0,39
Ca	1965	459	936	554	615	216	291	767	349	585	402
Cd	<0,1	<0,1	<0,1	0,15	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
Co	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Cr	2,51	0,73	0,94	0,42	3,21	0,53	2,48	0,62	0,25	0,93	0,97
Cu	3,71	3,20	4,50	3,63	6,15	3,85	4,16	3,18	3,13	2,58	3,22
Fe	52,75	50,40	20,9	25,5	67,17	80,17	76,49	118	82,61	66,74	25,71
K	2371	666,4	3289	3922	7608	48,97	4685	3098	4933	5652	3318
Li	0,25	<0,2	<0,2	<0,2	<0,2	<0,2	<0,2	<0,2	<0,2	<0,2	<0,2
Mg	499	444	601	260	570	324	335	635	352	670	602
Mn	1,24	1,33	1,88	0,97	0,72	1,81	0,81	0,72	0,59	0,48	1,24
Mo	<1	<1	<1	0,15	<1	1,25	<1	<1	<1	<1	<1
Na	32,44	21,35	17,50	14,97	13,56	34,05	8,88	21,13	30,18	54,77	32,44
Ni	5,47	2,14	6,11	1,77	3,09	0,78	2,05	4,91	0,80	3,91	1,21
P	319	834	559	454	577	398	295	109	461	391	350
Pb	4,24	3,99	3,97	3,85	3,84	3,82	3,68	3,47	3,42	3,37	3,01
Sr	1,16	0,66	0,82	0,68	1,06	0,57	0,40	0,87	0,70	0,56	0,73
V	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Zn	57,8	116,9	313,7	72,5	54,6	29	44,6	217,1	3,6	334,4	57,8

The concentration of chromium available for plants in most soils is low. The chromium concentration in plant dry matter ranges from 0.1 to 1 mg kg^{-1}. Based on the standard of Slovenia and in the literature (Bergmann 1976), normal values of chromium in plants range from <0.1 -1 mg kg^{-1} of dry matter. Critical values would be if it is in higher concentrations than 1 mg kg^{-1}. Plants that grow in the serpentine lands may contain up to 100 mg kg^{-1} chromium. In our research, three potato samples exceeded the critical values of chromium.

The average concentrations of nickel in plants range from 0.1 to 5 mg of dry matter. The tolerant plant value is 5-20 mg kg^{-1}, while higher concentrations are critical for plants (Bergmann 1976). Based on the standard of Slovenia, the normal value of nickel in plants ranges from 0.1 -5 mg kg^{-1} of dry matter. In our samples nickel exceeded the critical values in two sample spots.

The maximum allowable amount of cadmium in fruit and vegetables (excluding leafy and root vegetables, potatoes) ranges from 0.050 mg / kg of wet mass. The maximum value allowed leafy vegetables, root and potato is 0.10 mg / kg of wet mass. By comparing our results with maximum concentrations allowed by the Slovenian Standards, it can be concluded that only one sample of potatoes exceeded the maximum allowable value.

CONCLUSION

Based on our analysis of the presence of heavy metals (Pb, Cd , Zn , Cu , Ni , Cr) in 11 potato samples, we conclude that the concentration of heavy metals in soils cultivated potatoes in the vicinity of power plants in Kastriot resulted higher when compared to natural concentrations and limit concentrations of heavy metals in fruits and vegetables. Lead has exceeded the maximum permissible concentration in all samples, cadmium in one sample, zinc in three samples, chromium in three samples, nickel in two samples, while copper has not exceeded the maximum permissible concentration based on the Slovenia Standard which we took for comparison purposes.

The pollution is caused by the activity results of thermo plants that emit heavy metals in the soil. Higher presence of heavy metals in the soil compared to natural values has contributed to higher bioaccumulations of heavy metals in potatoes.

For this reason it is necessary to ensure the monitoring of heavy metals in soil and plants in order to follow the situation of environmental quality, protection of health population and undertaking measures to reduce the emission of pollutants in the first place metal heavy from thermo plants.

REFERENCES

E. Öztürk, E. Atsan*, T. Polat and K. Kara, The Journal of Animal & Plant Sciences, 21(2): 2011, Page: 235-239 ISSN: 1018-7081;
Ellen, G., J.W. Loon and K. Tolsma (1990). Heavy metals in vegetables grown in the Netherlands and in domestic and imported fruits. Z. Lebensm. Unters. Forsch., 190, 34-39;
M.B.Rajković 1 , L.Perić 1 and Divna Kovačević 1, Journal of Agricultural Sciences Vol. 47, No 2, 2002 Pages 161-177, UDC: 633.491:546.4/5:632.95.028 Original scientific paper;
Al-Chaarani B, El-Nakat JH, Obeid PJ, Aouad S. Measurment of levels of heavy metals in vegetable grown and sold in selected areas in Lebanon, JJC, 2009, Pages 303-315;
Samara C, Misaelides P, Tsalev D, Anousis I,Kouimtzis Th. Trace elements distribution invegetables grown in the industrial area of Thessaloniki, Greece. Fresenius *Environ. Bull, 1992, pages 577-582;*
Berghof application report, Microwave digestion of foods, page 19
http://www.onlinecas.com/Berghof/CATALOGUE%20BERGHOF/Micro-onde%20MWS3+/Applications%20MWS3+/AR_MWS-3plus_Food-Pharma-Cosmetics_140405.pdf;
Bergmann, Pflanzendiagnose und Pflanzenanalyse, (1976), Jena, DOI: 10.1002/jpln.19771400325;

PAPER 067

USING DIATOMITE AS PADDING MATERIAL IN WATER PROOFING MEMBRANES

Hilmi Kısa, Erol Pehlivan*[2]

[1]Selcuk University, Graduate School of Natural and Applied Science, Campus, Konya-Turkey;
[*2]Department of Chemical Enginering, Selçuk University, Campus, 42071 Konya Turkey;

Email: erolpehlivan@gmail.com;

ABSTRACT

Water entering into insulating membranes causes a threat to their structure in terms of their strength. Water entering the building structure disturbs the system. Corrosion of the carrier portion is considered as important and it causes a decrease of the load carrying capacity. Water in the structure of building integrity of concrete, freezes in winter, and it evaporates in summer and leads to formation of cracks in the concrete. Water enters the concrete skeleton leads to the formation of some organic materials, mold and fungi which are dangerous for the human health. In this research, two types of water resistance membranes were compared according to their performance. The membranes can be produced with diatomite and calcite. Diatomite is a building material which has a higher chemical stability and is lighter than calcite. It will be more advantages over conventional calcite because it has a high strength and melting temperature as 1430 °C. Artificial aging and waterproofing resistance against chemicals were tried in the experimental tests. Diatomite provided a lighter weight to the membrane module. The 3 mm thickness of the membrane has lower mass (35 kg) compared to calcite membrane (40 kg). After the chemical resistance against water resistance test, the diatomite-filled prototype sample yielded a higher water resistance to the pressure of 60 kPa. However, the calcite-filled prototype yielded until 20 kPa water resistance and lost its waterproofing properties in low pressures values. This is because the calcite can expose to hydrochloric acid, sulfuric acid, acetic acid, and nitric acids which used in the production of membrane and they enter the micro pores of calcite and changes its properties. This is why membrane made by diatomite instead of calcite. The pressure-strength has increased by adding diatomite to the structure. Water resistance test after artificial extensibility resulted in significant differences in two prototype membrane modules.

Keywords: Diatomite, filler material, waterproofing membrane

INTRODUCTION

All applications of protection against water or moisture are called the waterproofing. Water entering the building structure; interrupting corrosion of the carrier portions of the structure and causes a decrease in load bearing capacity. Water may enter into the structures in many ways. Leaking can be formed from raining and snowing. The soil moisture and ground water are the most important factor for leaking.

Waterproofing membranes are produced as reinforced by modifying by bitumen and polymeric plastics. There is bitumen on the basis of waterproofing membrane production. Bitumen is an important component of the waterproofing because it is a hydrophobic insulation material. However, the use of bitumen in its pure form is very difficult for the membrane production. This material has a weak resistance to the environmental conditions. Polypropylene is added to the bitumen to give it a good resistance and stability. Polypropylene is often used in production of waterproofing membrane. The melting temperature of polypropylene is around 160 °C and polypropylene provides an extra viscosity to bitumen. Bitumen is brittle in low temperature, and liquid in high temperature. Polymer modification that means addition of polypropylene into bitumen is the most important application of the waterproofing membrane production. Polymers are mixed to the structure of bitumen at high temperatures. A process of the production of the membrane dough was showed in the Fig. 1.

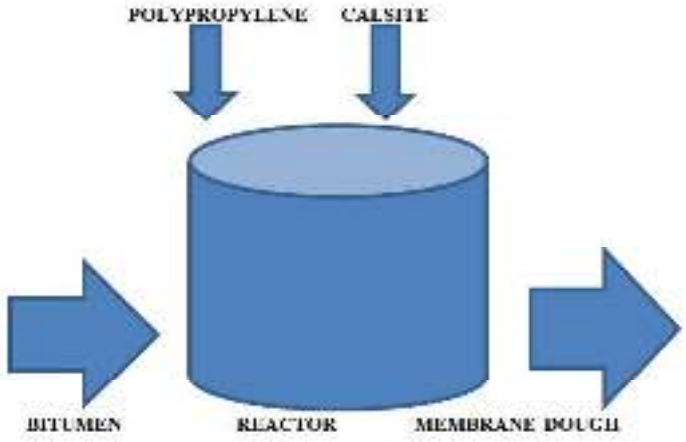


Fig. 1. Processes of membrane dough

When this processes finished, the prepared dough sent to inosculate with a polyester carrier and polyethylene films are pasted top and down of the plastered carrier to complete waterproofing membranes (Fig. 2.).

Diatomaceous earth or diatomite, or kieselgur/kieselguhr, is a naturally occurring, soft, siliceous sedimentary rock that is easily crumbled into a fine white to off-white powder. It has a particle size ranging from less than 3 micrometers to more than 1 millimeter, but typically 10 to 200 micrometers. The typical chemical composition of oven-dried diatomaceous earth is 80 to 90 % silica, with 2 to 4 % alumina and 0.5 to 2 % iron oxide [1]. Diatomite exists by the accumulation of the amorphous silica (opal, $SiO_2 \cdot nH_2O$) remains of dead diatoms (microscopic single-celled algae) in lacustrine or marine sediments. Diatomite is inert material against a lot of chemical; it is affected only strong base such as NaOH and and strong acid such as HF at high temperature [2, 3]. The most important property of diatomite is the low density through high porosity. Its density is near 0.15-0.40 g/cm^3 in the dry state. Opal hardness of diatomite is about 4.5-6.0 [4].

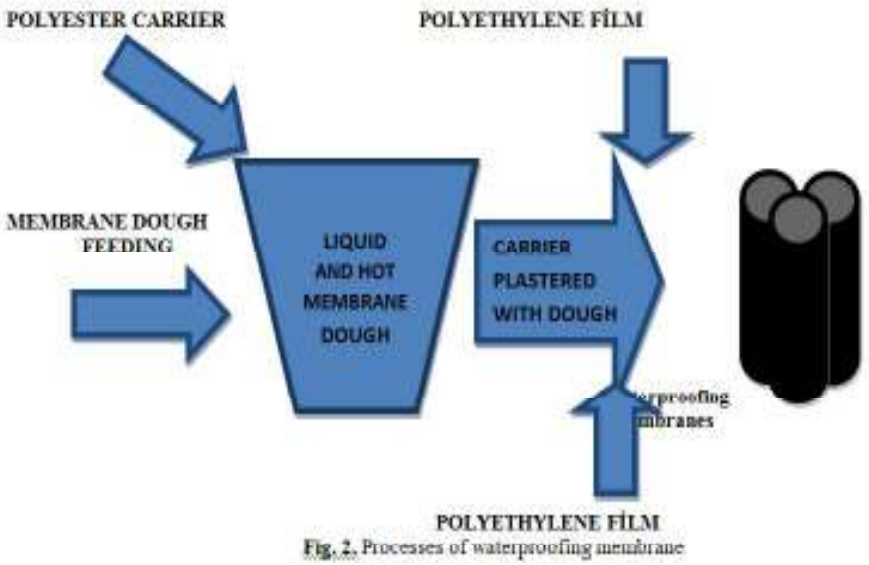


Fig. 2. Processes of waterproofing membrane

MATERIALS AND METHODS

Calcite is a traditional padding material used in producing of waterproofing membranes. Calcite is formed with calcium carbonate ($CaCO_3$). Acidic solutions enter to the structure of calcite and that will cause porosity on the

membrane surface so the strength of waterproofing will decrease. Waterproofing membranes become heavier due to high density of calcite. Diatomite is lighter and more inert than the calcite. Diatomite is affected only with HF at high temperature. It is not affected with sulfuric acid (H_2SO_4), nitric acid (HNO_3) and hydrochloric acid (HCl). Waterproofing membranes become lighter when lower density diatomite was inserted in their structure. The diatomite was purchased from Ata Madencilik Ltd. Şti Aydın-Turkey and calcite, Niğtaş Ltd. Şti Niğde-Turkey.

2.1. Thickness test

This test is made according to TS EN 1849-1 standard. This Standard covers to methods of detecting the mass per unit area and thickness of the bitumen sheets which is using on the roofs. The mass per unit area test is used for determine this type of products. Thickness of the sheet is measured to take data from 10 different areas of sheet width and data save ass the arithmetical average of the sheet thickness [5].
The thickness measuring device should measure the planar way with the thickness of 0.01 mm accuracy and 20 kPa should be applied to this 10 mm diameter of the surface of membrane. The sheet should be in 100 mm length and width for the test. All measurements were realized in ambient conditions. The sheet and measuring tool are cleaned before the application test [6].

2.2. Determination of water tightness

This standard has been prepared by CEN/TC 254 purpose of determining waterproofing property of waterproofing sheets. This standard is just about waterproofing sheets and is not related to the waterproofing systems which are used in the workplace flooring [5]. Test samples across the width of the plate edges must be properly dispersed within 100 mm. Direction length of the sample tested must be marked parallel to the direction of manufacture. Number of test samples of not less than three, which is prepared as specified in the relevant standard. The pressure was gradually increased up to the specified test pressure. When the test pressure is reached, this pressure was allowed to stand for 24 hours. Waterproofing of the test sample was checked at the end of the test period (A sudden pressure drop and the water present on the surface exposed to the pressure of the test sample) [7].

2.3. Artificial ageing method

This test is made according to TS EN 1296 standard. This Standard has been prepared for the classification of the bitumen, plastic and plastic sheets. [8]. Test sample prepared by cutting enough large and number for making the test. Heating is provided with air circulating furnace. Otherwise, it must be subjected to the test rating simultaneously with the materials exposed to heat after a sufficient number of reference materials is waited at (23 ± 2) °C temperature and %(50±5) RH in a dark place. Furnace temperature is set near at (70±2)°C. Surface of the test samples put in the furnace so that exposure to air circulating. Sub-surface is deposited on a silicon paper. The exposure time is specified in the relevant product standard. This period may be 4, 8, 16, 24 weeks. The preferred exposure time for plates used in the experiments conducted by exposure to heat is 24 weeks. After the test samples were exposed to heat, before being subjected to the evaluation test must stand for at least 24 hours at a (23 ± 2) °C and (50 ± 5) % relative humidity. Samples should be inspected visually before and after exposure to heat [8].

2.3. Methods for exposure to liquid chemicals, including water

This test is made according to TS EN 1847 standard. The purpose of this standard is classification and description plastics and waterproofing sheets. It should be applied to the membrane system used in waterproofing [8]. Experiments performed immediately after the dipping process is made for detect to influence of chemical liquid on the sample.

RESULTS

The prototypes were produced in the production system of factory and the waterproofing membranes were made of two different filler dough. These prototypes were produced in the same weight and same size (Fig. 3).

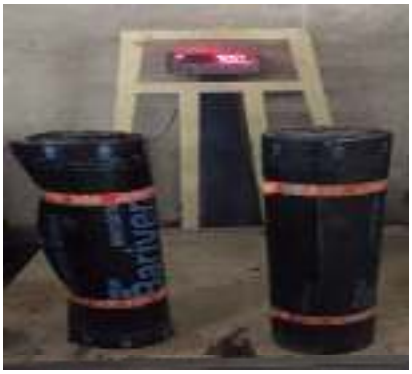


Fig. 3. Waterproofing membrane with same weight and size.

The calcite membrane has reached 3 mm thickness to 40 kg. Diatomite waterproofing membrane has reached 3 mm thickness to 35 kg. The following chart shows the thickness of the same weight for the filled membranes.

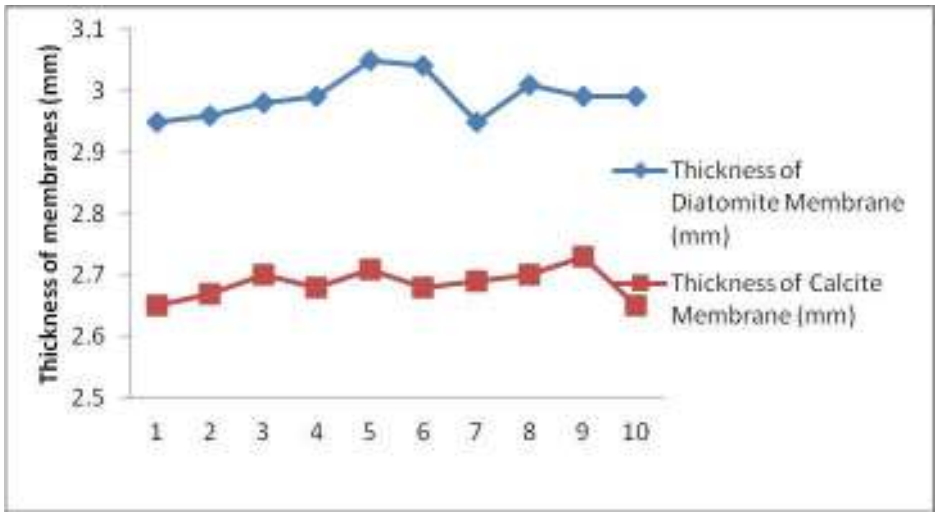


Fig. 4. Thickness of different filled waterproofing membranes

In the resistance test, two types of waterproofing membranes were compared according to their chemical resistance performance. The waterproofing membranes were inserted into 10% H_2SO_4, 5% HNO_3, 10% HCl and 10% CH_3COOH one by one. The experiment was completed in a week. Test specimens were prepared in size 400 cm^2. Then the samples were put into a deep bowl that chemicals found in 3200 ml. We do visual inspection with sensitive lens on the membrane surface which stored for one week in room temperature. We have detected very small irritation traces on the calcite membrane surface.

After the chemical resistance against water resistance test, the diatomite-filled prototype sample yielded a higher water resistance to the pressure of 60 kPa. However, the calcite-filled prototype yielded until 20 kPa water resistance and lost its waterproofing properties in low pressures values. This is because the calcite can expose to hydrochloric acid, sulfuric acid, acetic acid, and nitric acids which used in the production of membrane and they enter the micro pores of calcite and changes its properties. This is why membrane made by diatomite instead of calcite. The pressure-strength has increased by adding diatomite to the structure. Fig. 5. shows the pressure resistance of two filled membranes.

The price of the membranes is important. Diatomite is more expensive than calcite although diatomite reduces waste of the tenfold or twentyfold expensive materials than calcite but the cost of the diatomite and calcite filled waterproofing membrane are same for the sample membranes. Although that, diatomite will increase life of waterproofing membrane because of chemical inertness. In addition to this, the shipping cost is less compared to the calcite membrane reduced because of decreasing the weight of the membrane. Using diatomite as padding material in membrane will be gainful investment in the future for the producers.

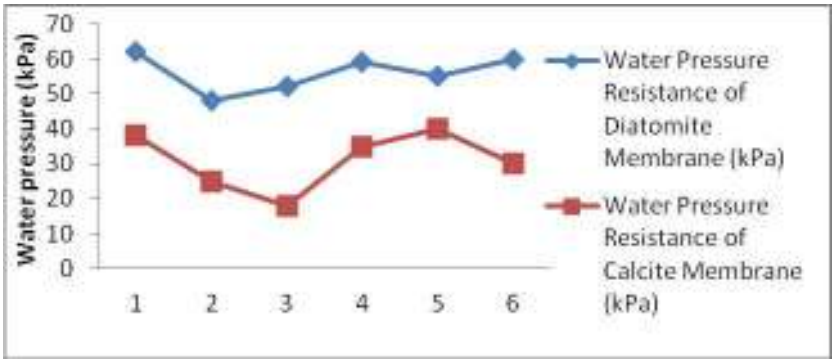


Fig. 5. Water pressure resistance of different filled waterproofing membranes

REFERENCES

Venedik, D., 2006, Sulardaki Krom(III) Kirliliğinin Diatomit İle Giderilmesi, Yüksek Lisans Tezi, *Gazi Üniversitesi Fen Bilimleri Enstitüsü, Ankara,* 22-24.

Anonim, 2010, *Diatomit*[online], http://www.marbleport.com/dogal kaynaklar/38/diatomit [Ziyaret Tarihi: 28 Haziran 2014].

Marques, J.A. and Lopes, J. G., Correia, J. R., 2011, Durability Of The Adhesion Between Bituminous Coatings and Self-protection Mineral Granules of Waterproofing Membranes, Construction and Building Materials, *Elsevier,* Lisbon, Portugal 25(1), 138-144.

Anonim, 2002, Diatomit[online], http://www.karamanmadencilik.com/icerik/2/17/ diatomit [Ziyaret Tarihi: 28 Haziran 2014].

Anonim, 2002a, TS EN 1849-1 Su Yalıtımı İçin Esnek Levhalar-Kalınlık ve Birim Alan Kütlesinin Tayini-Bölüm 1: *Çatı Su Yalıtımı İçin Bitümlü Levhalar, Ankara*, 1-3.

Anonim, 2007, TS EN 1928 Esnek Levhalar-Su Sızdırmazlık İçin-Çatı Su Sızdırmazlığı için Bitüm, Plastik ve Lastik Levhalar-Su Geçirmezlik Tayini, *Ankara*, 1-7.

Anonim, 2004, TS EN 1296 Esnek Levhalar-Çatılarda Su Yalıtımı için Plastik ve Lastik Levhalar-Uzun Süre Yüksek Sıcaklıklara Maruz Bırakarak Yapay Yaşlandırma Metodu, *Ankara,* 1-2.

Anonim, 2002b, TS EN 1847 Esnek Levhalar-Çatılarda Su Yalıtımı için Plastik ve Lastik Levhalar-Su Dahil, Sıvı Kimyasallara Maruz Bırakma Metotları, *Ankara,* 1-5.

PAPER 068

BIOMONITORING OF ATMOSPHERIC DEPOSITION OF HEAVY METALS USING MOSS FROM THREE REGIONS IN ALBANIA

Ilva Gjikaj[1], Majlinda Vasjari[2], Majlinda Terpo[3]

[1]Chemistry Department, Faculty of Mathematical Engineering and Physical Engineering, Polytechnic University of Tirana, Albania;
[2]Chemistry Department, Faculty of Natural Sciences, University of Tirana, Albania;
[3]Biochemistry Department, Faculty of Natural Sciences, University "Eqrem Çabej", Gjirokastra, Albania;

E-mail: ilva_gjika@yahoo.com

ABSTRACT

The insidious accumulation of heavy metals over large areas and long periods, resulting in slow damage to living organisms, necessitates careful monitoring of the input, movements and effects of such pollutants. Mosses have demonstrated the ability to absorb and accumulate atmospheric pollutants in tissue, so the moss biomonitoring technique was applied to air pollution studies in our country. Samples of terrestrial mosses *Hypnum cupressiforme* were collected at 13 sites during October-September 2010 following the the guidelines of the UNECE ICP Vegetation. The elements like aluminum, lead, zinc, copper and cadmium were analysed by ICP-AES technique. Geographical distribution maps of the elements over the sampled territory were constructed using GIS technology. The most contaminated sites with heavy metals resulted to be those with high road traffic, high population density and in the vicinity of different residential and industrial activities.

Key words: air pollution, biomonitor, moss, heavy metals, ICP-AES.

INTRODUCTION

The atmosphere is subjected to large inputs of anthropogenic contaminants produced by both stationary sources (power plants, industries and residential heating) and mobile sources related to traffic. The emission of toxic substances into the environment has spread mainly from industrialized countries. However, many industrial plants and especially road traffic may emit heavy metals into the atmosphere. Leygonie (1993) noted that, fossil fuels contain many kinds of heavy metals which are emitted during the combustion of those fuels. Furthermore, the wear of auto tires, degradation of parts and especially paint, and metals in catalysts are all suspected as potential sources of heavy metal pollution (Wei & Morrison, 1994; Monaci *et al.,* 2000; Ozaki *et al.,* 2004; Suzuki *et al*., 2009). Generally, traffic related pollutants include toxic metals like lead, cadmium, copper and zinc (Viard *et al.,* 2004).
Trace elements are widely dispersed in the environment and their interactions with different natural components result in toxic effects on the biosphere. The transport and mobilization of trace elements have already attracted much attention. Most of trace elements in terrestrial ecosystems originate from atmospheric wet and dry deposition. From a biogeochemical perspective, the characterization of atmospheric deposition is relevant in order to identify the variability and sources of the atmospheric pollutants (M. Anicic et al., 2008). On the other hand, some trace metals are essential in plant nutrition, but plants growing in a polluted environment can accumulate them at high concentrations (Hovmand *et al.,* 1983; Huckbee *et al.,* 1983; Alloway, 1990; Vousta *et al.,* 1996; Sharma *et al.,* 2004).
An alternative, simple and inexpensive method of investigating metal deposition from the atmosphere was suggested in the late 1960s by Swedish scientists (Rühling and Tyler, 1968, 1971) and further developed during the last 30 years in a majority of European countries. Many studies have demonstrated the ability of mosses to absorb and accumulate atmospheric pollutants in tissue. Root and cuticle absence makes them find their nutritive elements in wet and dry atmospheric deposition (Rühling and Tyler, 1968). This moss biomonitoring technique was recently adopted by the United Nations Economic Commission for Europe (UNECE) as a method of investigating heavy metal deposition in Europe (Buse *et al.*, 2003). *Hypnum cupressiforme*, which was used in this study, is one of the

moss species recommended for passive biomonitoring purposes (Miris Castello, 2007). For the first time this technique has been applied to a systematic study of air pollution with heavy metals. This study is only a part of the survey that covers all the territory of Albania. With this survey Albania attended for the first time the *European moss survey* in 2010/11, through the *UNECE ICP Vegetation Programme*. The aim of this study was the monitoring of air pollution at three regions in Albania, identifying the most polluted areas and defining different pollution sources.

MATERIALS AND METHODS

Hypnum cupressiforme moss samples were collected at three regions of Albania (Tirane, Durres and Lezhe), following the guidelines of the UNECE ICP Vegetation. The moss samples were collected during September-October 2010 at 13 locations. In the laboratory, after manual removal of all adhering material (plant remains, soil particles, etc.), only the green–brown moss shoots were subjected to analysis as they correspond approximately to the deposition over the last three years. Then the moss samples were dried to constant weight at 30–40°C for 48 h and homogenized to a fine powder in agate mill.

Moss samples were digested by using of Microwave digestion system (Marsx, CEM, USA). All of the reagents used for this study were with analytical grade: nitric acid, trace pure (Merck, Germany), hydrogen peroxide, p.a. (Merck, Germany), and redistilled water. About 0.5 g of moss material was placed in a Teflon vessel and treated with 7 ml of concentrated nitric acid (HNO_3) and 2 ml hydrogen peroxide (H_2O_2) overnight. The procedure was continued with full digestion of moss material in microwave digestion system (Mars, CEM, USA). Digests were filtrated and quantitatively transferred to 25 ml calibrated flasks.

The content of elements in the moss samples were determined by inductively coupled plasma – atomic emission spectrometric (ICP-AES) method performed at the *"Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia"*. The certified M2 and M3 moss samples were used for quality control of ICP-AES analysis. These certified moss samples were prepared within the monitoring program "The European Moss Survey".

RESULTS

In Figure 1. is shown the survey area together with the locations of sampling sites. The names of sampling sites of moss samples and the content of elements Al, Pb, Zn, Cu and Cd (in µg/g dry weight), are given in Table 1. In Figures 2-4 are shown the maps of geographical distribution of elements Zn, Cu and Al. These maps were prepared at *"Joint Institute for Nuclear Research, Dubna Moscow Region, Russia"*, using the Geographic Information System (GIS).

Figure 1. *Survey area with the location of sampling sites (red dots).*

Table 1. The sampling sites of moss samples and the content of elements obtained in this study (μg/g, dry weight).

Sampling sites	Elements				
	Al	Pb	Zn	Cu	Cd
Berxulle	806	2.85	2.08	5.58	0.08
Karrec	1520	2.37	6.05	5.75	0.10
K. Botanik	1051	2.09	15.32	5.00	0.13
Dajt	573	1.64	15.90	4.67	0.12
Lalm	1269	1.98	17.16	5.35	0.12
Ndroq	1267	2.40	14.10	6.25	0.08
Shkafane	1625	1.48	11.90	5.62	0.08
Manez	2254	2.31	3.95	2.96	0.05
Golem	2331	2.21	21.09	8.21	0.06
Krrabe	1244	2.55	19.63	7.84	0.12
Milot	2722	3.76	24.77	15.55	0.26
Lezhe	1712	2.84	17.51	7.46	0.11
Kruje	1492	3.43	46.87	7.09	0.37

Our results are compared with the corresponding data from similar studies in the neighboring Balkan countries (Frontasyeva et al., 2004; Spiric et al., 2009; Barandovski et al., 2008). In Table 2. are given the ranges (min-max) of elements. For comparison with a pristine territory, the corresponding data for northern Norway (E. Steinnes, 2007) are shown also in the right-hand column. As it is seen from Table 2, the maximum values of each element in our results are within the ranges reported from all other countries, except Norway. So, the results of our study show that in comparison to the Balkan countries our survey area is cleaner, however, compared to a clean area such as Norway our area is influenced by pollution (except for Zn which is lower even than Norway).

Table 2. Comparison of the results obtained in the present study with other Balkan countries and Norway (μg/g, dry weight).

Elements	Albania	Serbia	Romania	Kroatia	Macedonia	Norway
Al	573-2722	1280-22090	830-23000	398-21460	825–17600	67-820
Zn	2.08 - 46.87	14 - 415	39 - 2950	12 - 283	14 - 203	7.9 - 173
Cu	2.96 - 15.55	6.31-3140	815 - 21340	320 - 12140	424 - 17380	2.1 - 9.2
Cd	0.05 - 0.37	30 - 2340	27 - 1470	20 - 1421	37 - 1475	0.025 - 0.171
Pb	1.48 - 3.76	-	6.45-31.5	0.06-82.4	1.5–37.2	0.64-6.12

Aluminium

Aluminium is the third most abundant element in the lithosphere. Most naturally occurring aluminium compounds are sparingly soluble and bioavailable; therefore, relatively small quantities of aluminium are found in most biological samples unless contaminated with soil (dust) (Pais *et al.*, 1997). The largest source of airborne aluminium-containing particulates is the flux of dust from soil and the weathering of rocks (Lee and Von Lehmden 1973; Sorenson et al. 1974). Human activities, such as mining and agriculture, contribute to this wind-blown dust (Eisenreich 1980; Filipek et al. 1987). The major anthropogenic sources of aluminium-containing particulate matter include coal combustion, aluminium production, and other industrial activities, such as smelting that process crustal minerals (Lee and Von Lehmden 1973). Away from local pollution sources, aluminium is a good indicator of mineral particles, mainly windblown soil dust, as it is present at high concentrations in the earth's crust. Therefore, the spatial pattern of aluminium concentrations in mosses might provide an indication of the contribution of wind re-suspension to the deposition of metals to mosses, reflecting to some extent historical deposition of heavy metals. A

higher accumulation of soil dust does not necessarily translate into a higher deposition flux for all metals in the same way. The deposition flux of metals depends on the particle size distribution.
The geographical distribution of aluminium is typical of the group of crustal elements predominantly supplied to the moss by windblown soil dust, showing relative uniform mean values between regions. Enhanced levels of aluminium in mosses are observed mainly at Milot (2722 µg/g), Golem (2331 µg/g) and Manez (2254 µg/g) and this seems to be related to the soil dust created during different human activities in these areas. In Golem it is related to the soil dust created as a result of diggings, because massive constructions have been and still continue to be carried out in this area. While in Milot and Manez aluminium is related to the soil dust created from agricultural activities in these lands. Previously in Milot existed a place which was used for the collection of various minerals coming from different parts of Albania, in order to be transported later to different destinations by train, for example to the ex-chemical-metallurgical factory in Laç or other factories or to the port of Durres to be exported. So, the enhanced level of aluminium in Milot could also originate from the past activities related to the collection of minerals in this area and also as a result of processing various minerals at the ex-chemical-metallurgical factory in Laç (near Milot).

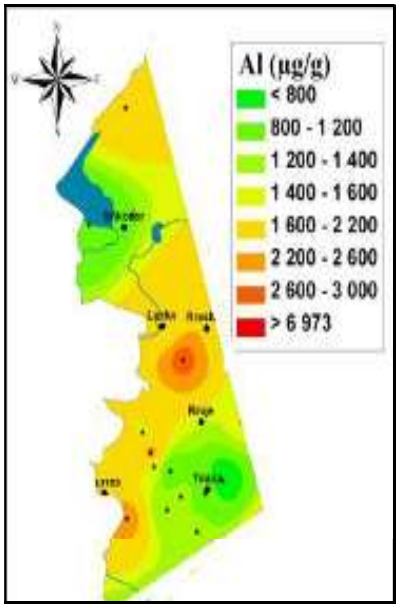


Figure 5. *The geographical distribution of element Al.*

Zinc

Zinc is one of the most widely used metals in the world. The major industrial sources of zinc include electroplating, smelting and ore processing, and drainage from both active and inactive mining operations (Mirenda 1986). Furthermore, zinc is an important component of brass, bronze, die casting metal, other alloys, rubber, and paints. The environmental releases of zinc from sources of human origin far exceed the releases from natural sources (Fishbein 1981). Anthropogenic releases of zinc and its compounds to the atmosphere are from dust and fumes from mining, zinc production facilities, processing of zinc-bearing raw materials (e.g., lead smelters), brass works, coal and fuel combustion, refuse incineration, and iron and steel production (EPA 1980d; Ragaini et al. 1977). The four most important sources of zinc in soil were estimated to be smelter slugs and wastes, mine tailings, coal and bottom fly ash, and the discharge of commercial products such as fertilizers. Tire debris contains significant quantities of zinc, which may contaminate soils near roads (Loranger et al. 1996).
The highest value of zinc was found in the area of Kruje (46.87 µg/g) followed by Milot (24.77 µg/g), Golem (21.09 µg/g), Krrabe (19.63 µg/g) and Lezhe (17.51 µg/g). This particularly high value of zinc in Kruje has its origin from the lime kilns that used to operate for a long time and in an uncontrolled manner in this area, in which large quantities of automobile tires were burned. In these lime kilns coal, petroleum products and by-products and other different wastes were also burned. The areas of Milot, Golem Krrabe and Lezhe have national roads in their vicinity, so the high concentrations of zinc in these areas reflect the contamination of soil from tire debris. Another source of

zinc in Milot is related to the past activities of the ex-factory in Laç. In this factory, which is very near to Milot, copper ores used to be processed where zinc is found in the secondary copper ores, as it is for example the mineral sphalerite (ZnS).

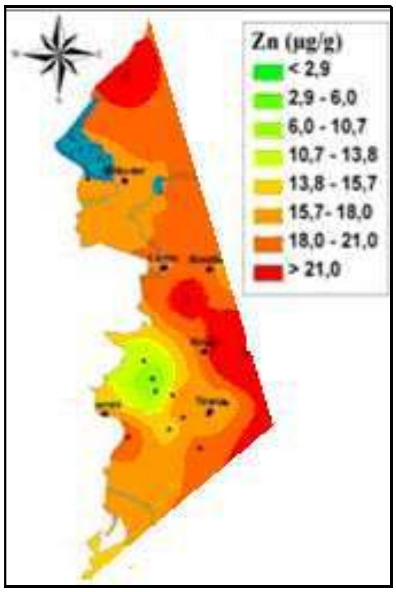


Figure 2. The geographical distribution of element Zn.

Copper

Anthropogenic sources of release of copper to the environment include mining operations, copper smelters, copper and iron ore processing, iron and steel production, municipal incinerators, copper sulfate production, gray iron foundries, primary lead and zinc smelting, ferroalloy production, coal combustion, oil and gasoline combustion, brass and bronze production, carbon black production, agriculture, sludge from publicly-owned treatment works and municipal and industrial solid waste (Hutchinson 1979; Romo-Kröger et al. 1994; Weant 1985). Other sources of copper release into the environment originate from domestic waste water, combustion processes, wood production, phosphate fertilizer production, and natural sources (e.g., windblown soil dust, volcanoes, decaying vegetation, forest fires, sea spray, etc.) (Georgopoulos et al. 2001; Harrison 1998). Sources of copper in urban areas include coal combustion, soil, tire wear, and automobile emissions (Kim and Fergusson 1994).
The highest value of copper was found in Milot (15.55 µg/g). The other sites have more similar copper values, but however we can also distinguish the sites Golem (8.21 µg/g), Krrabe (7.84 µg/g), Lezhe (7.46 µg/g) and Kruje (7.09 µg/g). This high value of copper in Milot has its origin from the past activities of ex-copper smelter and refining plant in Laç, which are very near to Milot. Also, another source of copper in Milot are the batches of copper minerals that previously used to be deposited in this area. The origin of copper in Golem is from the million of tones of mineral and coal collected in the port of Durres, from the dust created during the massive constructions in all of the coastal area and in areas nearby Golem and from the sea spray. In Kruje copper comes from the burning of coal, wood, petroleum by-products and other wastes in the lime kilns and from the different kind of fuels used in the cement factory. One common characteristic of the sites Milot, Golem, Krrabe and Lezhe is that they are found in the vicinity of national roads, reflecting in this way the pollution from road traffic as a result of gas exhaust from the fuel combustion and from tire debris.

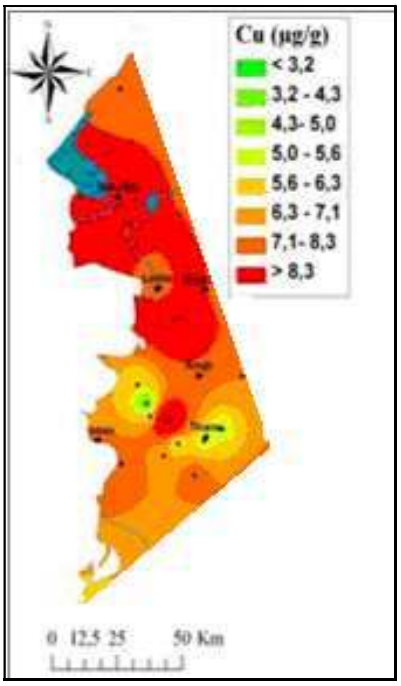


Figure 3. The geographical distribution of element Cu.

Lead

Lead is dispersed throughout the environment primarily as the result of anthropogenic activities. Because it is strongly adsorbed to soil, it generally is retained in the upper layers of soil and does not leach appreciably into the subsoil and groundwater. Lead minerals are found in association with zinc, copper, and iron sulfides as well as gold, silver, bismuth, and antimony minerals. Lead also occurs as a trace element in coal, oil, and wood. (EPA 2001a). Anthropogenic sources of lead can result from the mining and smelting of lead ores, as well as other ores in which lead is a by-product or contaminant, manufacture of lead-containing products, combustion of coal and oil, and waste incineration. Lead is found in building material (brick, concrete, painted and unpainted wood, roofing, and vinyl), and automotive sources (brakes, used oil), which contribute to runoff (Davis et al. 2001).
The concentration of lead does not vary evidently through the monitoring sites, reflecting in this way the anthropogenic pollution, which is mainly due to combustion of fuel and oil in the vehicle's engines and their brake consumption. However, from all the monitoring sites we can distinguish the sites of Milot (3.76 µg/g) and Kruje (3.43 µg/g). In Milot, besides the road traffic, the lead is found in the environment from the past activities of the ex-factory in Laç (near Milot), where as a result of the copper and iron ore processing, huge quantities of technological remnants are deposited, which among others contain considerable quantities of lead. It is known that in copper and iron ores are found secondary minerals such as galena (PbS). In Kruje lead is found in the environment from the burning of different fuels in lime kilns like coal, wood, petroleum by-products, motor oil and other wastes and also from burning of fuel at the cement factory.

Cadmium

Cadmium occurs in the earth's crust is commonly associated with zinc, lead, and copper ores. Cadmium is refined and consumed for use in batteries, pigments, coatings and platings, stabilizers for plastics, and nonferrous alloys, photovoltaic devices, and other (USGS 2008). Industrial activities are the main sources of cadmium release to air (EPA 1985a), and emissions from anthropogenic sources have been found to exceed those of natural origin (IARC 1993). Major industrial sources of cadmium emissions include zinc, lead, copper, and cadmium smelting operations, coal and oil-fired boiler, fossil fuel combustion, waste incineration other urban and industrial emissions, phosphate fertilizer manufacture, road dust, and municipal and sewage sludge incinerators (Alloway and Steinnes 1999;

Morrow 2001). Additional sources of cadmium are rubber tire wear, motor oil combustion, cement manufacturing, and fertilizer and fungicide application (Wilber et al. 1992).
The sites of Kruje (0.37 μg/g) and Milot (0.26 μg/g) have the highest levels of cadmium. The concentration of cadmium in Kruje originates from burning of different materials in lime kilns like tires, coal, petroleum products and by-products, different plastics, etc. and also from the production of cement and burning of fuel at the cement factory found nearby. Knowing that cadmium is found in the copper ores, its high concentration in Milot originates from the copper ore gathering in that area, as well as from Laç where the ex-factory of copper smelting and refining is located.
A Pearson′s correlation test was carried out to investigate the correlation between metal concentrations (significance was attributed to values of $P < 0.05$). Results have not indicated any correlation between the crustal element Al and the elements Zn, Cd, Pb and only a moderate correlation between Al-Cu. This indicates for their mainly anthropogenic origin. Their geogenic origin is related to the deposition of windblown soil dust in mosses. The fact that all these elements have high levels in Milot, Golem and Kruje indicates that their origin is also from the soil dust created from various anthropogenic activities, like the windblown soil dust created as a result of massive constructions and from the depositions of various minerals and coal. Other anthropogenic activities are the burning of various combustible materials and road traffic.

CONCLUSIONS

This was the first study of the atmospheric environment within the Republic of Albania and it adds this country to the European moss network. In comparison with neighboring countries where similar studies have been made, the results of our study show that in comparison to the Balkan countries our survey area is cleaner, however, compared to a clean region such as Norway our area is influenced by pollution (except Zn which is lower even than Norway). The most polluted areas, with Cd, Pb, Cu and Zn of this biomonitoring, resulted to be Milot, Kruje, Golem, Lezhe and Krrabe. The main anthropogenic sources of these elements are the windblown soil dust as a result of massive constructions, the depositions of various minerals and coal, the burning of various combustible materials and road traffic.

Acknowledgements: The authors gratefully acknowledge Prof. Trajçe Stafillov of Sts. Cyril and Methodius University, Skopje, Macedonia and Prof. Marina Frontasyeva of Joint Institute for Nuclear Researches, Dubna, Russia for their collaboration.

REFERENCES

Alloway B.J. 1990. *Heavy metals in soils.* Blackie Academic & Professional, Glasgow, 339 p.
Alloway BJ, Steinnes E. 1999. Anthropogenic additions of cadmium to soils. In: Cadmium in soils and plants. Kluwer Academic Publishers, 97-123.
Barandovski, L., Cekova, M., Frontasyeva, M.V., Pavlov, S.S., Stafilov, T., Steinnes, E., Urumov, V. (2008). Atmospheric deposition of trace element pollutants in Macedonia studied by the moss biomonitoring technique. Environ. Monit. Assess. 138, 107-118. http://dx.doi.org/10.1007/s10661-007-9747-6
Buse, A., Norris, D., Harmens, H., Buker, P., Ashnden, T., and Mills, G., 2003: *Heavy Metals in European Mosses:2000/2001 Survey*, UNECE ICP Vegetation.
Davis A, Shokouhian M, Ni S. 2001. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. Chemosphere 44:997-1009.
E. Steinnes, T. Berg, H. Uggerud, M. Vadset. Atmospheric Deposition of Heavy Metals in Norway. Nation-wide survey in 2005. State Program for Pollution Monitoring, Report 980/2007. Norwegian State Pollution Control Authority, Oslo 2007. 36 pp. (In Norwegian).
Eisenreich SJ. 1980. Atmospheric input of trace metals to Lake Michigan (USA). Water Air Soil Pollut 13(3):287-301.
EPA. 1980d. Exposure and risk assessment for zinc. Washington, DC: U.S. Environmental Protection Agency, Office of Water Regulations and Standards (WH-553). EPA440481016. PB85212009.
EPA. 1985a. Cadmium contamination of the environment: An assessment of nationwide risk. Washington, DC: U.S. Environmental Protection Agency, Office of Water Regulations and Standards. EPA 440485023.

EPA. 2001a. Lead and lead compounds. Guidance for reporting releases and other waste management quantities of toxic chemicals. Washington, DC: U.S. Environmental Protection Agency.
Filipek LH, Nordstrom DK, Ficklin WH. 1987. Interaction of acid mine drainage with waters and sediments of West Squaw Creek in the West Shasta mining district, California. Environ Sci Technol 21:388-396.
Fishbein L. 1981. Sources, transport, and alterations of metal compounds: An overview: 1. Arsenic, beryllium, cadmium, chromium, and nickel. Environ Health Perspect 40:43-64.
Frontasyeva, M.V., Galinskaya, T.Ye., Krmar, M., Matavuly, M., Pavlov, S.S., Radnovic, D., Steinnes, E. (2004). Atmospheric deposition of heavy metals in northern Serbia and Bosnia Herzegovina studied by moss biomonitoring, neutron activation analysis and GIS technology. Journal of Radioanalytical and Nuclear Chemistry 259(1), 141-147.
Georgopoulos AR, Yonone-Lioy MJ, Opiekun RE, et al. 2001. Environmental copper: Its dynamics and human exposure issues. J Toxicol Environ Health Part B Crit Rev 4(4):341-394.
Harrison BJ. 1998. Table 1. Copper concentrations in the environment. In: Copper information sourcebook- 1998- the world's scientific literature on copper in the environment and health, 21-62.
Hovmand M.F., J.C. Tjell H. Mosbaek. 1983. Plant uptake of airborne cadmium. - *Environmental Pollution,* 30: 27-38.
Huckabee J.W., F. Sanz Diaz S.A. Janzen J. Solomon. 1983. Distribution of mercury in vegetation at Almaden Spain. - *Environmental Pollution,* 30: 211-224.
Hutchinson TC. 1979. Copper contamination of ecosystems caused by smelter activities. In: Nriagu JO, ed. Copper in the environment. Part I: Ecological cycling. New York: John Wiley and Sons Inc.
IARC. 1993. Cadmium and certain cadmium compounds. In: IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Beryllium, cadmium, mercury and exposures in the glass manufacturing industry. IARC monographs, Vol. 58. Lyon, France: World Health Organization. International Agency for Research on Cancer, 119-236.
Kim ND, Fergusson JE. 1994. The concentrations, distribution and sources of cadmium, copper, lead and zinc in the atmosphere of an urban environment. Sci Total Environ 144:179-189.
Lee RE Jr, Von Lehmden DJ. 1973. Trace metal pollution in the environment. J Air Pollut Control Assoc 23(1):853-857.
Leygonie R. 1993. Heavy metals in the atmosphere: sources, emissions, measurement, effects. - *Pollution Atmospherique,* 35: 63-74.
Loranger S, Tetrault M, Kennedy G, et al. 1996. Manganese and other trace elements in urban snow near an expressway. Environ Pollut 92:203-211.
M. Aničič, M. Tasič, M.V. Frontasyeva , M. Tomaševič, S. Rajšič, Z. Mijič, A. Popovič. Active moss biomonitoring of trace elements with Sphagnum girgensohnii moss bags in relation to atmospheric bulk deposition in Belgrade, Serbia, 2008.
Mirenda RJ. 1986. Acute toxicity and accumulation of zinc in the crayfish *Orconectes virilis* (Hagen). Bull Environ Contam Toxicol 37:387-394.
Miris, Castello.(2007): A Comparison Between Two Moss Species Used as Transplants for Airborne Trace Element Biomonitoring in NE Italy. Environ Monit Assess 133:267–2
Monaci F., F. Moni E. Lanciotti D. Grechi R. Bargagli. 2000. Biomonitoring of airborne metals in urban environments: New tracers of vehicle emissions, in place of lead. -*Environmental Pollution,* 107: 321-327.
Morrow H. 2001. Cadmium and cadmium alloys. In: Kirk-Othmer encyclopedia of chemical technology. John Wiley & Sons, Inc., 471-507.
http://www.mrw.interscience.wiley.com/emrw/9780471238966/kirk/article/cadmcarr.a01/current/pdf?hd=All%2Ccadmium. April 29, 2008.
Ozaki I., I. Watanabe. K. Kuno. 2004. As, Sb and Hg distribution and pollution sources in the roadside soil and dust around Kamikochi, Chubu Sangaku National Park, Japan. -*Geochemical Journal,* 38: 473-484.
Pais, I., Benton, J., and Jones, Jr., 1997: *The Handbook of Trace Elements*, St. Lucie Press, Boca Raton, Florida, pp. 82.
Ragaini RC, Ralston HR, Roberts N. 1977. Environmental trace metal contamination in Kellogg, Idaho, near a lead smelting complex. Environ Sci Technol 11:773-781.
Romo-Kroger CM, Morales JR, Dinator MI, et al. 1994. Heavy metals in the atmosphere coming from a copper smelter in Chile. Atmos Environ 28(4):705-711.
Rühling, Å . and Tyler, G., 1968: An ecological approach to the lead problem, *Bot Notiser.* 12, 321–342.
Rühling, Å. and Tyler, G., 1971: Regional differences in the heavymetal deposition over Scandinavia, *J. Appl. Ecol.* 8, 497–507.

Sharma O., P. Bangar, K.S. Rajesh Jain, P.K. Sharma. 2004. Heavy metals accumulation in soils irrigated by municipal and industrial effluent. - *Journal of Environmental Science and Engineering,* 46(1): 65-73.
Sharma P., Dubey R.S. 2005. Lead toxicity in plants. Brazilian journal of plant physiology, 17, 1: 35-52.
Sorenson JRJ, Campbell IR, Tepper LB, et al. 1974. Aluminum in the environment and human health. Environ Health Perspect 8:3-95.
Spiric, Z., Frontasyeva, M.V., Stafilov, T., Steinnes, E., Bukovec, D., Gundorina, S.F., Ostrovnaya, T.M., Enimiteva, V. (2009) Multielement atmospheric deposition study in Croatia using moss biomonitoring, NAA, AAS and GIS Technologies. Submitted to «Journal of Hazardous Materials» E18-2009-149.
Suzuki K., T. Yabuki Y. Ono. 2009. Roadside leaves as bioindicators of heavy metal pollution in traffic areas of Okayama, Japan. – *Environmental Monitoring and Assessment,* 149: 133-141.
USGS. 2008. Cadmium. Mineral commodity summaries. U.S. Geological Survey. http://minerals.usgs.gov/minerals/pubs/commodity/cadmium/mcs-2008-cadmi.pdf. April 29, 2008.
Viard B., F. Pihan, S. Promeyrat, C. Pihan. 2004. Integrated assessment of heavy metal (Pb, Zn, Cd) highway pollution: bioaccumulation in soil, *Gramineae* and land snails. – *Chemosphere,* 55: 1349-1359.
Vousta D., A. Gramanis C. Samara. 1996. Trace elements in vegetables grown in an industrial area in relation to soil and air particulate matter. - *Environmental Pollution,* 94: 325-335.
Weant GE. 1985. Sources of copper air emissions. Research Triangle Park, NC. Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency. EPA 600/2/-85-046.
Wei C., M. Morrison. 1994. Platinum in road dust and urban river sediments. - *The Science of the Total Environment,* 146/147: 169-174.
Wilber GG, Smith L, Malanchuk JL. 1992. Emissions inventory of heavy metals and hydrophobic organics in the Great Lakes basin. In: Schnoor JL, ed. Fate of pesticides and chemicals in the environment. John Wiley and Sons, Inc., 27-50.

PAPER 069

BIOMONITORING OF ARSENIC AIR POLLUTION

Ilva Gjikaj[1], Majlinda Vasjari[2], Majlinda Terpo[3]

[1]Chemistry Department, Faculty of Mathematical Engineering and Physical Engineering, Polytechnic University of Tirana, Albania;
[2]Chemistry Department, Faculty of Natural Sciences, University of Tirana, Albania;
[3]Biochemistry Department, Faculty of Natural Sciences, University "Eqrem Çabej", Gjirokastra, Albania;

E-mail: ilva_gjika@yahoo.com

ABSTRACT

Arsenic and many of its compounds are especially potent poisons. Releases of arsenic to the environment from anthropogenic sources far exceed those from natural sources. Monitoring of trace element air pollution using bioindicators is a more economical alternative than direct ambient air measurements and especially relevant for monitoring large areas. The selection of moss species and sampling was carried out according to the guidelines of the UNECE ICP Vegetation. The moss *Hypnum cupressiforme* was collected during September-October 2010 at 13 localities in Albania. The content of arsenic and other elements were determined by ICP-AES technique. The arsenic content varies from 0.08 mg/kg to 0.68 mg/kg. The highest values were found in Milot, Manez and Kruje areas. Geographical distribution maps of the elements were constructed using GIS technology.

Keywords: air pollution, biomonitor, moss, arsenic, ICP-AES.

INTRODUCTION

Elemental arsenic and arsenic compounds are classified as "toxic" and "dangerous for the environment" in the European Union under directive 67/548/EEC. Arsenic is widely distributed in the Earth's crust, which contains about 3.4 ppm arsenic (Wedepohl 1991). Arsenic is present in more than 200 mineral species. It is mostly found in nature in minerals, such as realgar (As_4S_4), orpiment (As_2S_3), and arsenolite (As_2O_3) the most common of which is arsenopyrite (FeAsS) and only found in its elemental form to a small extent. Elemental arsenic is produced by reduction of arsenic trioxide (As_2O_3) with charcoal. As_2O_3 is produced as a by-product of metal smelting operations. While arsenic is released to the environment from natural sources such as wind-blown soil and volcanoes, releases from anthropogenic sources far exceed those from natural sources. Mining, smelting of non-ferrous metals and burning of fossil fuels are the major industrial processes that contribute to anthropogenic arsenic contamination of air, water and soil. Historically, use of arsenic-containing pesticides has left large tracts of agricultural land contaminated (Cucu-Man *et al.,* 2004). The use of arsenic in the preservation of timber has also led to contamination of the environment. Most anthropogenic releases of arsenic are to land or soil, primarily in the form of pesticides or solid wastes. However, substantial amounts are also released to air and water.
The emissions of heavy metals cause severe problems in plants, animals, and humans, depending on the concentrations of specific elements (Alloway, 1990; Bargagli, 1988a). Therefore, it is necessary to conduct close analyses of the heavy metal depositions into atmospheric, terrestrial biotic and aquatic environments. In recent decades, a few new cheaper and more reliable methods have been preferred. The use of moss as a biomonitor is a convenient way to determine the levels of atmospheric deposition (Puckett, 1988). Uptake of metals by mosses occurs largely from atmospheric deposition, and there is usually a high correlation between the levels of a particular element in moss samples and the levels of that element in bulk deposition samples at the same site (Alloway, 1990).
Hypnum cupressiforme is one of the moss species recommended for passive biomonitoring purposes (Miris Castello, 2007). For the first time this technique has been applied to a systematic study of air pollution with heavy metals. This study is only a part of the survey that covers all the territory of Albania. With this survey Albania attended for the first time the *European moss survey* in 2010/11, through the *UNECE ICP Vegetation Programme*. The aim of this study was the monitoring of air pollution at three regions in Albania, identifying the most polluted areas and defining different pollution sources.

MATERIALS AND METHODS

Hypnum cupressiforme moss samples were collected at three regions of Albania (Tirane, Durres and Lezhe), following the guidelines of the UNECE ICP Vegetation. The moss samples were collected during September-October 2010 at 13 locations. In the laboratory, after manual removal of all adhering material (plant remains, soil particles, etc.), only the green–brown moss shoots were subjected to analysis as they correspond approximately to the deposition over the last three years. Then the moss samples were dried to constant weight at 30–40°C for 48 h and homogenized to a fine powder in agate mill.

Moss samples were digested by using of Microwave digestion system (Marsx, CEM, USA). All of the reagents used for this study were with analytical grade: nitric acid, trace pure (Merck, Germany), hydrogen peroxide, p.a. (Merck, Germany), and redistilled water. About 0.5 g of moss material was placed in a Teflon vessel and treated with 7 ml of concentrated nitric acid (HNO_3) and 2 ml hydrogen peroxide (H_2O_2) overnight. The procedure was continued with full digestion of moss material in microwave digestion system (Mars, CEM, USA). Digests were filtrated and quantitatively transferred to 25 ml calibrated flasks.

The content of elements in the moss samples were determined by inductively coupled plasma – atomic emission spectrometric (ICP-AES) method performed at the *"Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia"*. The certified M2 and M3 moss samples were used for quality control of ICP-AES analysis. These certified moss samples were prepared within the monitoring program "The European Moss Survey".

RESULTS

In Figure 1. is shown the survey area together with the locations of sampling sites. The names of sampling sites of moss samples and the content of elements As, Al, Li, Sr (in µg/g dry weight), are given in Table 1. In Figure 2 are shown the maps of geographical distribution of elements As and Al. These maps were prepared at *"Joint Institute for Nuclear Research, Dubna Moscow Region, Russia"*, using the Geographic Information System (GIS).

Figure 1. *Survey area with the location of sampling sites (red dots).*

Table 1. *The concentration of elements obtained in this survey (µg/g, dry weight).*

Sample number	Sampling sites	Elements			
		As	Al	Li	Sr
Alb-24	Berxulle	0.09	806	0.46	17.3
Alb-25	Karrec	0.39	1520	0.96	23.5
Alb-26	K. Botanik	0.08	1051	0.67	21.3
Alb-27	Dajt	0.17	573	0.28	17.5
Alb-28	Lalm	0.13	1269	0.97	22.9
Alb-29	Ndroq	0.31	1267	0.98	17.9
Alb-30	Shkafane	0.14	1625	1.14	16.5
Alb-31	Manez	0.64	2254	1.41	20.0
Alb-32	Golem	0.15	2331	1.74	20.6
Alb-33	Krrabe	0.19	1244	1.13	25.61
Alb-49	Milot	0.68	2722	2.77	24.31
Alb-50	Lezhe	0.29	1712	2.28	25.59
Alb-51	Kruje	0.51	1492	1.65	18.47

Our results are compared with the corresponding data from similar studies in the neighboring Balkan countries (Frontasyeva et al., 2004; Spiric et al., 2009; Barandovski et al., 2008). In Table 2. are given the ranges (min-max) of elements. For comparison with a pristine territory, the corresponding data for northern Norway (E. Steinnes, 2007) are shown also in the right-hand column. As it is seen from Table 2, the maximum value of arsenic in our results is within the ranges reported from all other countries, except Norway. So, the results of our study show that in comparison to the Balkan countries our survey area is cleaner, but, compared to a clean area such as Norway it is influenced by pollution, still with no big difference between them.

Table 2. *Comparison of the results obtained in the present study with other Balkan countries and Norway (μg/g, dry weight).*

Elements	Albania	Serbia	Romania	Kroatia	Macedonia	Norway
As	0.08-0.68	0.46-61	0.59-45.1	0.10-6	0.12-8.0	0.020-0.505
Al	2.40-11.68	1.14-22	2.72-51.9	0.76-33	2.33-122	0.10-4.2
Sr	16.5-25.6	6.8-95	1.8-290	4-125	11.8-136	3.6-43.3

Aluminium

Most naturally occurring aluminium compounds are sparingly soluble and bioavailable; therefore, relatively small quantities of aluminium are found in most biological samples unless contaminated with soil (dust) (Pais *et al.*, 1997). The largest source of airborne aluminium-containing particulates is the flux of dust from soil and the weathering of rocks (Lee and Von Lehmden 1973; Sorenson et al. 1974). Human activities, such as mining and agriculture, contribute to this wind-blown dust (Eisenreich 1980; Filipek et al. 1987). The major anthropogenic sources of aluminium-containing particulate matter include coal combustion, aluminium production, and other industrial activities, such as smelting that process crustal minerals (Lee and Von Lehmden 1973). Away from local pollution sources, aluminium is a good indicator of mineral particles, mainly windblown soil dust, as it is present at high concentrations in the earth's crust. Therefore, the spatial pattern of aluminium concentrations in mosses might provide an indication of the contribution of wind re-suspension to the deposition of metals to mosses, reflecting to some extent historical deposition of heavy metals. A higher accumulation of soil dust does not necessarily translate into a higher deposition flux for all metals in the same way. The deposition flux of metals depends on the particle size distribution.

The geographical distribution of aluminium is typical of the group of crustal elements predominantly supplied to the moss by windblown soil dust, showing relative uniform mean values between regions. Enhanced levels of aluminium in mosses are observed mainly at Milot (2722 μg/g), Golem (2331 μg/g) and Manez (2254 μg/g) and this seems to be related to the soil dust created during different human activities in these areas. In Golem it is related to the soil dust created as a result of diggings, because massive constructions have been and still continue to be carried out in this area. While in Milot and Manez aluminium is related to the soil dust created from agricultural activities in

these lands. Previously in Milot existed a place which was used for the collection of various minerals coming from different parts of Albania, in order to be transported later to different destinations by train, for example to the ex-chemical-metallurgical factory in Laç or other factories or to the port of Durres to be exported. So, the enhanced level of aluminium in Milot could also originate from the past activities related to the collection of minerals in this area and also as a result of processing various minerals at the ex-chemical-metallurgical factory in Laç (near Milot).

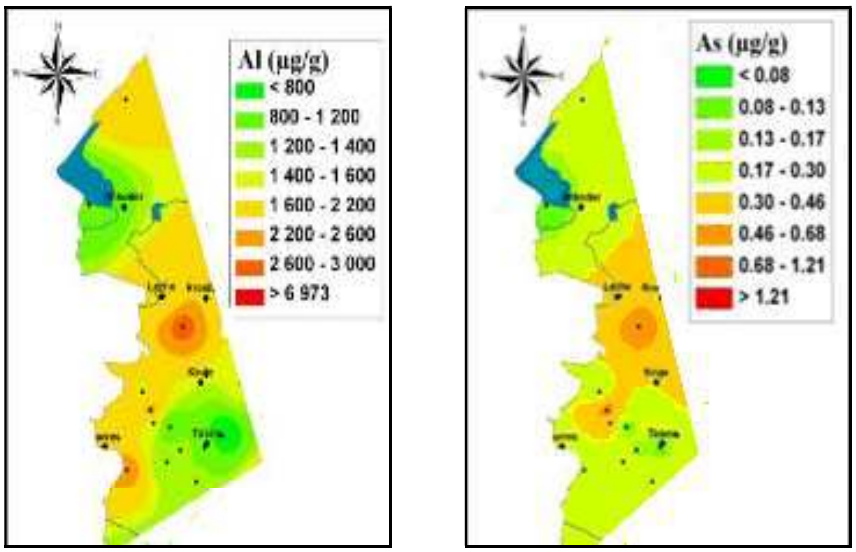


Figure 2. *The geographical distribution of elements Al and As.*

Arsenic

Arsenic is widely distributed in the Earth's crust, which contains about 3.4 ppm arsenic (Wedepohl 1991). It is mostly found in nature in minerals, such as realgar (As_4S_4), orpiment (As_2S_3), and arsenolite (As_2O_3), and only found in its elemental form to a small extent. There are over 150 arsenic-bearing minerals (Budavari et al. 2001; Carapella 1992). While arsenic is released to the environment from natural sources such as wind-blown soil and volcanoes, releases from anthropogenic sources far exceed those from natural sources. Anthropogenic sources include nonferrous metal mining and smelting (especially copper), pesticide application, coal combustion, wood combustion, and waste incineration. Arsenic is found in soil either naturally occurring or from anthropogenic releases forms insoluble complexes with iron, aluminum, and magnesium oxides found in soil surfaces, and in this form, arsenic is relatively immobile. Arsenic is largely immobile in agricultural soils; therefore, it tends to concentrate and remain in upper soil layers indefinitely (Sanok et al. 1995).

As it is seen from the graph in Figure 3. the highest concentrations of arsenic are found in the monitoring sites of Alb-49 (Milot), Alb-31 (Manez) and Alb-51 (Kruje). The origin of arsenic in Milot is from the past activities of ex-copper smelter and refining plant in Laç, which are very near to Milot. Arsenic is combined with the copper ores, so after the processing of copper ores for various purposes, their tailings rich in arsenic used to be deposited in the surrounding environment. Another source of copper in Milot are the batches of copper ores that previously used to be deposited in this area, in order to be transported later to different destinations by train. Also, in the vicinity of Milot is located Fushe Milot, an area with agricultural lands, so the elevated arcenic level may originate from the use of pesticides in this lands. In Manez which is also a developed agricultural area, arsenic is believed to be due to the use of pesticides. While in Kruje the high content of arsenic comes as a result of burning various materials in the lime kilns or the cement factory like coal, wood or various residues. Besides the above mentioned monitoring stations, the stations of Alb-25 (Karrec), Alb-29 (Ndroq) and Alb-50 (Lezhe) can also be distinguished. Even though they have a lower content of arsenic than the three previous stations, they can also be distinguished from the rest of the monitoring stations. It is noticed that all of these three stations have agricultural lands in their vicinity, therefore the origin of arsenic in these areas may be due to the use of pesticides in these lands.

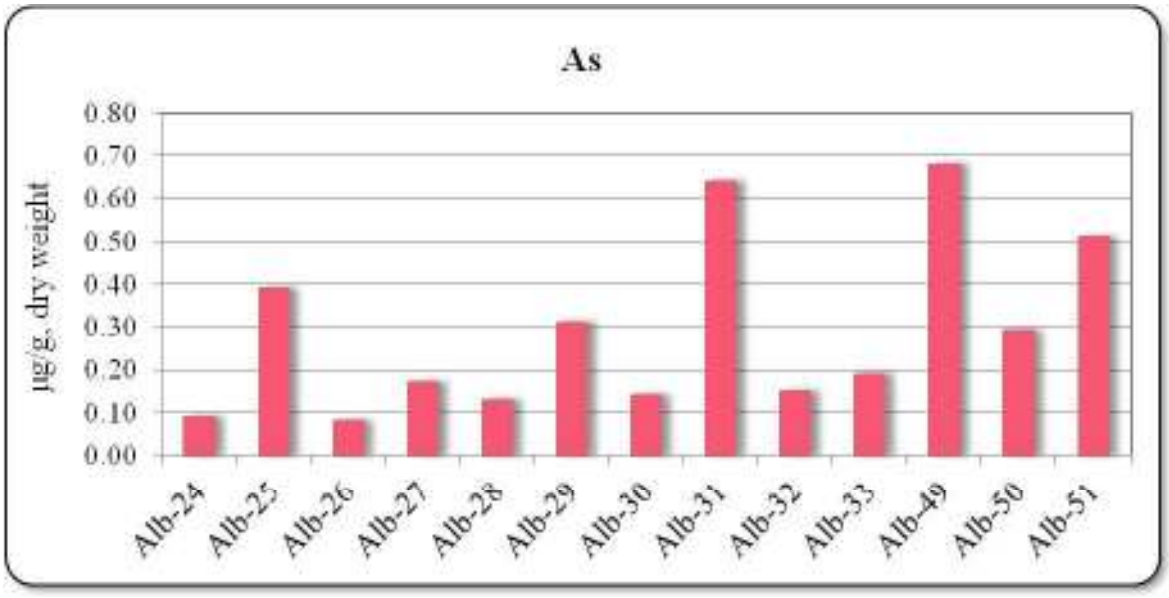


Figure 3. *The concentration of arsenic in mosses according to the monitoring sites.*

In order to investigate the correlation between metal concentrations, a Pearson′s correlation test was carried out (significance was attributed to values of $P < 0.05$). Results have indicated moderately positive correlations ($r > 0.5$) between arsenic and the crustal elements aluminium and lithium. This indicates for its dual origin, geogenic and anthropogenic. Contamination by arsenic was similar to the pattern for aluminum because of the similar emission sources related to soil particles, even though in some areas the origin of arsenic in soil is as a result of anthropogenic processes, such as the use of pesticides. In Kruje the increase of arsenic, unlike aluminum and lithium, indicates for its deposition in mosses directly from air where it is released as a result of burning various materials.

CONCLUSIONS

In comparison with neighboring countries where similar studies have been made, the results obtained for Albania are within the ranges reported from all other countries, except Norway, showing that in comparison to the Balkan countries our survey area is cleaner, but, compared to a clean area such as Norway it is influenced by pollution, still with no big difference between them. The most polluted areas with arsenic resulted to be Milot, Manez, Kruje, Karrec, Ndroq and Lezhe. The main anthropogenic sources of arsenic are the pesticide application in agricultural lands, depositions and processing of various arsenic containing minerals and the burning of various combustible materials. This was the first study of the atmospheric environment within the Republic of Albania and it adds this country to the European moss network.

Acknowledgements: The authors gratefully acknowledge Prof. Trajçe Stafillov of Sts. Cyril and Methodius University, Skopje, Macedonia and Prof. Marina Frontasyeva of Joint Institute for Nuclear Researches, Dubna, Russia for their collaboration.

REFERENCES

Alloway, B.J. (1990). Heavy metals in Soils. London: Blackie andSon Ltd., 368.
Barandovski, L., Cekova, M., Frontasyeva, M.V., Pavlov, S.S., Stafilov, T., Steinnes, E., Urumov, V. (2008). Atmospheric deposition of trace element pollutants in Macedonia studied by the moss biomonitoring technique. Environ. Monit. Assess. 138, 107-118. http://dx.doi.org/10.1007/s10661-007-9747-6
Bargagli, R (1988a). Trace elements in terrestrial food chains. In *Trace Elements in Terrestrial Plants.* Berlin: Springer-Verlag, p.263.

Budavari S, O'Neil MJ, Smith A, et al., eds. 2001. The Merck index an encyclopedia of chemicals, drugs and biologicals. 13th ed. Whitehouse Station, NJ: Merck & Co., Inc., 440, 462.
Carapella SC. 1992. Arsenic and arsenic alloys. In: Kroschwitz JI, Howe-Grant M, eds. Kirk-Othmer encyclopedia of chemical technology. Vol. 3. New York, NY: John Wiley and Sons, 624-633.
Cucu-Man, S., Mocanu, R., Culicov, O., Steinnes, E., and Frontasyeva, M. (2004). Atmospheric deposition of metals in Romania studied by biomonitoring using the epiphytic moss *Hypnum cupressiforme. Intern. J. Environ. Anal. Chem.* 84, 845–854.
E. Steinnes, T. Berg, H. Uggerud, M. Vadset. Atmospheric Deposition of Heavy Metals in Norway. Nation-wide survey in 2005. State Program for Pollution Monitoring, Report 980/2007. Norwegian State Pollution Control Authority, Oslo 2007. 36 pp. (In Norwegian).
Eisenreich SJ. 1980. Atmospheric input of trace metals to Lake Michigan (USA). Water Air Soil Pollut 13(3):287-301.
Filipek LH, Nordstrom DK, Ficklin WH. 1987. Interaction of acid mine drainage with waters and sediments of West Squaw Creek in the West Shasta mining district, California. Environ Sci Technol 21:388-396.
Frontasyeva, M.V., Galinskaya, T.Ye., Krmar, M., Matavuly, M., Pavlov, S.S., Radnovic, D., Steinnes, E. (2004). Atmospheric deposition of heavy metals in northern Serbia and Bosnia Herzegovina studied by moss biomonitoring, neutron activation analysis and GIS technology. Journal of Radioanalytical and Nuclear Chemistry 259(1), 141-147.
Lee RE Jr, Von Lehmden DJ. 1973. Trace metal pollution in the environment. J Air Pollut Control Assoc 23(1):853-857.
Miris, Castello.(2007): A Comparison Between Two Moss Species Used as Transplants for Airborne Trace Element Biomonitoring in NE Italy. Environ Monit Assess 133:267–2
Pais, I., Benton, J., and Jones, Jr., 1997: *The Handbook of Trace Elements*, St. Lucie Press, Boca Raton, Florida, pp. 82.
Puckett, K.J. (1988). Bryophytes and lichens as monitors of metal deposition, lichens. In: *Bryophytes and Air Quality*. Berlin: Band 30, J. Cramer, p. 240.
Sanok WJ, Ebel JG, JR, Manzell KL, et al. 1995. Residues of arsenic and lead in potato soils on long island. Chemosphere 30(4):803-806.
Sorenson JRJ, Campbell IR, Tepper LB, et al. 1974. Aluminum in the environment and human health. Environ Health Perspect 8:3-95.
Spiric, Z., Frontasyeva, M.V., Stafilov, T., Steinnes, E., Bukovec, D., Gundorina, S.F., Ostrovnaya, T.M., Enimiteva, V. (2009) Multielement atmospheric deposition study in Croatia using moss biomonitoring, NAA, AAS and GIS Technologies. Submitted to «Journal of Hazardous Materials» E18-2009-149.
Wedepohl KH. 1991. The composition of the upper earth's crust and the natural cycles of selected metals. Metals in natural raw materials. Natural resources. In: Merian E, ed. Metals and their compounds in the environment. Occurrence, analysis, and biological relevance. New York, NY: VCH, 3-17.

PAPER 071

FLOW CYTOMETRY IMMUNOPHENOTYPING AND DIFFERENTIAL DIAGNOSIS OF HAIRY CELL LEUKEMIA

Valentina Semanaj, Teuta Curaj, Genc Sulcebe

Laboratory of Immunology and Histocompatibility, University Hospital Center "Mother Teresa", Tirana, Albania;

E-mail: vsemanaj@yahoo.com

ABSTRACT

Introduction: Hairy cell leukemia (HCL) is an uncommon mature B-cell lymphoproliferative disorder which has distinct clinical features and a particular cellular morphology and immunophenotype. The neoplastic cells in this disease express a variety of pan-B markers, such as CD19, CD20, and CD22 and, are positive for FMC7 but negative for CD5 and CD23. The coexpression of CD103, CD11c, and CD25 is considered as a unique feature of HCL and is often used as an absolute criterion for establishing the diagnosis of HCL. Materials and methods: The applied methodology is a four color flow cytometry multiparametric immunophenotyping technique using EDTA bone marrow or peripheral blood samples taken from 197 patients diagnosed with Chronic lymphoproliferative disorders. The following fluorescent stained monoclonal antibodies were used: CD3, CD4, CD5, CD8, CD11c, CD19, CD20, CD23, CD25, CD103, FMC7, and kappa/lambda light chains. Results: From all the 197 patients tested, 144 of them (73,1 %) resulted with Chronic lymphocytic leukemia(CLL), 36(18,2%) patients with non-Hodgkin lymphoma (NHL) and 17(8,6%) of them resulted with HCL. In this group, the age of the patients ranged from 47 to 70 years (mean: 60.6 years). Twelve (70.5%) of them were males and 5 (29,4%) females, rate 2,4:1.The cell membrane marker positivity results observed on the abnormal cell populations of all the patients with HCL were: CD19 (100%), CD20 (100%), CD103(100%), light chain (100%), CD11c (94,1%), CD25 (70,6%). The cell marker profile CD11c+ CD25+CD103+ resulted with high specificity in HCL patients since they were concomitantly found in % of patients with this disorder.The diagnosis HCL–variant was established in 4 cases. Conclusion: Cellular immunophenotyping is an essential tool for the diagnosis of HCL, in order to distinguish them from other B-cell malignancies and also for monitoring and assessing the response to therapy.

Key words: Hairy cell leukemia; immunophenotyping; flow cytometry; monoclonal antibodies.

INTRODUCTION

Hairy cell leukemia (HCL) is an uncommon mature B-cell lymphoproliferative disorder. It affects primarily elderly men and is characterized by splenomegaly, pancytopenia, and monocytopenia. The major sites of disease involvement are bone marrow (BM) and spleen with small number of leukemic cells in the peripheral blood (P.Zinzani et al. 2010). The disease has distinct clinical features and a particular morphology, histopathology, and immunophenotype (O.Babusíková 2003).The distinction between HCL and other chronic B-cell lymphoproliferative disorders is clinically important because patients with HCL do not respond well to conventional lymphoma chemotherapy (E.Matutes 2006). The pathologic diagnosis of HCL is based mainly on morphologic findings in PB and BM and flow cytometric immunophenotyping of leukemic cells (fig.1). The neoplastic cells in this disease express a variety of pan-B markers, such as CD19, CD20, and CD22 and, are positive for FMC7 but negative for CD5 and CD23 cell markers. The coexpression of CD103, CD11c, and CD25 cell markers is considered as unique for HCL and is often used as an absolute criterion for establishing the diagnosis of HCL (E.Jaffe et al. 2001, M.Else et al. 2009). HCL has a characteristic immunophenotypic profile and light scatter characteristics in flow cytometry. In the scoring system that is used to differentiate CLL from other B-cell malignancies, HCL—like other non-CLL malignancies—has low scores that range from 1 to 0 in contrast to CLL in which scores range from 3 to 5 (R.Dillman 2008). However, atypical immunophenotypes have been reported in otherwise typical HCL (M.Cessna et al. 2005). Several studies showed that CD10, a marker for B-cell neoplasms of follicular center origin, was positive in HCL cases at frequencies ranging from 5% to 26% (Ref). The distinction between typical HCL and

HCL-variant is based on the clinical features (normal monocyte count and high white blood cell count in the HCL-variant), morphology, and immunophenotype (Y. Chen, Y et al. 2006).

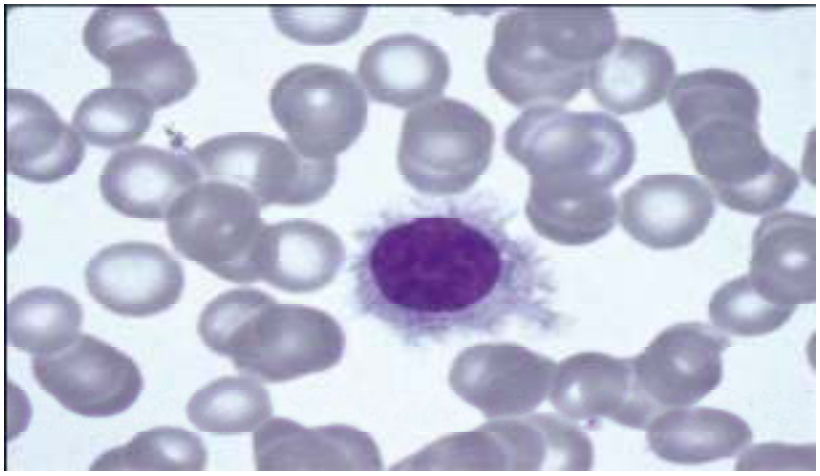


Figure 1: Peripheral blood – Classic hairy cell morphology.

MATERIAL AND METHODS

Patients and samples studied.
This study was carried out at the Laboratory of Immunology and Tissue Typing of the UniversityHospital Center Mother Teresa in Tirana, during the time interval 2011-2013. During this period, 197
consecutive samples from suspected and not yet treated chronic lymphoproliferative dissorders (CLPD) patients were studied through FCMI. Of these, 67 were bone marrow samples, and130 peripheral blood samples. Anticoagulant K3EDTA tubes were used for the biological sample collection.
Flow cytometry multiparametric immunophenotyping methodology.
The data collection and analysis were performed on a standard 4-color Beckman-Coulter XL flow cytometer. (Coulter Epics XL-MCL, CA, USA). This instrument measure ssimultaneously Forward Scatter (FS - distribution of light in a straight line), and Side Scatter (SS - distribution of light at the right angle), which provide data for cell size and cell granularity respectively.
At the same time the instrument enables the measurement of four different fluorescent dyes (FITC, PE, ECD and PC5). The monoclonal fluorescent antibodies used were as following: anti-CD3, CD4, CD5, CD7, CD8, CD10, CD11c , CD19,CD20, CD23, CD45, CD56, CD103, kappa, lambda and FMC7. Four-color panels were used with different cocktail fluorochrome-conjugated antibodies. In each panel the CD45-FITC marker was used for gating the normal and abnormal cell populations studied.
Statistical analysis
The GraphPad software (GraphPad Software, Inc.La Jolla, CA USA) was used in order to evaluate
the differences between categorical variables through the Fischer s exact test and also for the elaboration of continuous data.

RESULTS

General data about the patients studied
From all the 197 CLPD patients studied, 156 (79,9 %) of them were males and 41(20,1%) were females,
with a ratio of 3,8:1. Median age were 64.8±8.9 years, 95% CI 63.5-66.06 years.
After FCMI, according to the immunophenotypic criteria the HCL diagnosis was established in 17 patients. 12 (70.5%) of them were males and 5 (29.4%) females, ratio 1:2.4. Median age were 62.7±9.5 years.
Anemia, leukopenia, absolute monocytopenia, thrombocytopenia, and splenomegaly were present in 76%, 88,2%, 100%, 94,1%, and 100% of patients, respectively.
Cytomorphology bone marrow and peripheral blood examination of these patients, described lymphoid cells bearing hair-like projections from the cytoplasm in all cases .

Table 1. Classification of CLPD according to multiparametric flow cytometry immunophenotyping

	CLL	NHL-B	NHL -T	HCL	MCL
Female/nr/%	26 (18.0%)	6 (23.0%)	2 (28.5%)	5 (29.4%)	0 (0.0%)
Male/nr/%	118 (81.9%)	20 (76.9%)	5 (71.4%)	12(70.5%)	3 (100.0%)
Total	144 (73.1%)	26 (13.2%)	7 (3.5%)	17 (8.6%)	3 (1.5%)

FCMI in patients with diagnosis of Hairy cell leukemia.
In each panel CD45-FITC was used for "gate"-ing normal and abnormal cell populations. All cases showed increased SS (side scatter) compared with normal lymphoid population (Fig. 2).

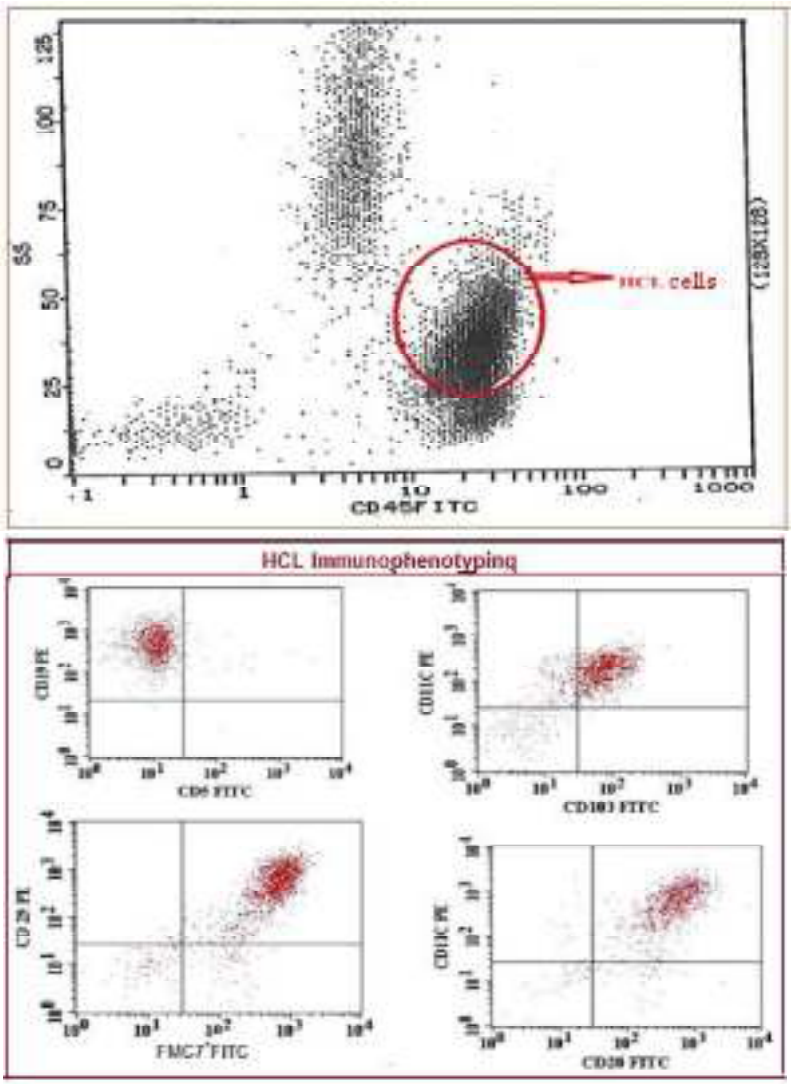


Figure 2. Flow cytometry dot plots of HCL cases showing the characteristico CD45/SS, and immunophenotypic profile.

The cellular markers of pathological population in CLPD are shown in Table 2 . In addition to the classic B lymphoid cell line markers such as, CD19 and CD20, who resulted high intensively positive in all HCL patients, the CD11c and CD103 markers resulted also positive in all HCL cases. CD25 resulted positive in 12 (70.6%) of

HCL patients. All cases were CD5 negative, thecell marker profile CD11c+ CD25+CD103+ displayeded high specificity in HCL patients (n %).

Table 2. Cell marker expression in CLL, HCL, MCL, NHL.

CD cell markers studied	CLL N=144	HCL N=17	MCL N=3	NHL-B N=26	p* value
CD19+	144 (100%)	17 (100%)	3 (100%)	26 (100%)	ns
CD5 +	144 (100%)	0 (0%)	3 (100%)	2 (7.6 %)	P=0.0001
CD23 +	138 (95.8%)	4 (23.5%)	0 (0.0%)	2 (7.6%)	P=0.0001
CD20 +	56 (38.8%)	17 (100%)	3 (100%)	26 (100%)	ns
mLC +	135 (93.7%)	17 (100%)	3 (100%)	26 (100%)	ns
CD38 +	37 (25.6%)	2(11.7%)	3 (100%)	11(42.3%)	ns
FMC-7+	0 (0%)	15(89.3%)	3 (100%)	7 (26.9%)	P=0.0001
CD11c+	0 (0%)	16(94.1%)	0 (0.0%)	1 (3.8%)	P=0.0001
CD25+	0 (0%)	12(70.6%)	0 (0.0%)	1(3.8%)	P=0.0001
CD103+	0 (0%)	17(100%)	0 (0.0%)	0 (0.0%)	p=0.0001

*** Fisher's exact test $p \leq 0.05$**

Many CLPD can mimick each other. In addition to the classical cytology, several diagnostic tools such as FCMI, immunohistochemistry or cytogenetic and molecular biology methods are needed in order to establish a precise CLPD diagnosis (J.Bennett, et al.1989). The correct diagnosis of HCL is critical because therapy with purine analogues is associated with high complete response rates and long relapse-free survival in patients with HCL (W.Flinn et al. 2000). The diagnosis of HCL usually is made by examining the morphologic features of the PB and BM in conjunction with the characteristic immunophenotype as determined by flow cytometric analysis. Many studies on immunophenotype define HCL as a monoclonal B-cell disease with coexpression of CD103, CD11c and CD25 (B.Cornfield et al. 2001). In our series all cases were positive for CD11c+CD103+. Therefore, it is not surprising that cases that lack CD103 or CD25 could be excluded from consideration of a diagnosis of HCL (H.Cessna et al. 2005). The major differential diagnosis would include other CD5 negative lymphoproliferative disorders such as (HCL-V) and splenic marginal zone lymphoma.

Negativity for CD25 is frequently seen in HCL-V, and in our sdudy it was shown in 4 cases. Unlike typical HCL, patients with HCL-V commonly present with a high WBC count, an absence of monocytopenia and have a poor response to purine analogue therapy (E. Matutes et al. 2003). The CD10 marker, which isfound in lymphoid cells of germinal center origin, has been reported positive in HCL in a relatively higher percentage compared with other small B-cell leukemias or lymphomas of non–germinal center origin. The frequencies of CD10 expression in HCL in the reported studies ranged from 5% to 26% (T.Jasionowski et a.l 2003). In our 17 HCL cases, we identified 2 patients with expression of CD10 (11.6%). Among the CD10+ HCL patients, we did not find any morphologic or clinical feature that could differenciate them from those HCL patients with a typical immunophenotype. CD23 positivity has been reported in approximately 20% of HCL cases in some studies (Juliusson et al. 1994). In our study the CD23 positivity was observed in 4 (23,5%) of 17 HCL patients and in a relatively high percentage of their leukemic cells.

CONCLUSION

Multi parametric flow cytometry immunophenotyping is an essential tool for the diagnosis of HCL in order to distinguish them from other B-cell malignancies, for the disease monitoring and for assessing the response to therapy.

REFERENCE

Cornfield DB, Mitchell Nelson DM, Rimsza LM, et al. (2001). The diagnosis of hairy cell leukemia can be established by flow cytometric analysis of peripheral blood, even in patients with low levels of circulating malignant cells. Am J Hematol; 67:223-226.

Jaffe ES, Harris NL, Stein H, et al. (2001). Pathology and Genetics of Tumours of Haematopoietic and Lymphoid Tissues. Lyon, France: IARC Press; World Health Organization Classification of Tumours.
Cessna MH, Hartung L, Tripp S, et al. (2005). Hairy cell leukemia variant: fact or fiction. Am J ClinPathol; 123:132-138.
Dillman RO. (2008). Immunophenotyping of Chronic Lymphoid Leukemias. JCO, 26: 8 1193-1194.
Wu ML, Kwaan HC, Goolsby CL. (2000). Atypical hairy cell leukemia. Arch Pathol Lab Med.;124:1710-1713. 6.
Flinn IW, Kopecky KJ, Foucar MK, et al. (2000). Long-term follow-up of remission duration, mortality, and second malignancies in hairy cell leukemia patients treated with pentostatin. Blood.;96:2981-2986.
Cessna MH, Hartung L, Tripp S, et al. (2005). Hairy cell leukemia variant: fact or fiction. Am J Clin Pathol: 123:132-138.
Jasionowski TM, Hartung L, Greenwood JH, et al. Analysis of CD10+ hairy cell leukemia. Am J Clin Pathol. 2003;120:228-235.
Juliusson G, Lenkei R, Liliemark J. (1994) Flow cytometry of blood and bone marrow cells from patients with hairy cell leukemia: phenotype of hairy cells and lymphocyte subsets after treatment with 2-chlorodeoxyadenosine. Blood.;83:3672-3681.
Matutes E, Wotherspoon A, Catovsky D.(2003). The variant form of hairy-cell leukaemia. Best Pract Res Clin Haematol;16:41-56.
Matutes, E., Wotherspoon, A., Brito-Babapulle, V. Catovsky, D. (2001). The natural history and pathological features of the variant form of hairy cell leukaemia. Leukemia: 15; 184-186
Zinzani, P.L., Pellegrini, C., Stefoni, V., Derenzini, E., et al. (2010). Hairy cell leukaemia: evaluation of the long-term outcome in 121 patients. Cancer; 116: 4788-4792.
Chen, Y.H., Tallman, M.S., Goolsby, C. and Peterson, L. (2006). Immunophenotypic variations in hairy cell leukemia. American Journal of Clinical Pathology, 125, 251-259.
Babusíková O, Tomová A. (2003). Hairy cell leukemia early immunophenotypical detection and quantitative analysis by flow cytometry.Neoplasma. 50(5):350-6.
Matolcsy A. (2005). Immunophenotypic Markers in the Diagnosis of Non-Hodgkin's Lymphomas. Immunophenotypic Analysis, Second Edition, chapter 3.
Else M, Dearden CE, Matutes E, et al. (2009). Long-term follow-up of 233 patients with hairy cell leukaemia, treated initially with pentostatin or cladribine, at a median of 16 years from diagnosis. Br J Haematol;145(6):733-740.
Matutes E. (2006). Immunophenotyping and differential diagnosis of hairy-cell leukemia.Hematol Oncol Clin North,Am;20(5):1051-1063
Bennett, J.M., Catovsky, D., Daniel, M.T., Flandrin, G., Galton, D.A., Gralnick, H.R. & Sultan, C. (1989) Proposals for the classification of chronic (mature) B and T lymphoid leukaemias. French-American-British (FAB) Cooperative Group. J Clin Pathol, 42, 567-584.

PAPER 072

MAMMAL PREY IN THE PELLETS OF THE LITTLE OWL, *ATHENE NOCTUA*. DATA FROM THE ANTIGONE COMMUNE, GJIROKASTËR, ALBANIA

Gligor Paspali[1], Etleva Hysaj[1], Ferdinand Bego[2]

[1] Department of Biology and Chemistry, University "Eqrem Çabej", Gjirokastra, Albania
[2] Department of Biology, Faculty of Natural Sciences, University of Tirana, Albania

Email:gpaspali@yahoo.com

ABSTRACT

The Little Owl,*Athene noctua,* is a small nocturnal bird of prey that based on our studies is less common than the Barn Owl,*Tyto alba,* in the southern region of Albania. In some stations the Little Owl is sympatric with *T.alba*. In this study we for the first time provide more complete data on the mammal prey content in the Little Owl diet though analysis of 290 pellets collected in some stations within the territory of Antigone commune during a three years period (2011-2014). Pellets are collected in all seasons, although the majority of them belong to winter time. From the analysis of the pellets some 170 mammal prey items were identified. Mammal diet of the Little Owl is largely dominated by rodents (93%), while insectivores (Soricomorpha) provides a small contribution to the mammal prey of the little owl (only 7%). The Thomas' vole,*Microtus thomasi,* is the most preferable type of prey for the little owl with about 68% of the total mammal prey. Other small mammals, such as *Suncus etruscus* and *Neomys anomalus,* already identified in the pellets of the *T. alba* in the southern region of Albania are not part of the little own diet.

Key words: pellets,*Athene noctua*, small mammals, Antigone, Gjirokastër

INTRODUCTION

Little Owls *Athene noctua* are small predators that nest in cavities and feed mainly on small mammals and invertebrates,hunting mostly at night and dusk. The Little Owl's suitable habitat is commonly described as open agri-pastoral areas, meadows and rural settlements. In Europe, Little Owl populations have suffered a marked reduction during the last decades, mainly due to large-scale habitat changes associated with the intensification and mechanization of agriculture, which have in return caused a reduction in prey and nest-site availability (M.Tucker and F.Heath 1994). In Central Europe, the Little Owl is a relatively well-studied species (E.Glue and G.Scott 1980; M.Exo 1992). In theMediterranean area, however, the species is still quite abundant and occurs in different habitats, but relatively little research has been conducted on it (C.Génot 2001b).
Studies on the diet of the Little Owl are very scarce in Albania and mainly covering the lowland coastal zone of the Middle Albania and the Southern region of Albania. Our study aims to provide new and more complete data on the mammal content in the Little Owl diet from the Southern region of Albania.

MATERIAL AND METHODS

Study area
The commune of Antigone (fig. 1) is situated between the Drinos river and the western facing slopes of the Lunxhëri mountain (190-1000m above sea level). Five villages are part of the commune: Asim Zeneli, Arshi Lengo,Krinë,Tranoshishtë and Saraqinishtë. The territory of the Antigone commune is about 2800 ha, and the relief is predominantly hilly-mountainous: 771 ha are occupied with arable land, 1739 ha are pastures and 180 ha are covered with shrubs and forests. The terrain is very broken and drained by torrents (Nimica and Suha) and streams (Hosi and Tranoshishta), that are all tributaries to the Drinos river. The climate is typical of the Mountain-Mediterranean Climate Zone, characterized by abundant precipitations, dry summer and cold winter. The territory of Antigone commune is distinguished for its very rich flora, dominated by shruby vegetation composed of almond-leaved pear(*Pyrus amygdaliformis*), tree heath(*Erica arborea*),oriental hornbeam(*Carpinus orientalis*), strawberry

tree(*Arbutus unedo*), Jerusalem sage(*Phlomis fruticosa*), terebinth tree(*Pistacia terebinthus*), blackthorn(*Prunus spinosa*), manna ash(*Fraxinus ornus*),common hazel(*Corylus avellana*), field maple(*Acer campestris*),etc.. Oak and oriental plane are main tree species in the area. Main crops in arable land are wheat, corn, onion, potatoe and beans.

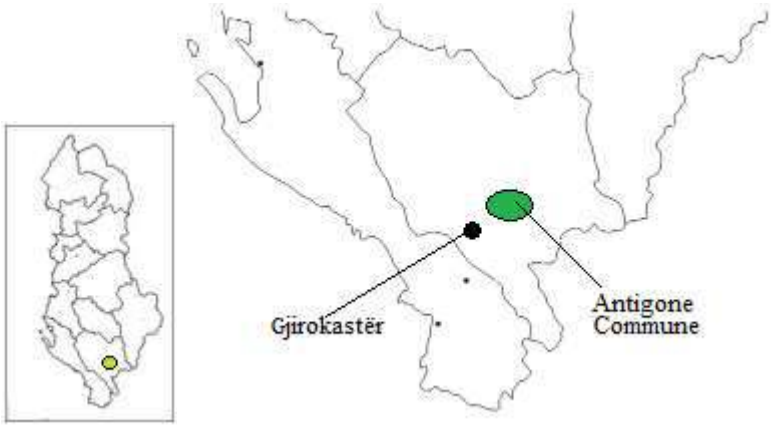


Figure 1.Study area where the Little Owl pellets were collected

Methods

Searching, collection and analysis of the Little Owl pellets was the main method to study the mammal prey content in the diet of the little owl. Pellets were collected in almost all seasons of the year during a three-year period of time (2011- 2014). They were found in abandoned houses of 4 villages (Saraqinisht, Krinë,Tranoshishtë and Asim Zeneli)of the Commune Antigone,Gjirokastër.In this study we have taken into consideration only those pellets that were well preserved as a whole, excluding those that were damaged or broken parts. Pellets were processed for analysis of the prey items using a pincet, while the species determination of the remaining bones was done under the stereomicroscope. Each pellet was treated as a single sample and was opened and analysed separately. Skeleton residues, mainly cranial remaining of prey, found in each pellets, such as skulls and jaws were put in separate plastic envelopes. Prey was identified at genius and species level, using reference books and articles (J.Niethammer and F.Krapp 1977, 1982, 1983; W.Yalden 1977; J.Erfurt 2003). For proper determination of sibling species of genus *Mus* references to scientific papers were made(M.Macholán 1996; B.Kryštufek and M.Macholán 1998).The whole small mammal collection found and selected from the little owl pellets is preserved at the research laboratory of the Biology-Chemsitry Department, University of Gjirokastra.

RESULTS

A total of 290 pellets were collected and analysed over the three-year period of time (2011-2014), out of which 170 small mammal individuals were found. The size of the pellets varied from 1.5 cm to 5.5 cm in length and 1.41 cm in width, in average. The mean value of their weight was 1.03 gr. The mean value of the mammal prey items in each pellet was about 0.6. In Spring and Summer the dominant collour of the pellets was black-blue, due to the high content of invertebates, mostly insects, while their consistence was soft and delicate. In Autumn and Winter the collour of the pellets became grey, due to the high content of mammal's hair in the pellets, while their consistence became hard and more solid(fig. 2).100% of little owl pellets had remains of invertebrates, 50% of them had remains of invertebrates only, and 2.7% of the pellets had remains of birds. From the examination of the skeleton residues (skulls and jaws) 7 species of small mammals were identified, of which 2 insectivore species (Soricomorpha) and 5 rodents (Rodentia). The mammal prey in the diet of the Little Owl is dominated by rodents (F= 93%), while insectivores contribute with only 7% of the mammal prey.

Figure 2. Pellets of the little owl collected in the Commune Antigone, Gjirokaster

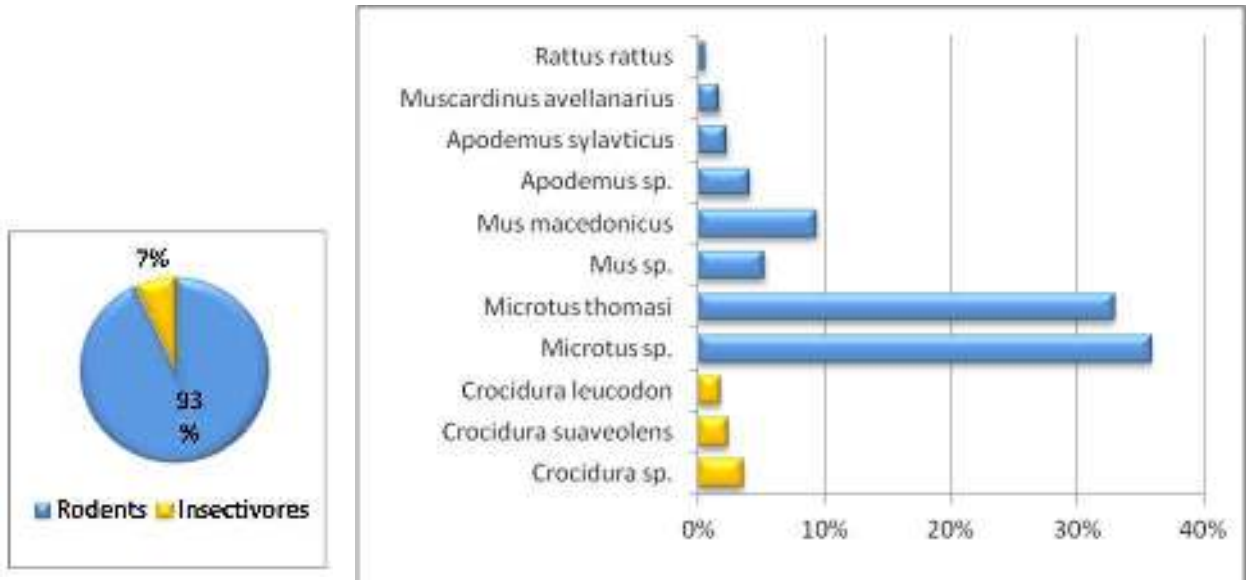


Figure 3. Composition of the mammal prey in the pellets of the little owl, in percentage

It seems that the Little Owl demostrates a high preference to voles that contribute with about 68 % of the mammal prey in the Little Owl's diet, followed by macedonian mouse,*Mus macedonicus,*with a relative freqeuncy 9%. All the remaining mammal prey species were less frequented by the little owl, and their relative frequency was less than 4%(fig.3). Analyzing the content of prey in the little owl pellets showed a drastic decrease of mammal prey from one year to the other. Thus, pellets collected in winter, spring and autumn during the period 2011-2012 contained residues of mammal prey at 91% , while those collected in winter and spring of 2013-2014 had only 14% mammal prey items, with the majority of prey items being represented by invertebrates, largely dominated by insects. At the same time, the rodents' porportion in the mammal prey showed a decrese of about 10-11% each year, while the contribution of insectivores increased each year by 10-11% (Environmental Index, i/r: 0.03; 0.15; 0.33) (fig. 4).

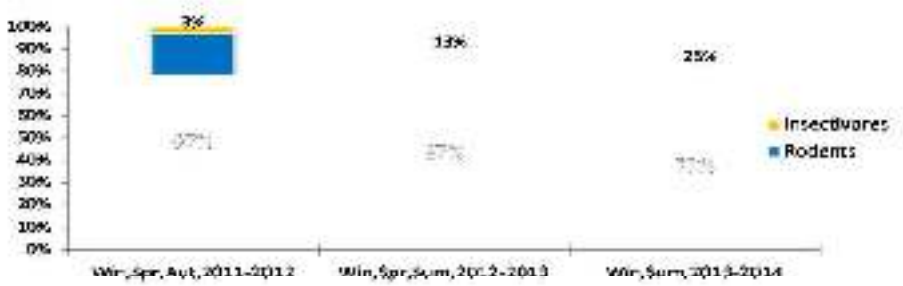


Figure 4. Dynamics of rodents and insectivores in the diet of the little owl during 2011-2014

Voles*(Microtus thomasi,Microtus sp.)*are the most prefered mammal prey by the little owl as they represent the most widely distributed and most common species in the Southern region of Albania (G.Paspali et al. 2013) regardless the geographical fluctuations of its population in different parts of the study area, and the differences in habitat structures and composition.

Voles are active during all seasons, and do not hibernate or undergo torpor (F.Merritt et al. 2001).The presence of voles in the little owl's diet is significantly higher during Winter 2011-2012 (F=77.3%), while in the following years they became less frequent in the little owl's diet, dominated by insects in the following years and seasons. This can probably be explained by the fact that Little Owls hunt inside buildings where loose grain is stored that provides good habitats for certain insects. If there is no snow, which,strongly reduces hunting efficiency, owls avoid exposure to wind and low temperatures, which would require additional energy when hunting in the natural environment(I.Kitowski and K. Pawlega 2010). In addition, during winter the abandoned houses are used by the local shepherds to host herds of sheep and goats, whose droppings attract insects that are an easy prey to catch by the little owl.

Mice *(Mus macedonicus,Mus sp.)*were the second most preferred mammal prey by the little owl. They became less important in the diet in all three winter seasons (2011-2014), with relative frequency (F) that fluctuated between 12% and 0 % (winter 2011-2012,F=12%; winter 2012-2013,F=5%; winter 2013-2014,F=0%). On the contrary, in springs of the three investigation years (2012-2014) the relative frequency (F) of the mice gradually incresased from 7.3% to 33.3%. We believe that such phenomenon may be explained with the increased abundance of mice in the hunting area of the little owl due to favourable clime conditions characterised by an increase of temperature and humidity. In recent years a gradual increase of temperatures associated with an increase of precipitation intensity was registered in the study area. The arable land along the Drinos valley that is part of the study area during the last years became more and more cultivated with perennial and annual crops such as, wheat, corn and alfalfa, which are known to provide preferred habitats and feeding grounds for mice.

The increase of temperatures and precipitation intensity associated with increased incidence of heavy rains and floods might have negatively influenced voles'population undergoing thus a drastic decline of their presence in the little owl's diet in all three spring seasons (2012-2014). The relative frequency (F) for the voles decreased from 83% in spring 2012, to 36% in spring 2013 and 17% in spring 2014. Thus, the frequency of catching voles by the little owl dropped down by two times from one year to another. The increased temperatures might have forced voles to dig deeper in the ground to protect themselves against higher temperatures and drought, making voles less active on the ground and a more difficult prey to catch by the little owl, while the increased incidence of heavy rains associated in those years with massive flooding, may have caused massive mortality of voles inside their underground dens.

Other small mammals, such as *Suncus etruscus* and *Neomys anomalus,* already identified in the pellets of the *T. alba* in the southern region of Albania (G.Paspali et al. 2013) were not part of the little owl's diet. This may be explained with the fact these prey species are pretty scarce in the region (G.Paspali et al. 2013) and consequently a very difficult prey to hunt by the little owl.

CONCLUSIONS

Mammal content in the diet of the Little owl comprises 7 small mammal species, of which *M.thomasi,M.macedonicus, A.sylvaticus* and *C. suaveolens* are most preferred prey by the little owl.
Rodents notably dominate the mammal prey in the little owl's diet in comparison with insectivores (rodents are present with five species while insectivores with two species only).
Small mammals are a preferred prey by the little owl during winter time, associated with the increased energy demand of the little owl in winter and the easier way to catch the prey in the absence of the vegetation coverage.
During 2011-2014, from one year to another, there was evidenced a considerable decrease of the small mammal prey content in the little owl's diet. Thus, in winter, spring and summer 2013-2014 small mammal prey was identified in only 13% of the pellets.
Invertebrates, notably insects, represent the most preferred prey by the little owl, as they were present in all pellets and in all seasons.
Antigone Commune, especially the village Saraqinishtë, represents a special case within the southern region of Albania for the Little Owl, as being the only commune where pellets of the little owl were collected all year around.
Climate and rich vegetation and flora, along with its proximity to Drinos field and human settlements associated with a high number of abandoned houses suitable to host little owls, are believed to be some of the main factors that make this commune a preferred place for the little owl.

REFERENCES

Erfurt, J. (2003). Bestimmung von Säugetierschädeln in Fraßresten und Gewöllen [Determination of mammalian skulls in nutrition remnants and pellets],Methodenfeldökol.Säugetierforsch 2, 471–535 (in German).
Exo, K.M. (1992). Population ecology of Little Owls Athene noctua in Central Europe: a review.In The ecologyand conservation of European owls. Joint Nature Conservation Committee UK Nature Conservation No 5 (ed. Galbraith, C. A., Taylor, I.R.&Percival, S.): 64–75. Peterborough, U.K.
Génot, J.C. (2001). Overview of Little Owl Athene noctua literature.In The Little Owl in Flanders in its internationalcontext. Proceedings of the Second InternationalLittle Owl Symposium, Oriolus 67 (ed. VanNieuwenhuyse, D., Leysen, M.&Leysen, K.): 84–87. Geraardsbergen, Belgium.
Glue, D.E. and Scott, D. (1980). Breeding biology of the little owl, British Birds 73, 167–180.
Kitowski, I. and Pawlega, K. (2010). Food Composition of the Little Owl Athene noctua in Farmland Areas of South East Poland, Belgium Journal of Zoology 140 (2), 203-211.
Kryštufek, B. and Macholán, M. (1998). Morphological differentiation in Mus spicilegus and the taxonomic status of mound-building mice from the Adriatic coast of Yugoslavia, Journal of Zoology, London 245, 185–196.
Macholán, M. (1996). Key to European house mice (Mus), Folia Zoologica 45(3), 209–217.
Merritt, J.F., Lima, M., Bozinovic, F. (2001). Seasonal regulation in fluctuating small-mammal populations: Feedback structure and climate,Oikos94, 505–514.
Niethammer, J. and Krapp, F. (1977). Handbuch der SaugetiereEuropas – Band 1, Nagetiere 1 [Manual of the European Mammals,Volume 1, No 1], AULA–Verlag, Wiesbaden (in German).
Niethammer, J. and Krapp, F. (1982). Handbuch der SaugetiereEuropas – Band 2/1, Nagetiere 2 [Manual of the European Mammals, Volume 2/1, No 2], AULA–Verlag, Wiesbaden (in German).
Niethammer, J. and Krapp, F. (1983). Handbuch der Saugetiere Europas – Band 3/1, Insektenfresser – Herrentiere [Manual of European Mammals, Volume 3/1, Insectivora], AULA–Verlag, Wiesbaden (in German).
Paspali, G., Oruci, S., Koni, M., Wilson, F.I., Krystufek, B., Bego, F. (2013). Seasonal variation of small mammals in the diet of the barn owl (Tyto alba) in the Drinos river valley, southern Albania, Turkish Journal of Zology 37, 97-105.
Tucker, G.M. and Heath, M.F.(eds.).(1994). Birds in Europe: their conservation status. BirdLife International,Cambridge.
Yalden, D.W. (1977). The identification of remains in owl pellets. Occasional Publication Mammalogical Society, London,UK.

PAPER 074

TAXONOMIC STUDY OF THE ORDER ODONATA IN KORÇA REGION

Shkëmbi Enilda[1*], Paparisto Anila[1], Mulla Noila[1], Halimi Eltjon[1], Qirinxhi Xhuliana[2]

[1]University of Tirana, Faculty of Natural Science, Department of Biology, Albania
[2]University Fan S Noli, Faculty of Natural and Human Sciences, Department of Nursing, Albania

*e-mail: enilda07@gmail.com

ABSTRACT

The purpose of this paper is to provide a contribution to the recognition and identification of the biodiversity of the order Odonata, the class Insecta, in Korça region. This is done in order to complement the data on entomofauna in Albania. This study was conducted in 2013. The collection of the material was performed within 22 days of expeditions in 11 stations. Each station has been visited 2 times. Expeditions were conducted near areas with rivers, reservoirs, lakes, during 9^{oo}-13^{oo}. According to the analysis of the collected data, 16 species, 11 genus and 7 families of the order Odonata are determined. The most represented is suborder Zygoptera with 9 species, and suborder Anisoptera represented by 7 species. Family Coenagrionidae and Libellulidae are families represented, both with 3 genus and five species. Of the 11 stations in the study, Boboshtica is the station with the largest number of species, that is 9. In this paper were reported 8 new species of Odonata order for the region of Korça. New species are: *Lestes barbarus* Fabricius, 1798; *Enellagma cyathigerum* Charpentier, 1840; *Ischnura pumilio* Charpentier, 1825; *Orthetrum albistylum* Selys, 1848; *Orthetrum brunneum* Fonscolombe, 1837; *Crocothemis erythroea* Brulle, 1832 *Sympetrum depressiusculum* Selys, 1841 and *Anax imperator* Leach, 1815. This number is added to the 17 species referred to in the literature, bringing the number of known species of the order Odonata in Korça to 25.

Key words: Odonata, Korça, variety, new records

INTRODUCTION

Order Odonata includes about 6000 species known in the world. 120 species are found in Europe (J.Silsby 2001). Studies for this group to our country have so far been sporadic and mainly conducted by foreign authors, especially in recent years. In 2013 Murányi and Kovács published a list of the species collected in our country during the collecting trips between 1992 and 2007. Also during the years 2006-2008 expeditions by E. Halimi, A. Paparisto and K. Misja were conducted in the areas: Shengjin, Kavaja, Divjake, Patok, Karavasta and Spille. We have these data for the area of Korça: 7 Odonata species according to Dumont et al. (1993); 12 species according to D. Muranyi (2013) and 14 species collected by us.

MATERIALS AND METHODS

To carry out this research, expeditions have been undertaken during 2013, in June, July and August. 11 stations have been visited in 22 days of expeditions. Expeditions were carried out near areas with rivers, reservoirs, streams, lakes, during the morning hours 900-1300. Each station has been visited equally 2 times. Habitats and species in the study areas are photographed by the camera Panasonic Lumix DMC-LZ30. Geographic information to measure the height above sea level is taken with GPS and MapAltitude program. On the map below,(Fig. 1) are listed 11 stations distributed in the region of Korça. A common entomological net air with a 34 cm diameter is used for the collection of Odonata. The suborder Anisoptera is difficult to capture in flight. They have delicate body and can be damaged by the movement of the net in the opposite direction of their movement. In this case these species are caught when they are at rest, during the process of copulation or when eggs are deposited. As for the suborder Zygoptera, the capture is simpler because they fly slower and not too far away from their place of residence (P. Corbet 1962). After the catch, insects are put into entomological envelopes, where the date, place of capture and special notes on the collection time are written. The species are determined by StereoMicroscopes ZEISS (Carl Zeiss) and 10x optical microscope Pi W / 23. One of the parameters that we analyzed is the constant of the species. This is an important

indicator as habitats in the study area are diverse. The value of the constant shows the ecological valence of the species. The constant is given by the formula:

$$K = \frac{a}{p} \times 100$$

a- shows the number of stations where the specie is present, P-shows the total number of stations (N.Peja 1995). By calculating the number of stations meeting and knowing the total number of stations (11), we calculate the value of the constant species.

The determination of species is based on the keys: "Some Key to the family of Odonata" by author Paul Choate (2000); "Field key to adult California dragonflies (Odonata) by the author: Kathy Biggs (2009); "Field guide to the dragonflies of Britain and Europe" by Klaas-Douwe B Dijkstra (2006).

Figure 1. Map of the stations visited in the area of Korça

RESULTS

The analysis of 211 specimens, collected during 22 days of expeditions, in 11 stations of the Korça district, have given these results:Suborder Zygoptera represented by 4 families, 6 genera and 9 species.
Family Coenagrionidae, collected individuals belonging to this family are part of 3 genera: genus *Erythromma (E. viridulum and E.lindenii)*, genus *Enellagma* (*E. cyathygerum*) and genus *Ischnura (I. elegans and I. pumilio)*.
Family Calopterygidae, only one genus, genus *Calopteryx (C. virgo and C. splendens)*.
Family Platycnemididae, only one genus, genus *Platycnemis (P.pennipes)*.
Family Lestidae, only one genus, genus *Lestes (L.barbarus)*.
Suborder Anisoptera represented by 3 families, 5 genera and 7 species.
Family Cordulegastridae, only one genus, genus *Cordulegaster (C.bidentatus)*.
Family Libellulidae, there are 3 genera: genus *Sympetrum (S.sanguineum and S.depressiusculum),* genus *Orthetrum (O.albistylum and O. brunneum),* genus *Crocothemis (C. erythrea)*
Family Aeshnidae, only one genus, genus *Anax (A.imperator*)

ANALYSIS OF NUMBER AND FREQUENCIES OF SPECIES, GENERA AND FAMILIES

After determining individuals collected in the area of Korça, we conclude that the order Odonata in this area is represented by 16 species, 11 genera and 7 families. Suborder Zygoptera is represented by 9 species and 56.25% frequency, 6 genera and 54.54% frequency and by 4 families with 57.14% frequency. Suborder Anisoptera is represented by 7 species and 43.75% frequency, by 5 genera and frequency of 45.46% and 3 families and frequency of 42.86% (Table 1)

Table 1. Number and frequencies of species, genera and families by suborders

Suborder	Number of species	Frequency of species	Number of genera	Frequency of genera	Number of families	Frequency of families
Zygoptera	9	56.25%	6	54.54%	4	57.14%
Anisoptera	7	43.75%	5	45.46%	3	42.86%
Total	16	100%	11	100%	7	100%

ANALYSIS OF FAMILIES BY GENERA AND SPECIES
By analyzing families based on genera and species we have this distribution:

Table 2: Distribution of number and frequencies of species and genera by families

Family	Number of species	Frequency of species	Number of genera	Frequency of genera
Calopterygidae	2	12.50%	1	9.09%
Lestidae	1	6.25%	1	9.09%
Coenagrionidae	5	31.25%	3	27.27%
Platycnemididae	1	6.25%	1	9.09%
Cordulegastridae	1	6.25%	1	9.09%
Libellulidae	5	31.25%	3	27.27%
Aeshnidae	1	6.25%	1	9.09
Totali	16	100%	11	100%

From data analysis, the most represented species are Coenagrionidae and Libellulidae families with 5 species each or a frequency of 31.25 % of all species; Calopterygidae family with two species or 12.50 %; Lestidae, Platycnemididae, Cordulegastridae and Aeshnidae families are represented only by one specie or 6.25% frequency. According to the genus composition, Coenagrionidae and Libellulidae families are represented with more genera, each with 3 genera or 27.27%; Calopterygidae, Lestidae, Platycnemididae, Cordulegastridae and Aeshnidae families represented by 1 genus or 9.09% frequency.

ANALYSIS OF CONSTANT SPECIES

From the analysis we see that *Platycnemis pennipes*, collected at 7 stations has the highest constant of species, and 63.63% frequency, followed by *Ischnura elegans* with a frequency of 45.45% , collected at 5 stations and *Ischnura pumilio* with constant species 27.27% frequency , collected at 3 stations; other species have a lower constant and are collected at 1 or 2 stations.

Table 3. Number of Species by constant and the number of encountered stations

Constant species	Number of encountered stations	Number of species
63.63% A	7	1
45.45% B	5	1
27.27% C	3	1
18.18 D	2	5
9.09% E	1	8

By analyzing the number of species per constant species and the number of encountered stations (Table 3) we have the following results: with a costant of 63.63 % and collected at 7 stations we have one specie; with a constant of 45.45 % and collected at 5 stations we have one specie; with a constant of 27.27 % and collected at 3 stations, we have one specie; we have 5 species with a constant of 18.18 % and collected at 2 stations; and we have 8 species collected at 1 station with a constant of 9.09%.

Table 4. Full list of the Odonata species according to the stations and Albanian names

Nr.	Scientific name	Boboshticë	Cangoni	Dardhë	Drenovë	Maliq	Moravë	Rehovë	Tushemisht	Voskopojë	Zvezdë	Prespë e vogël	Common albanian name
1	Order Odonata												Pilivesë
1	Suborder Zygoptera												Vajzë flutureset
1	Family Calopterygidae												Pilivesat krahëgjera
1	Genus Calopteryx Leach, 1815												
1	*Calopteryx virgo* Linnaeus, 1758							+		+			Vajzë e bukur
2	*Calopteryx splendens* Harris, 1782	+									+		Vajzë e bukur me shirit
2	Family Lestidae												Vajzë flutureese e holla
2	Genus Lestes Leach, 1815												
3	*Lestes barbarus* Fabricius, 1798						+						Vajzë smeralde jugore
3	Family Platycnemididae												Vajzë flutureese shpinë bardhë
3	Genus Platyncemis Burmeister, 1839												
4	*Platycnemis pennipes* Pallas, 1771	+	+		+	+			+	+	+		Vajzë flutureese pendëblu
4	Family Coenagrionidae												Vajzë flutureese krahëngushtë
4	Genus Ischnura Charpentier, 1840												
5	*Ischnura elegans* Vander Linden, 1820	+			+						+	+	Vajzë flutureese bisht blu
6	*Ischnura pumilio* Charpentier, 1825	+			+								Vajzë flutureese e vogël e bukur
5	Genus Erythromma Charpentier, 1840												
7	*Erythromma viridulum* Charpentier, 1840	+											Vajzë flutureese e vogël sykuqe
8	*Erythromma lindenii* Selys, 1840	+											Vajzë flutureese e vogël syblu
6	Genus Enellagma Charpentier, 1840												
9	*Enellagma Cyathigerum* Charpentier, 1840	+											Vajzë flutureese blu
2	Suborder Anisoptera												
5	Family Cordulegastridae												Vajzë flutureese bishtdhëmbëzuar
7	Genus Cordulegaster Leach, 1815												
10	*Cordulegaster bidentatus* Selys, 1843			+			+						Vajzë flutureese unazëverdhë
6	Family Libellulidae												Pilivesa me vela
8	Genus Sympetrum Newman, 1833												
11	*Sympetrum depressiusculum* Selys, 1841		+										Hedhësi me njolla
12	*Sympetrum sanguineum*											+	Pilivesë livadhi

													kuq e blu
9	Genus Orthetrum												
13	*Orthetrum albistylum* Selys, 1848					+							Pilivesa shkumore bishtbardhë
14	*Orthetrum brunneum* Fonscolombe, 1837	+			+								Pilivesa shkumore e jugut
10	Genus Crocothemis Brauer, 1868												
15	*Crocothemis erythraea* Brulle, 1832	+										+	Vajzë fluturuese e kuqe e ndezur
7	Family Aeshnidae												
11	Genus Anax												
16	*Anax imperator* Leach, 1815											+	Pilivesa e madhe mbretërore

CONCLUSIONS

Odonata in Korça district are represented by 16 species, 11 genus and 7 families. The most represented suborder is Zygoptera with 9 species and frequency of 56.25 % and suborder Anisoptera with 7 species and a frequency of 43.75%. Most represented in the genera and species are Coenagrionidae and Libellulidae families each of them with 3 genera and a frequency of 27.27% and with 5 species and 31.25% frequency. The most represented station in species is Boboshtica, with 9 species. The stations with the smallest number of species are: Rehova, Tushemisht, Dardha which are represented by only 1 specie. Based on our research, the number of known odonata species in Korça area is 25 species, 8 of which are reported for the first time. These species are: *Lestes barbarus* Fabricius, 1798; *Enellagma cyathigerum* Charpentier, 1840; *Ischnura pumilio* Charpentier, 1825; *Orthetrum albistylum* Selys, 1848; *Orthetrum brunneum* Fonscolombe, 1837; *Crocothemis erythraea* Brulle, 1832; *Sympetrum depressiusculum* Selys, 1841 and *Anax imperator* Leach, 1815.

REFERENCES

Biggs, K. (2009) Field key to adult California Dragonflies (Odonata).
Corbet, P.S. (1962) A biology of Dragonflies. Quadrangle, Chicago.(Reprinted by E.W. Classey in 1983). Witherby, London.
Corbet P.S., (1999) Dragonflies: Behavior and Ecology of Odonata. Harly Books Colchester. Essex. New York.
Choate, P. (2000) Key to some families of odonata.
Silsby, J. (2001) Dragonflies of the world. Natural History Museum in association with CSIRO publishing, UK and Europe.
Dumon, H.J., Mertens, J., Miho, A. (1993) A contribution to the knowledge of the odonata of Albania. Opuscula Zoolgical Fluminensia. Casa d'Uros. Postfach 34 Ch-8896 Flumserberg/ Bergheim. Schewiz 113 (1993): 1-10.
Fraser, F.C. (1957) A reclassification of the order Odonata. R. Zool. Soc., NSE, Sydney: 121-132.
Halimi, E., Paparisto, A., Topi, D., Misja, K. (2011) Environmental Impact on Biodiversity and Habitats of Aquatic Insects from Shkumbin and Ishëm delta Rivers (Albania)**.** Journal of Environmental Protect and Ecology. ISSN 1311-5065. (Editorial Board & Impact Factor = 0.168). Vol. 12. Nr.4. pp: 1619-1627.
Kalkman, V.J. (2000) Records on the dragonfly fauna of northwestern Albania (Odonata). Libellula, 19 (1-2): 107-111.
Dijkstra, K.D. (2006) Field guide to the dragonflies of Britain and Europe. British Wildlife Publishing. UK
Murányi, D. (2007) Contribution to the Odonata fauna of Albania. Folia Entomologica Hungarica 68: 41-53.
Murányi, D., Kovács, T. (2013) Contribution of the Odonata fauna of Albania and Montenegro. Folia Historico Naturalia Musei Matraensis 37: 29-41.

PAPER 075

ISOTHERM AND KINETIC ANALYSIS OF ADSORPTION OF COBALT AT VAN PUMICE

Salih ALKAN[1], Ali Rıza KUL[2], Sevda OCAK[3] Veysel BENEK[4]

[1]Ordu University, Department of Chemistry,52000Ordu, Turkey;
[2]Yuzuncu Yil University, Vocational School of Health Care,65080,Van, Turkey;
[3]YuzuncuYıl University, Engineering-Architectures Faculty, Environmental Engineering Department, Van, Turkey;
[4]YuzuncuYıl University Department of Chemistry, 65080 Van, Turkey;

Email: sevdaocaktr@yahoo.com

ABSTRACT

This study was conducted by Van Pumice and $CoCl_2$ on pH = 5, one of the major physicochemical properties of the water in the adsorption mechanism of Co(II) concentrations (75 ppm, 100 ppm, 125 ppm) effect was investigated. The study includes an analysis of the 318 K temperature range. In this way, pH 5 Co(II) have been observed between different adsorption behavior Van pumices.

Key Words: Heavy Metals, Adsorption, Isotherm, Van Pumices, Thermodynamics

INTRODUCTION

Pumice is a volcanic rock which forms in volcanic activities and it is porous glassy, spongy, resistant to chemical and physical factors. (Sarıışık vd., 1998). Heat and sound insulation of pumice is very good because of high porosity. Its hardness is about 5-6 on the Mohs hardness scale and no crystal water exist in the structure. Chemical composition is 60-70% SiO_2, 13-15% Al_2O_3, Fe_2O_3 1-4%, 1-2% CaO, MgO 1-2%, 2-5% Na_2O, 3-4% K_2O and there are TiO_2, SO_3 and Cl in trace amounts. (İlhan vd., 1997; Tözüm, 2009). In fact, in terms of physical properties, the term of heavy metal is used for those of densities larger than 5 g/cm^3. More than sixty metals in this group, especially cadmium, chromium, iron, cobalt, copper, nickel, mercury and zinc are found in the earth, usually in stable compounds or silicates such as carbonate, oxide, silicate and sulfide. (Kahvecioğlu ve ark., 2003). Inhalation of air with cobalt dust and skin contact with cobalt salts cause poisoning. Inhaled cobalt powder cobalt is dissolved in lungs and mixed in blood and urine. Despite the absence of certain evidences that cobalt and cobalt compounds cause cancer in human beings, cobalt compounds are regarded as risky as a carcinogenic substances. In experiments on animals were found tumors on cobalt contained in the implanted in the regions, cobalt metal, it has proven cancer-causing compounds in water-soluble cobalt (Atanassova, 1999; Alacabey, 2014). Adsorption is a separation process which is based on transfer of atoms, ions and molecules in solution to an adsorbent surface. Adsorption stems from unbalanced intermolecular forces surface molecules in the absorbent. (Berkem ve Baykut, 1980; Sarıkaya, 1993). Since adsorption phenomenon occurs spontaneously at constant temperature and pressure, free enthalpy change (i.e. adsorption free enthalpy) is always negative during adsorption. (Sarıkaya, 1993; Çiçek, 2005).

2. EXPERIMENTAL WORKS

2.1. Adsorbents

Chemical composition of Van Pumices, which is used as adsorbent in this study is given in the table below.

Table 2.1. The Pumice used as adsorbent Chemical Components

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Loss on Ignition
Van Pumices	69.00	14.65	2.51	1.11	0.55	3.520	2.48	0.40	4.76

2.2. Used Chemicals

HCl was used to have solutions at pH 5. For the experiment, solutions were prepared at different concentrations (75 ppm, 100 ppm, 125 ppm) of cobalt.

2.3. Experimental Study

Heavy metal (Co) solutions of 75 ppm, 100 ppm, 125 ppm concentrations at pH 5 were prepared by shaking by Van Pumice at 45 ^{O}C temperature for different periods (5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 150, 180, 240 min).
All adsorption measurements were performed with TermoScientific ICE 300 Series AA.

3. RESULTS AND ASSESSMENTS

3.1. Effect of Concentration on Adsorption of Co (II) Solution on Van Pumices

To determine the effect of concentration on the adsorption capacity, concentration of solution was modified by using different solutions of the range of 75-125 ppm. Change in adsorptions of Co (II) onto Van Pumice by time for different concentrations are given on Figure 3.1, Figure 3.2 and Figure 3.3.

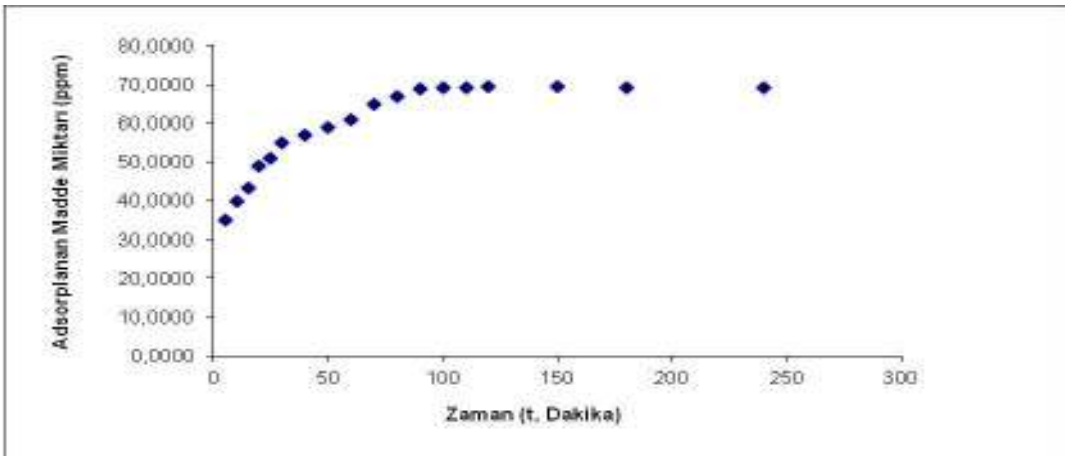


Figure 3.1. Change in adsorptions of Co (II) onto Van Pumice by time [Co(II), pH:5,C_1: 75ppm, T: 318K]

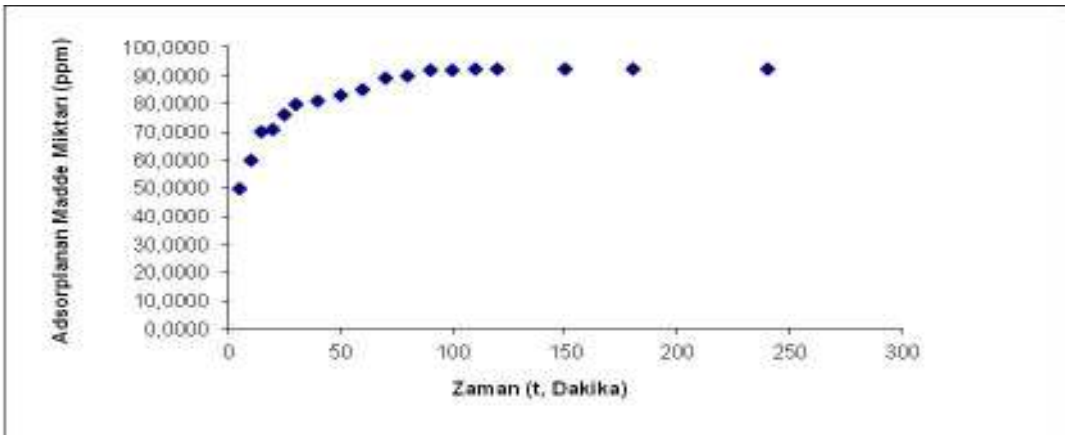


Figure 3.2. Change in adsorptions of Co (II) onto Van Pumice by time [Co(II), pH:5,C_2: 100ppm, T: 318K]

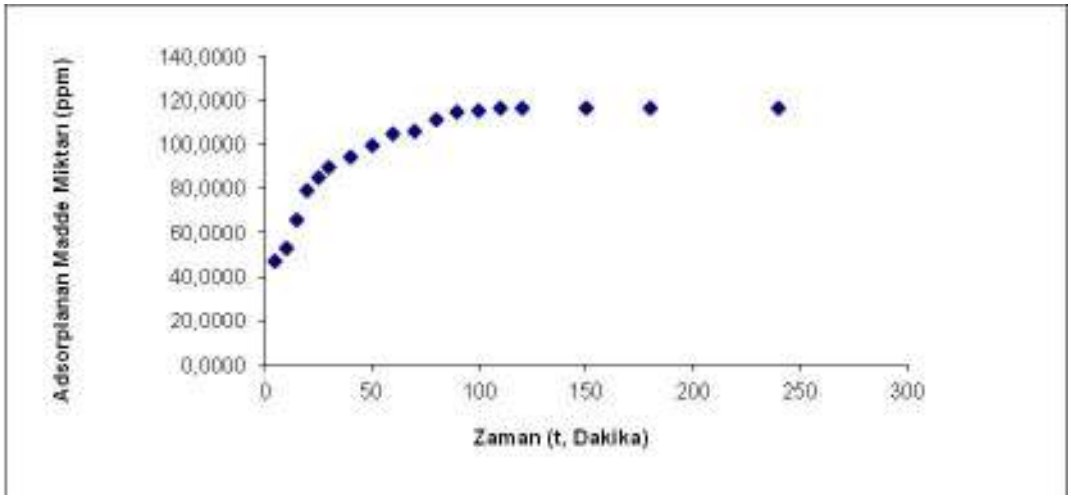


Figure 3.3. Change in adsorptions of Co (II) onto Van Pumice by time [Co(II), pH:5,C_3: 125ppm, T: 318K]

From Figures 3.1, 3.2 and 3.3 it is seen that adsorption increases with time and reaches equilibrium about 110 min.

3.2. Adsorption Isotherms

Isotherms are correlations between the amount of absorbed material (Ce) and the amount of substance adsorbed per gram in equilibrium (qe) at constant temperature. In short, it is the relationship between C_e and q_e. Here, Ce is amount of unadsorbed substance (mg/L), q_e amount of the substance adsorbed per gram (mg/g) in equilibrium.
Adsorption isotherms are required for studying equilibrium, finding capacity of adsorbent, determination for surface characteristics and assigning isotherms constant.
Experimental data were evaluated with Langmuir and Freundlich adsorptions models and Langmuir and Freundlich constants were determined by equalities 3.1 and 3.2 to find best model which is in agreement with experimental data.

Linear form of Langmuir equation is:

$$C_e/ q_e = 1/(Q_0. b) + C_e/ Q_0 \quad (3.1)$$

Where;
C_e: Amount of unabsorbed substance in solution (mg/L),
q_e: Amount of substance of adsorbed per gram of adsorbent (mg/g),
Q_0: Langmuir constant for expressing adsorption capacity (mg/g),
b: Langmuir constant for expressing adsorption energy (L/mg).

For calculating of Langmuir isotherms C_e/qe vs Ce graph is drawn. Slope of graph gives $1/Q_0$ while cut-off point is $1/b.Q_0$.

Linear form of Freundlich equation is:

$$\log q_e=\log K_f+n\log C_e \quad (3.2)$$

Where;
C_e: Amount of unabsorbed substance in solution (mg/L),
q_e: Amount of substance of adsorbed per gram of adsorbent (mg/g),
K_F: Adsorption capacity, calculated experimentally,
n: Adsorption strength.

K_F and n constants are gathered from Logqe vs logCe graph. Slope gives 1/n while cut-off point is $\ln K_F$.

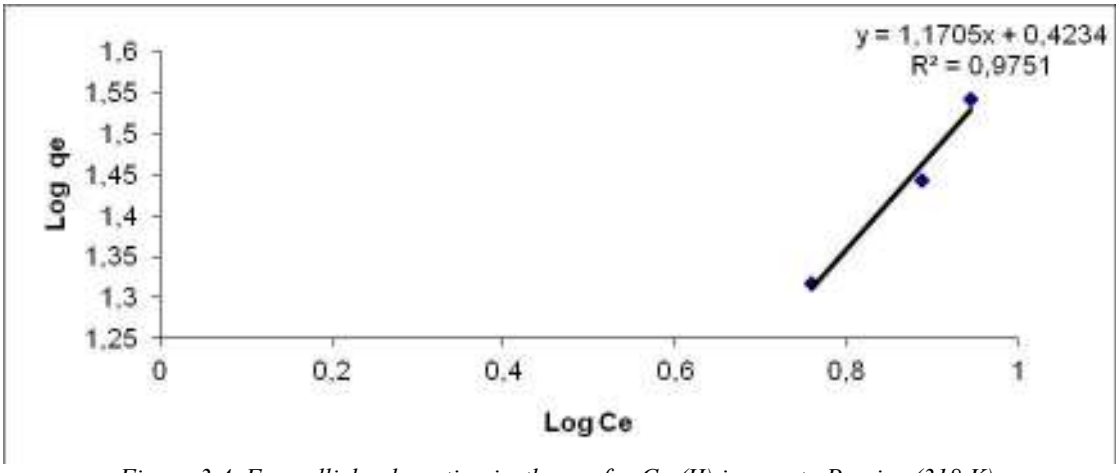


Figure 3.4. Freundlich adsorption isotherms for Co (II) ions onto Pumice (318 K).

Table 3.1. Calculated Langmuir and Freundlich parameters for adsorption of Co(II) ions on pumice.

T (K)	Langmuir			Freundlich		
	b (L/mg)	qm (mg/g)	R^2	n	K_F (mg/g)	R^2
318	-0.0210	-0.0067	0.5014	0.8543	1.5271	0.9751

Experimental data conforms Freundlich isotherm than Langmuir isotherm at 318 ^{0}K.

3.3. Adsorption Kinetics

Illumination of the mechanism of an events and the processes to be arranged are very important for interpretation of experimental data. Finding speed determining events of the process is essential. If adsorption kinetics is clear, then effective adsorbat-adsorbent contact time can be found. Kinetics is an important factor in understanding the adsorption process that affect the rate of adsorption steps.

Pseudo Fist-Order equation of rate, Lagergren equation:

$$\log (qe - qt) = \log qe - (k_1 / 2.303)\, t \qquad (3.3)$$

Where;
q_e: Amount of substance of adsorbed per gram of adsorbent at equilibrium (mg/g),
q_t: Amount of substance of adsorbed per gram of adsorbent at any time (mg/g),
k_1: Rate constant (dk^{-1}),
t: Contact time.

When log(qe-qt) vs t graph is drawn, slope gives k_1 and cut-off point is q_e.

Pseudo Second-Order rate equation

$$t / qt = [1 / k_2\, qe^2] + (1 / qe)\, t \qquad (3.4)$$

Here,
q_e: Amount of substance of adsorbed per gram of adsorbent at equilibrium (mg/g),
q_t: Amount of substance of adsorbed per gram of adsorbent at any time (mg/g),
k_2: Rate constant (g/mg.dk).
First adsorption rate is $h = k_2.qe^2$.
k_2 and theoretical qe values are calculated by slope and cut-off point of t/q_t vs t (time) graph.

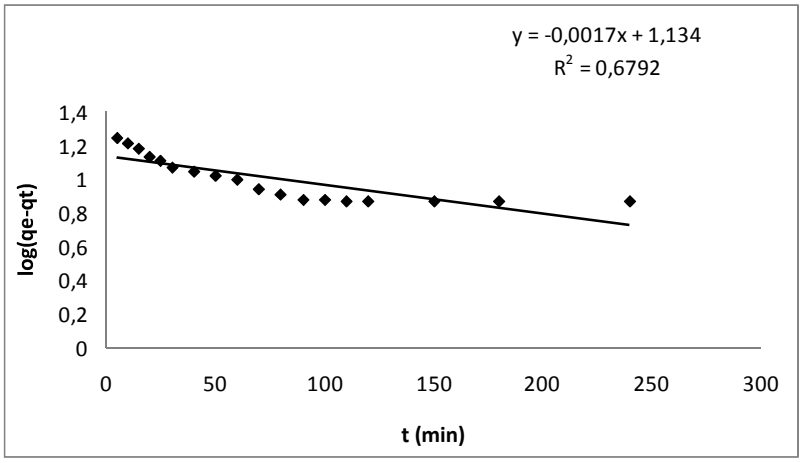


Figure 3.5. Approximated first order kinetics graph for adsorption of Co (II) ions (75 ppm, 318 K), on the Van Pumices.

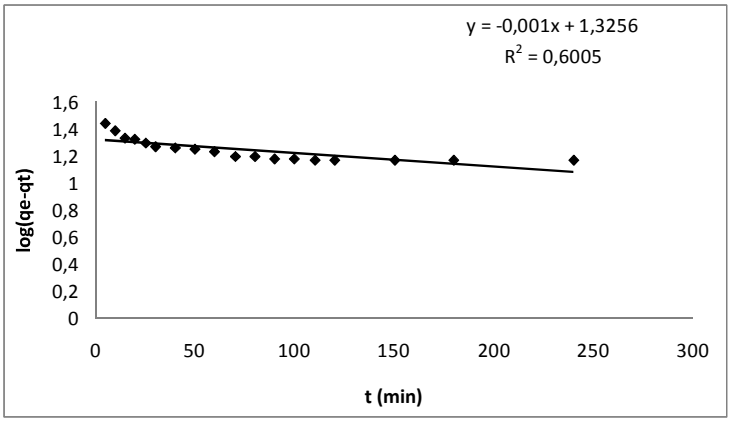


Figure 3.6. Approximated first order kinetics graph for adsorption of Co (II) ions (100 ppm, 318 K), on the Van Pumices.

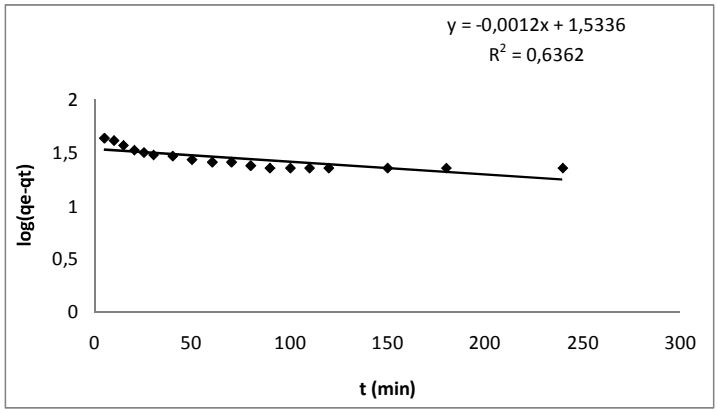


Figure 3.7. Approximated first order kinetics graph for adsorption of Co (II) ions (125 ppm, 318 K), on the Van Pumices.

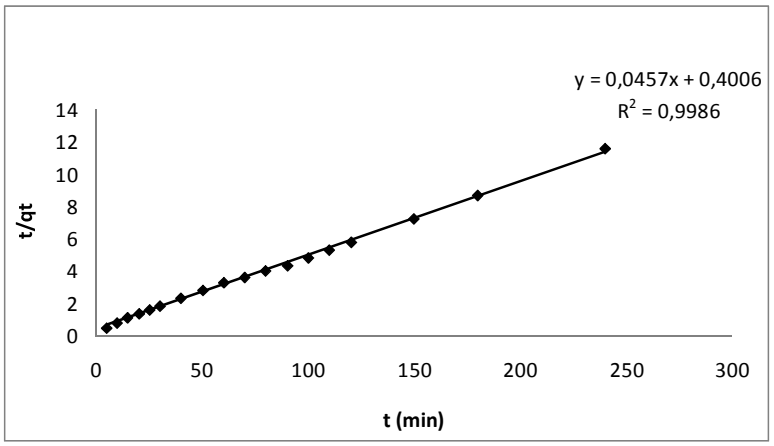


Figure 3.8. Approximated second order kinetics graph for adsorption of Co (II) ions (75 ppm, 318 K), on the Van Pumices.

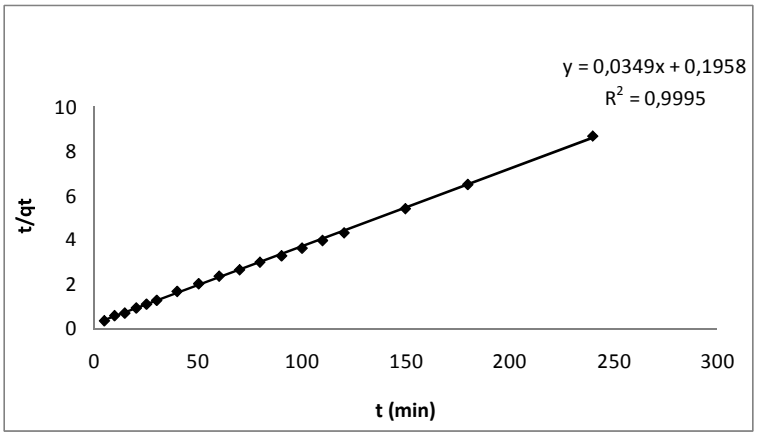


Figure 3.9. Approximated second order kinetics graph for adsorption of Co (II) ions (100 ppm, 318 K), on the Van Pumices.

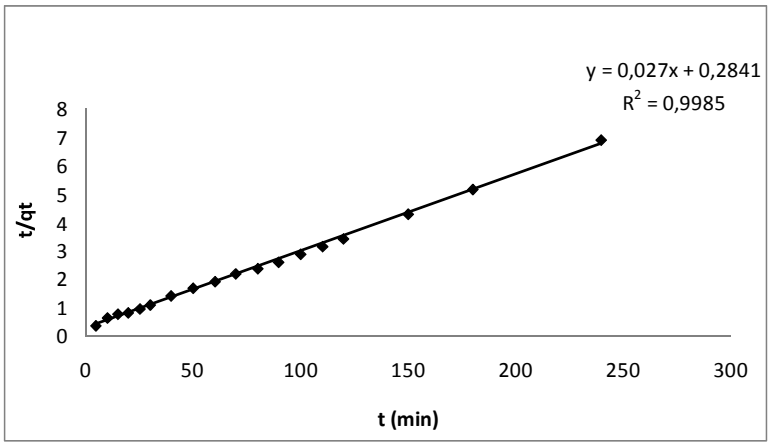


Figure 3.10. Approximated second order kinetics graph for adsorption of Co (II) ions (125 ppm, 318 K), on the Van Pumices.

3.4. Adsorption Thermodynamics

Gibbs free enthalpy (ΔG^o), adsorption entropy (ΔS^o) and adsorption enthalpy (ΔH^o) are very important for determining type of adsorption. They are calculated by (3.3), (3.4), (3.5), (3.6) equations, respectively.

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (3.3)$$

$\Delta G°$: Gibbs Free energy change (kJ/mol)
$\Delta H°$: Enthalpy change (kJ/mol)
ΔS^o : Entropy change (kJ/mol K)
T : The absolute temperature (Kelvin)

To find the Gibbs free energy of adsorption process conducted at a certain temperature, firstly equilibrium constant Kc, is calculated by equation 3.4.

$$K_c = C_a / C_e \quad (3.4)$$

K_c : Equilibrium constant
C_a : The concentration of material held by adsorbent material (mg/L)
C_e : Residual substance concentration in the solution (mg/L)

Kc vs C_0 graph is plotted and cut-off point, Kcº, is written in equality 3.7 to find Gibbs free energy of adsorption.

$$\Delta G^o = -R\ T\ \ln K_c^o \quad (3.5)$$

$$\ln Kc^o = (\ [\![\Delta S]\!]^o - [\![\Delta H]\!]^o)/ R\ x\ 1/T \quad (3.6)$$

R : Constant of Gas (8.314 J/mol K)

The slope of $\ln K_c^0$ vs 1/T graph, that ploted using equality 3.6, gives ΔH^0 and intersection point is ΔS^0. Positive values of ΔH^0 show endothermic adsorption, negative values of ΔG^0 shows spontaneous adsorption. In other words the applicability of the adsorption process can be understood by negative value of enthalpy and Gibbs free energy. Positive value of ΔS^0 means randomness shows the increase in at solid / solution interface (Kabak, 2008).

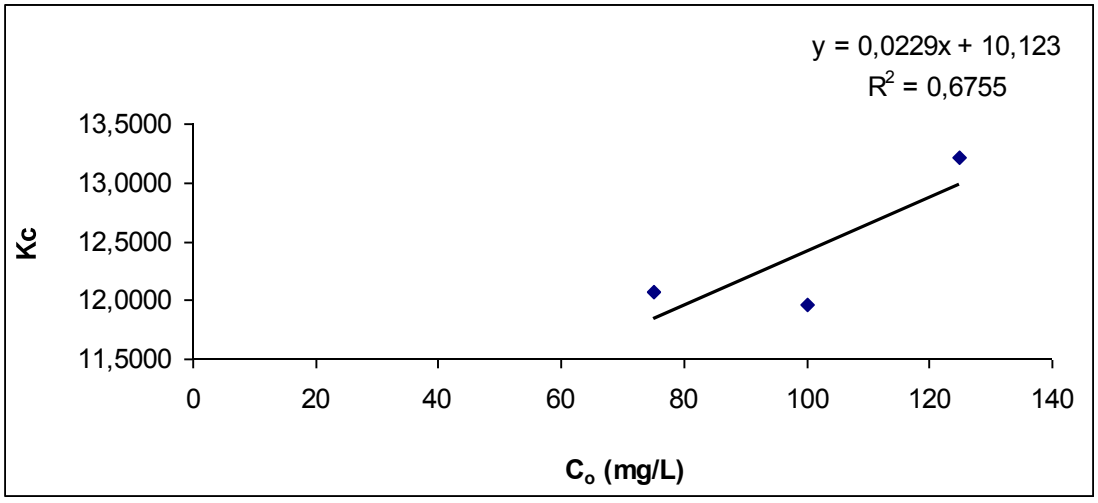


Figure 3.11. *Graph of Kc→C_0 for Co(II) ions at 318 K.*

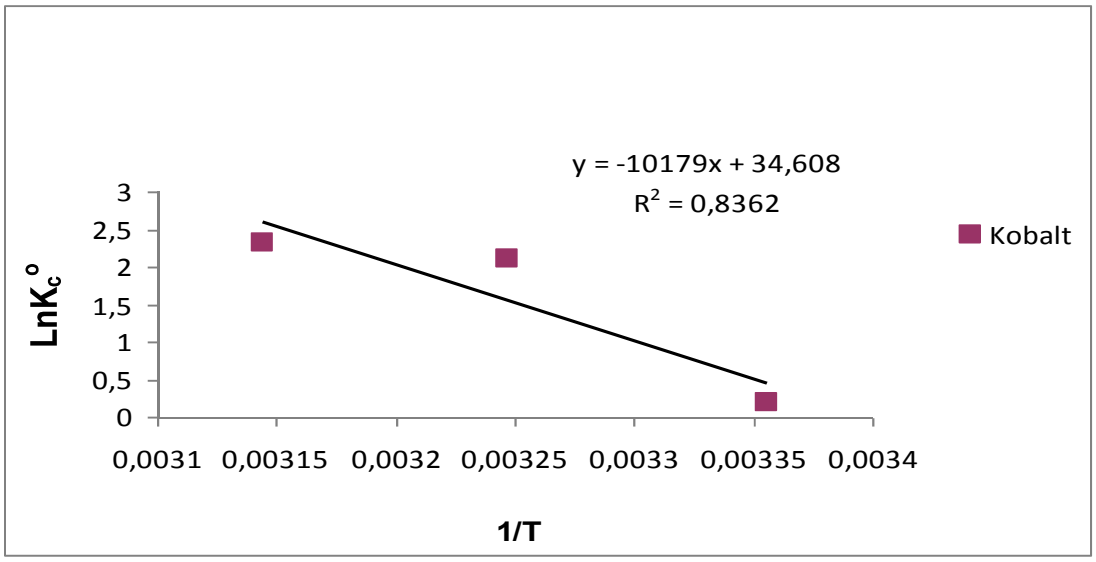


Figure 3.12. The graph of value lnKc^0 → 1/T for Co(II) ions.

Table 3.2. Calculated thermodynamic parameters of Co(II) ions on the pumices

Temp (K)	Kc°, Cons.	ΔG°, kJ/mol	ΔH°, kJ/mol	ΔS°, kJ/mol
318	10,123	-6,1200	-84,6282	0,2877

Negative value of ΔG° which was found by graphs shows that the adsorption is spontaneous.
Negative value of ΔH^0, that is a thermodynamic parameter for Co(II) ions on Van pumices means processes is exothermic.
Positive value of ΔS^0 indicates that during the sorption of cobalt solution and the irregularities increase at the interface of Van pumice.

RESULTS

Works for calculating Langmuir isotherms constant were done at pH=5. Correlation factor of Co(II) ions on Van pumices was calculated as R^2> 0.5014 at T = 318 K (See. Table 3.1). Freundlich isotherms constant was also calculated at same conditions. From graphs for correlation factor of Co(II) ions on Van pumices, for Freundlich it was found R^2> 0.9751 (See. Table 3.1). When correlation factors are examined, it is seen that sorption is not linear and it is in compliance with Freundlich adsorption isotherms.
Negative value of ΔH^0, that is a thermodynamic parameters for Co(II) ions on Van pumices means processes is exothermic (See. Table 3.2).
Positive value of ΔS^0 indicates that during the sorption of cobalt solution and Van pumice the irregularities increase at the interface. Entalpic and entropic contribution is caused by sorption processes that explain whether this is a spontaneous reaction (See. Table 3.2).
Negative values of Gibbs free enthalpy (ΔG) shows that adsorption occurs spontaneously on Van pumices (See. Table 3.2).

CONCLUSIONS

Adsorption increases in cobalt ion solution with Van pumice by increasing contact time. That increase is fast in first minutes, and then the increase slows down which is normal in adsorption process. The information in the literature supports this situation (Koyuncu ve ark., 2005; Çalışkan ve ark., 2005; Çokadar ve ark., 2003; Abollino ve ark., 2003; Akyüz ve ark., 2001; Kul, 1999).
The pH of the medium in adsorption processes, as known, is a very important factor. Because, the pH has an impact on the adsorbent surface charge and degree of ionization of adsorbent. In our study The effect of the different heavy

metals sorption on Van Pumice at pH = 5 were investigated. The work can be repeated at different pH for more clarity on the sorption process.

REFERENCES

Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., Mentasti, E., 2003. Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. *Water Research,* 37 (7) : 1619-1627.

Akyüz, S., Akyüz, T., Ozer N.M., 2001. FT-IR spectroscopic investigations of benzidine and bipyridyls adsorbed on diatomite form Anatolia. *Journal of Molecular Structure,* 565-566: 493-496.

Alacabey, İ., 2014. *Natural and Activated Van lake sediment (bottom sludge) isotherms of some heavy metals Adsorspsiyon of samples and Thermodynamic Analysis (doctoral thesis)* .Yüzüncü Yil University, Institute of Science, Ph.D. Thesis, Van.

Atanassova, I., 1999. Competitive effect of copper, zinc, cadmium and nickel on ion adsorption and desorption by soil clays. *Water, Air and Soil Pollutio*, 113 : 115 - 125.

Berkem , A.R., Baykut, S, 1980. *Physical Chemistry,* Istanbul University Publications, No: 42, Istanbul. p: 1111.

Çiçek, H., 2005. *The removal of phenol from waste water Obtained from Sugar Beet Pulp Using Active Carbon (*M.Sc.*)*. Firat University., Institute of Science and Technology, Elazig, 114 p.

Çalışkan, E., 2005. *Asi River Water, Sediment and catfish (Clarias gariepinus Burchell, 1822) t Investigation of Heavy Metal Accumulation* (M.Sc.). Mustafa Kemal University, Institute of Science and Technology, Hatay.

Çokadar, H., İleri R., Ateş, A., İzgi B.,2003. Removing the Nickel (II) ion in aqueous medium, granular activated carbon (GAK). *Çev-Kor Mag.,* 12,46 : 38-42.

İlhan, S., Nurbaş, M., Ekmekçi, S., Özdag, H., 1997. Use a pumice biotechnology as adsorbent, I. Isparta pumice Symposium, 26-28 June 1997, 39-46.

Kabak, H., 2008. *Live Activated Sludge of the biomass used some Medicinal Investigation of Adsorption Property by (doctoral thesis)*. Cukurova University, Graduate School of Science, Environmental Engineering Department, Adana.

Kahvecioğlu Ö., Kartal G., Güven A., Timur S., 2003. Metals Environmental Impacts. *Tmmob Metallurgical Engineers Journal*, 136: 47 – 53.

Koyuncu, H., Kul, A., Ceylan, H., Yıldız, N., Çalımlı, A., 2005. 3-Hydroxy Benzaldehyde natural and Activated bentonite on the Adsorption Equilibrium Studies. *12.Ulusal Clay Symposium Proceedings*. 5 to 9 September 2005, the Van. 243-244.

Kul, A.R., 1999. *Investigation on the commercial activated carbon adsorption of some organic substances in solution environment,* (doctoral thesis). Centenary University, Institute of Science, PhD Thesis, Van.

Sarıışık, A., Tozaçan, B., Davraz, M., Uğur, İ., Çankiran, O., 1998. *Pumice Technology,* S.D.Ü. Eng. Fak.-Isbaş, Isparta

Sarıkaya, Y., 1993. *Fizikokimya*, Gazi Bookstore, Ankara, s.633-653.

Tözüm, S., 2009. *Wastewater from olive pumice (Karasu) Adsorption of pollutants removal* (Master Thesis). Süleyman Demirel University, Science institute, Isparta.

PAPER 076

COPPER REMOVAL FROM WASTEWATER USING NATURAL PUMICE

Ali Rıza KUL[1], Salih ALKAN [2], Sevda OCAK[3], Veysel BENEK[4]

[1] *Yuzuncu Yil University, Vocational School of Health Care, 65080, Van, Turkey;*
[2] *Ordu University, Department of Chemistry, 52000, Ordu, Turkey;*
[3]*Yuzuncu Yil University, Engineering-Architecture Faculty, Environmental Engineering Department, 65080, Van, Turkey;*
[4]*Yuzuncu Yil University, Department of Chemistry, 65080 Van, Turkey;*

Email: sevdaocaktr@yahoo.com

ABSTRACT

This study was conducted on the pumice supplied from the Van Province, Turkey. The physicochemical properties of $CuCl_2$ at pH 5 were studied and the analyses were performed at a temperature of 308 °K at various concentrations (75 ppm, 100 ppm, 125 ppm) of Cu(II). In this study, we aimed to investigate the adsorption behavior between the Van pumice and Cu(II).

Key words: Heavy Metals, Adsorption, Isotherm, Van Pumice, Thermodynamics

INTRODUCTION

The word “Pumice” comes from Italian. However, it is named differently in other languages. It is termed "Ponce" in French, whereas in English, "Pumice" is used for the medium-grained form and "pumicite" for the naturally fine-grained form. In German, the coarser form of the rock is called "Bimstein" and the form with small grains is called “Bims”. In Turkish, however, it is known with three names: "Süngertaşı", "Köpüktaşı" and "Topuktaşı" (meaning, “spongerock”, “foamrock”, and “heelrock”, respectively) (Çevikbaş and İlgün, 1997).
During the formation of pumice, due to the rapid exsolution of gases and sudden cooling process, numerous pores at varying sizes occur in the body of the rock. Among these pores, particularly the tiny ones, there occur innumerable bubbles which contain translucent bubble walls. Due to these properties, pumice is a regarded as a good adsorbent (Bardakçı and Çiçek, 2005; Tözüm, 2009).
Acidic magma is more viscous and contains higher concentrations of silica compared to basic magma. Acidic magma is solid at the temperatures at which basic magma is liquid. Pumice is created when highly pressurized rock is violently ejected from a volcano, and the unusual foamy configuration of pumice happens because of simultaneous rapid cooling and rapid depressurization (Rittmann, 1976).
The term “heavy metal” is used for metals with a density greater than 5 g/cm^3 in terms of physical properties. Heavy metals are mainly released by production plants such as cement factories, iron and steel plants, thermal power plants, glass factories, and waste and mud incineration plants (Kahvecioğlu et al., 2003).
Copper is an essential element for living things (Stern et al. 2007). Copper, which has been known since 5,000 B.C., takes its name from the Latin word for Cyprus (*aescyprium*, *cyprium* and later *cuprum*) and it is one of the two elements that do not appear in metallic color in atmospheric conditions (Kartal et al. 2004). The impact of copper on plants and living beings depends on the size and chemical form of the being. Copper can be poisonous for small and simple structures, whereas it is the basic structural components for large creatures (Kartal et al. 2004).
Acute copper poisoning is a rare occurrence. Copper poisoning generally occurs from the ingestion of oxidized copper through acid foods cooked in uncoated copper cookware, or from the deliberate ingestion of copper salts, which is known as “Bakır Çalığı’’ in Turkish (meaning, “verdigris poisoning”) (Kartal et al. 2004; Dağhan, 2011).
Adsorption is a dissolution process based on the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. Adsorption occurs when the forces between the surface molecules of the adsorbent are not equivalent (Berkem and Baykut, 1980; Sarıkaya, 1993). Because the adsorption phenomenon occurs spontaneously at constant temperature and constant pressure, adsorption enthalpy released during the adsorption enthalpy change is always a negative sign (Sarıkaya, 1993; Çiçek, 2005).

MATERIAL AND METHODS

1. Adsorbents

The Van pumice was used as the adsorbent. Table 1 presents the chemical composition of the Van Pumice.

Table 1. Chemical Components of Van Pumice

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Loss on Ignition
Van Pumice	69.00	14.65	2.51	1.11	0.55	3.520	2.48	0.40	4.76

2. Chemicals Used

HCI was used in order to adjust the solutions at pH 5. For the experiment, the solutions of Cu(II) were prepared at different concentrations (75 ppm, 100 ppm, 125 ppm).

3. Experimental Studies

After the solutions were prepared at 75 ppm, 100 ppm, 125 ppm concentrations and at pH 5, they were shaken at 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 150, 180, 240 min and were centrifuged and then stored in a dark cool place.

All the adsorption measurements were performed with a TermoScientific ICE 300 Series AA spectrometer.

RESULTS

1. The Effect of Concentrations on the Cu (II) Adsorption with the Pumice

Various concentrations ranging between 75-125 ppm were used in order to determine the effect of concentration on the adsorption capacity. The changes in the Cu(II) adsorption resulting from various pumice concentrations are given in Figures 1,2, and 3.

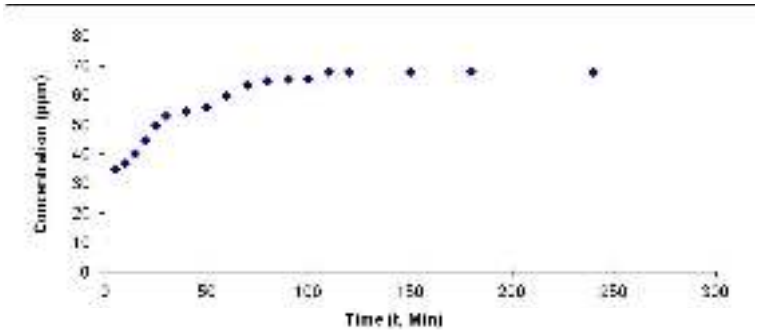


Figure 1. Cu(II) ions by adsorption on temporal changes of Van Pumice [Cu(II), pH:5,C_1: 75ppm, T: 308K]

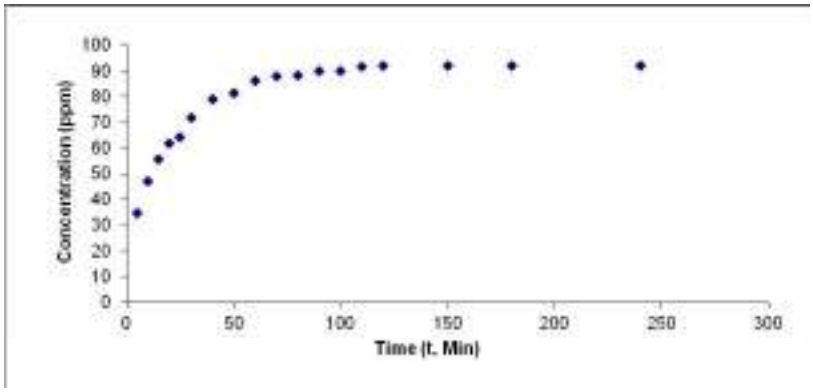


Figure 2. Cu(II) ions by adsorption on temporal changes of Van Pumice [Cu(II), pH:5,C_2: 100ppm, T: 308K]

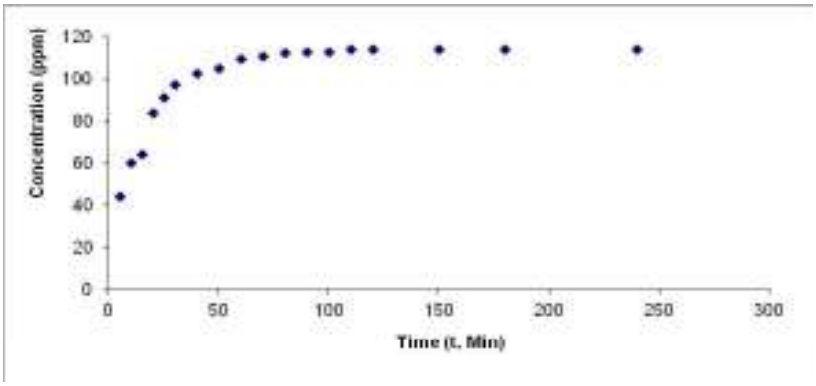


Figure 3. Cu(II) ions by adsorption on temporal changes of Van Pumice [Cu(II), pH:5,C_3: 125ppm, T: 308K]

2. Adsorption Isotherms

Isotherm is the correlation between the amount (Ce) of substance adsorbed by the adsorbent (pumice) and the amount of substance adsorbed per gram at equilibrium (qe) at constant temperature. In brief, it is the relationship between C_e and q_e, where Ce is the amount of the unadsorbed substance (mg/L) and q_e is the amount of the substance at equilibrium adsorbed per gram (mg/g). Adsorption isotherms are required for performing equilibrium studies, calculating the capacity of the adsorbent, determining the surface characteristics, and assigning the adsorption isotherm constants. Experimental data were evaluated through the Langmuir and Freundlich adsorption models and the Langmuir and Freundlich constants were determined using the equations 3.1 and 3.2. Moreover, an analysis was made to find out which model works better with the experimental data of the study.

Linear form of Langmuir equation;

$$C_e/ q_e = 1/(Q_0. b) + C_e/ Q_0 \quad (3.1)$$

Where;
C_e: Amount of unadsorbed substance in solution (mg/L),
q_e: Amount of adsorbed substance per unit (mg/g),
Q_0: Langmuir constant expressing the adsorption capacity (mg/g),
b: Langmuir constant expressing the adsorption energy (L/mg).

For the calculation of Langmuir isotherm, a graph was plotted against C_e/qe versus Ce. In this graph, the slope yields $1/Q_0$ and the cut-off point yields $1/b.Q_0$.

Linear form of Freundlich equation;

$$\log q_e=\log K_f+n\log C_e \quad (3.2)$$

Where;

C_e: Amount of unadsorbed substance in solution at equilibrium (mg/L),
q_e: Amount of substance adsorbed per unit at equilibrium (mg/g),
K_F: Adsorption capacity calculated experimentally,
n: Adsorption strength

The graph plotted against logqe versus C_e yields the K_F and n constants. The slope yields the value of 1/n and the cut-off point yields the value of $\ln K_F$.

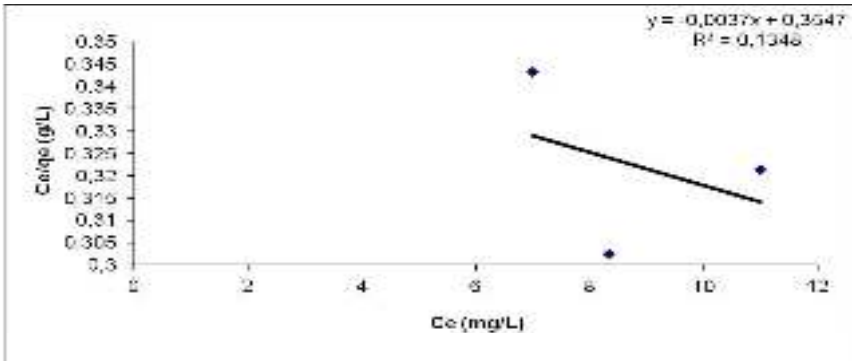


Figure 4. Langmuir adsorption isotherms for Pumice on Cu(II) ions (308 K).

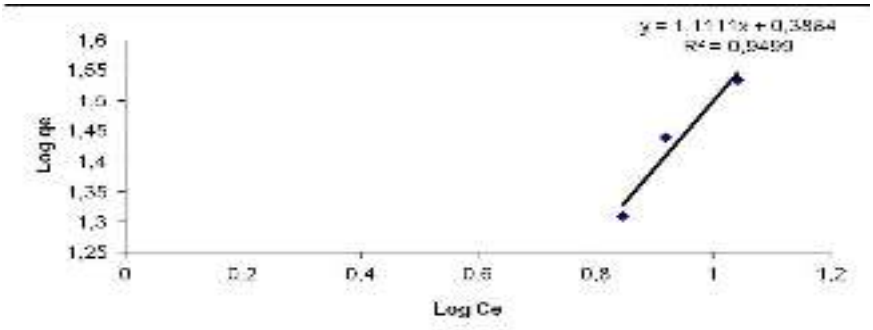


Figure 5. Freundlich adsorption isotherms for Pumice on Cu(II) ions (308 K).

Table 2. Calculated Langmuir and Freundlich parameters for adsorption Cu(II) ions on pumice.

T (K)	Langmuir			Freundlich		
	b (L/mg)	qm (mg/g)	R^2	n	K_F (mg/g)	R^2
308	-0.0104	-270.2703	0.1311	0.9000	1.4746	0.9499

The tables suggest that the experimental data are more consistent with the Freundlich isotherm than with Langmuir isotherm at 308 °K.

3. Adsorption Kinetics

An elucidation of the mechanism of events and interpretation of experimental data for the processes to be designed accordingly is highly important. To achieve this, a step should be designed to define the speed of the event. Once the adsorption kinetics are defined, the active adsorbate-adsorbent contact time, *i.e.* retention time, is calculated. Kinetics is an important step for understanding the adsorption steps affecting the rate of adsorption process.
Pseudo First-Order rate equation

$$\log (qe - qt) = \log qe - (k_1 / 2.303)\, t \quad (3.3)$$

Where;

q_e: Amount of substance adsorbed per gram of adsorbent at equilibrium (mg/g),
q_t: Amount of substance adsorbed per gram of adsorbent at any time (mg/g),
k_1: The rate constant (dk^{-1}),
t: Contact time.

In the graph plotted against log (qe-qt) versus t, the slope yields k_1 and the cut-off point yields the theoretical calculation of q_e.
Pseudo Second-Order rate equation

$$t / qt = [1 / k_2 qe^2] + (1 / qe) t \quad (3.4)$$

Where,
q_e: Amount of substance adsorbed per gram of adsorbent at equilibrium (mg/g),
q_t: Amount of substance adsorbed per gram of adsorbent at any time (mg/g),
k_2: The rate constant (g/mg.dk).

First adsorption rate is $h = k_2.qe^2$.

The rate constant, k_2, and the theoretical value of qe are calculated through the slope and cut-off point on the graph plotted against t/q_t versus t (time).

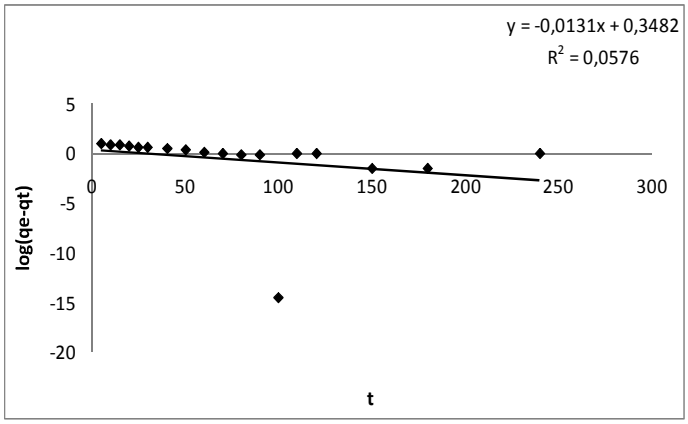


Figure 6. Kinetics of First Order Effects of Cu(II) ions (75 ppm, 308 K), on the Van Pumice for the Adsorption

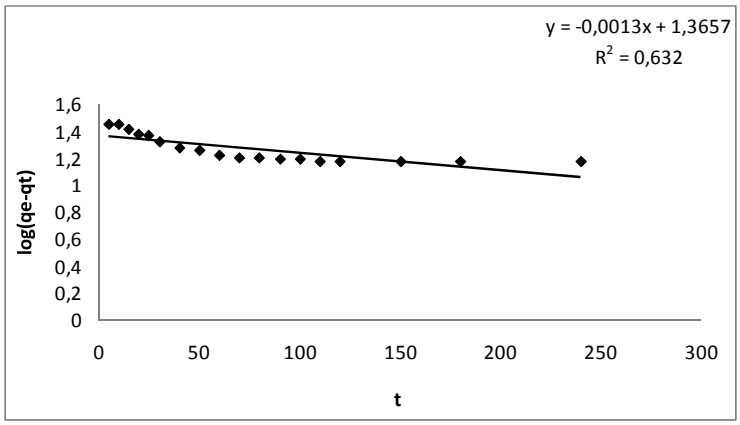


Figure 7. Kinetics of First Order Effects of Cu(II) ions (100 ppm, 308 K), on the Van Pumice for the Adsorption

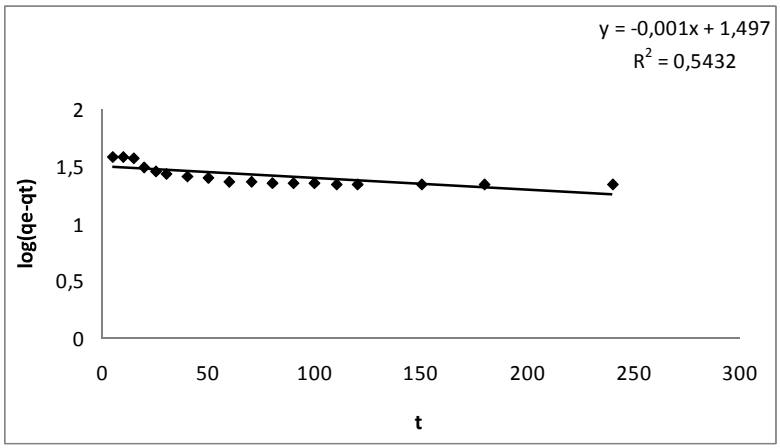


Figure .8. Kinetics of First Order Effects of Cu(II) ions (125 ppm, 308 K), on the Van Pumice for the Adsorption

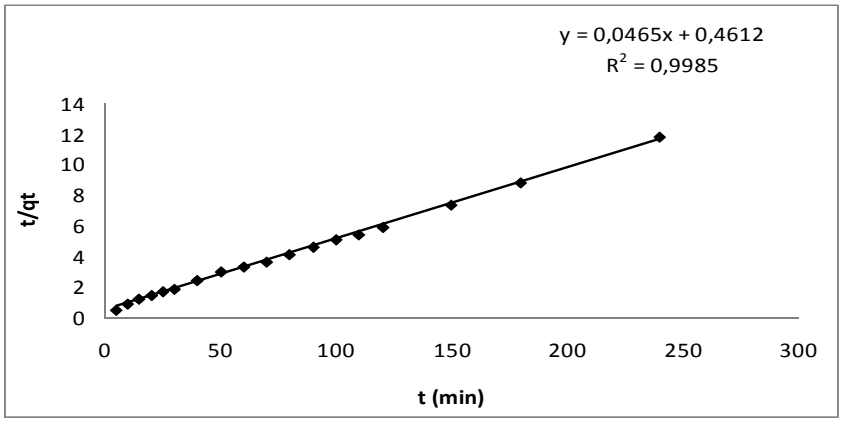


Figure .9. Kinetics of Second Order Effects of Cu(II) ions (75 ppm, 308 K), on the Van Pumice for the Adsorption

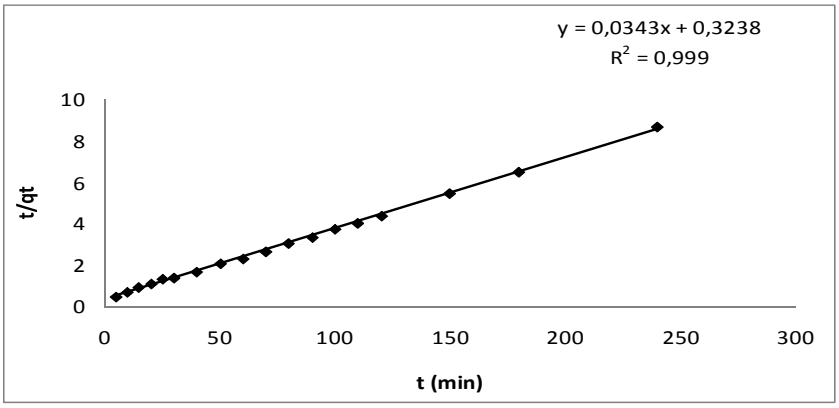


Figure 10. Kinetics of Second Order Effects of Cu(II) ions (100 ppm, 308 K), on the Van Pumice for the Adsorption

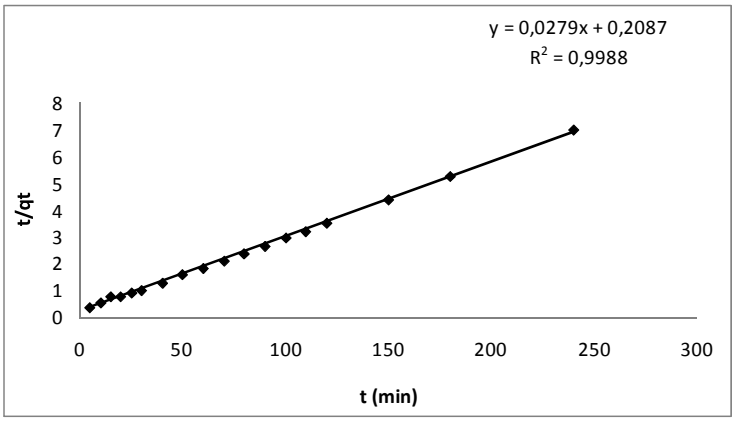


Figure 11. Kinetics of Second Order Effects of Cu(II) ions (125 ppm, 308 K), on the Van Pumice for the Adsorption

4. Adsorption Thermodynamics

Gibbs free enthalpy (ΔG^o), adsorption entropy (ΔS^o), and adsorption enthalpy (ΔH^o) are very important for the determination of the type of adsorption. These values are calculated using the equations 3.5, 3.6, 3.7, and 3.8.

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (3.5)$$

$\Delta G°$: Free energy change, Gibbs free energy (kJ/mol)
$\Delta H°$: Enthalpy change (kJ/mol)
ΔS^o: Entropy change (kJ/mol K)
T: The absolute temperature (Kelvin)

To find the Gibbs free energy of adsorption process at a certain temperature, firstly the equilibrium constant, Kc, is calculated by using the equation 3.6.

$$K_c = C_a / C_e \qquad (3.6)$$

K_c: Equilibrium constant
C_a: The concentration of the substance detained by the adsorbent (mg/L)
C_e: The concentration of the substance remained in the solution (mg/L)

A graph is plotted against the initial concentrations of Kc C_0. When the cut-off point of the graph (Kc^o) is placed onto its location on the equation 3.7, it yields the Gibbs free energy of adsorption.

$$\Delta G^o = -R\ T\ \ln K_c^o \quad (3.7)$$

$$\ln Kc^o = (\ [\![\Delta S]\!]^o - [\![\Delta H]\!]^o)/\ R\ x\ 1/T \qquad (3.8)$$

R : Constant of Gas (8.314 J/mol K)

On the equation 3.8, when the slope which occurs when the $\ln K_c^0$ is plotted against 1/T, it yields the ΔH^0 and the cut-off value of ΔS^0. Positive values of ΔH^0 show endothermic adsorption and the negative values show exothermic adsorption. Also, the negative values of ΔG^0 show spontaneous adsorption. In other words, the applicability of the adsorption process is dependent on the negative values of enthalpy and Gibbs free energy. Positive values of ΔS^0 indicate an increase in the randomness at the solid/solution interface (Kabak, 2008).

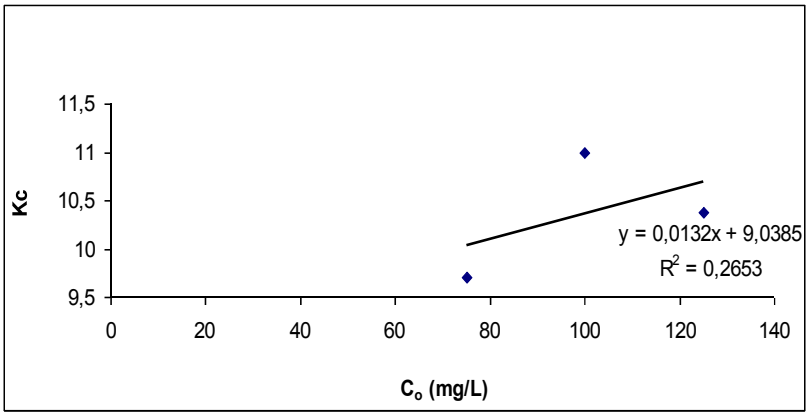


Figure 12. Kc→C_0 of Cu(II) ions at 308 K.

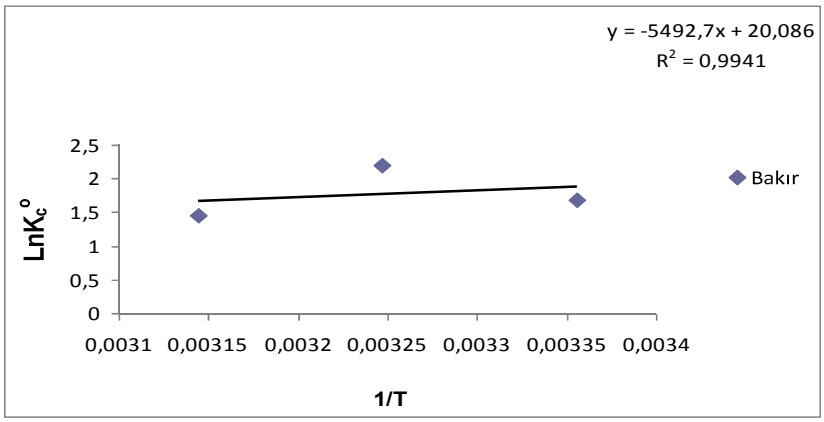


Figure 13. Value of $lnKc^0$→ 1/T for Cu(II) ions.

Table 3. Calculated thermodynamic parameters of Cu(II) ions on the pumice

Temperature (K)	Kc°, Constant	ΔG°, kJ/mol	ΔH°, kJ/mol	ΔS°, kJ/mol
308	9,0385	-5,6374	-45,6663	0,1670

Negative values of ΔG°, which are calculated with the help of graphs, indicate that the adsorption is spontaneous. Negative values of ΔH^0 indicate that the process is exothermic. Positive values of ΔS^0 indicate an increase in the irregularities at the interface between the Cu(II) solution and the pumice.

CONCLUSIONS

Adsorption of Cu(II) ions on the Van pumice at 35 °C and different concentrations (75 ppm, 100 ppm, 125ppm) was calculated. Retention time is the characteristic time it takes for the adsorbed substance to reach the constant value, and previous studies have reported the mean retention time as ~110 min.

It was revealed that the effectivity of adsorption was affected by the concentrations of Cu(II) ions and the stirring times.

The graphs for the calculation of the isotherm constants were plotted at pH 5. For the Langmuir model, the correlation factor of Cu(II) ions on the pumice was calculated as R^2> 0.1348 at T = 308 K (See Table 3.1). Under the same conditions, the Freundlich isotherm constants were calculated as R^2> 0.9499 at T = 308 K (See Table 2). When

the correlation factors were analyzed, it was revealed that the sorption of Cu(II) on the pumice was more consistent with the Freundlich adsorption isotherm.

The negative values of ΔH^0, which was a thermodynamic parameters for Cu(II) ions on the pumice, indicated that the process is exothermic (See Table 3).

The positive values of ΔS^0 indicated an increase in the irregularities at the interface between the Cu(II) solution and the pumice during sorption. The processes of sorption were aided by enthalpic and entropic contributions, which indicated whether the reaction was spontaneous (See Table 3).

Negative values of Gibbs free enthalpy (ΔG^0) revealed that the adsorption of the pumice was spontaneous (See Table 3).

The increase in the time of the contact between the solution of Cu(II) ions and the pumice generally led to an increase in the adsorption process. Also, the adsorption process was increased in proportion to the stirring time. This increase was initially faster but later remained stable, which is an expectable occurrence in the adsorption process. These results are consistent with the findings in the literature (Koyuncu et al., 2005; Çalışkan et al., 2005; Çokadar et al., 2003; Abollino et al., 2003; Akyüz et al., 2001; Kul, 1999).

The pH of the medium in adsorption processes, as is known, is a very important factor, because the pH has an impact on the adsorbent surface charge and the degree of ionization of the adsorbent.

REFERENCES

Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., Mentasti, E., 2003. Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances.Water Research,37 (7) : 1619-1627.

Akyüz, S., Akyüz, T., Ozer N.M., 2001. FT-IR spectroscopic investigations of benzidine and bipyridyls adsorbed on diatomite form Anatolia. Journal of Molecular Structure, 565-566: 493-496.

Bardakçı, B., Çiçek, E., 2005. Use the adsorption of radioactive waste of Isparta Pumice. Türkiye Pumice Symposium and Exhibition, 15 to 17 September 2005, the Isparta, 335-338.

Berkem , A.R., Baykut, S, 1980. Physical Chemistry, Istanbul University Publications, No: 42, Istanbul. p: 1111.

Çalışkan, E., 2005. Asi River Water, Sediment and catfish (Clarias gariepinus Burchell, 1822) t Investigation of Heavy Metal Accumulation (M.Sc.). Mustafa Kemal University, Institute of Science and Technology, Hatay.

Çevikbaş, A., İlgün, F., 1997. Geology and Economy of Turkey Pumice bed. I. Isparta pumice Symposium, 26 to 28 June 1997 Isparta, 13-18.

Çiçek, H., 2005. The removal of phenol from waste water Obtained from Sugar Beet Pulp Using Active Carbon (M.Sc.). Firat University., Institute of Science and Technology, Elazig, 114 p.

Çokadar, H., İleri R., Ateş, A., İzgi B.,2003. Removing the Nickel (II) ion in aqueous medium, granular activated carbon (GAK). Çev-Kor Mag., 12,46 : 38-42.

Dağhan, H., (2011). Human Health Effects of Heavy Metal Pollution on Natural Resources. MKU Faculty of Agriculture Journal, 16(2):15-25.

Kabak, H., 2008. Live Activated Sludge of the biomass used some Medicinal Investigation of Adsorption Property by (doctoral thesis). Cukurova University, Graduate School of Science, Environmental Engineering Department, Adana.

Kahvecioğlu Ö., Kartal G., Güven A., Timur S., 2003. Metals Environmental Impacts. Tmmob Metallurgical Engineers Journal, 136: 47 – 53.

Kartal G., A. Güven, Ö. Kahvecioğlu and S. Timur, 2004. Metals Environmental Impacts-II. TMMOB Metallurgical Engineers Journal, Number:137:46-531. http://www.metalurji.org.tr/dergi/dergi137/d137_4651.pdf

Koyuncu, H., Kul, A., Ceylan, H., Yıldız, N., Çalımlı, A., 2005. 3-Hydroxy Benzaldehyde natural and Activated bentonite on the Adsorption Equilibrium Studies. 12.Ulusal Clay Symposium Proceedings. 5 to 9 September 2005, the Van. 243-244.

Kul, A.R., 1999. Investigation on the commercial activated carbon adsorption of some organic substances in solution environment, (doctoral thesis). Centenary University, Institute of Science, PhD Thesis, Van.

Rittmann A. L., 1976, Volcanoes, Orbis Publishing, London.

Sarıkaya, Y., 1993. Fizikokimya, Gazi Bookstore, Ankara, s.633-653.

Stern, B.R., M. Solioz, D. Krewski, P. Aggett, T.C. Aw, S. Baker, K. Crump, M. Dourson,L. Haber, R. Hertzberg, C. Keen, B. Meek, L. Rudenko, R. Schoeny, W. Slob, and T.Starr, 2007. Copper and Human Health: Biochemistry, Genetics, and Strategies for Modeling Dose-response Relationships. J of Toxicol and Environ Health B CritRev., Apr-May;10(3):157-222.

Tözüm, S., 2009. Wastewater from olive pumice (Karasu) Adsorption of pollutants removal (Master Thesis). Süleyman Demirel University, Science institute, Isparta.

PAPER 080

DETERMINE OF CONCENTRATION OF THE IODINE IN THE SALT IN SOME DISTRICTS OF ALBANIA

Enkeleda Kadiu*, Jolanda Hyskaj, Entela Bushi*

*Department of Health and Environment, Institute of Public Health, Tirana, Albania;

Email: ledakadiu@hotmail.com

ABSTRACT

Objective: To determine the iodine concentration in the salt for human consummation. The principal aim is to do the identification and reduction of resources, which allow movement of the salt market without iodine, in order to achieve to the consumer iodized salt within the standards of the country. Methods: The iodometric titration method is used to analyze 204 samples of the salt. The iodine content of iodized salt samples is measured using a Standard iodometric titration prescribed by DeMaeyer, Lowenstein and Tilly (WHO, Geneva 1979). Iodine is liberated using sulfuric acid. The free iodine is titrated with sodium thyosulphate, using starch as an indicator. The samples are collected in the districts: Berat, Diber, Durres, Elbasan, Fier, Korce, Kruje, Kukes, Kucove, Lushnje, Pogradec, Vlore. Results and conclusions: The national mean iodine concentration of the salt was 29.6 mg/kg and the mean iodine concentration was 30.2 mg/kg. The minimum value encountered was 0 mg iodine / kg salt, while the maximum value 68.8 mg iodine / kg salt (or ppm). It should be noted that median overall sample, and in every district in particular is within the normal value appropriate iodization of salt for human consummation (≥ 20 mg iodine / kg salt). The analysis of levels of iodine in samples collected showed that 81.4% of samples had ≥ 20 ppm iodine content (according to parameters set by law), while 18.6% had no iodine or iodine content below 20 ppm.

Keywords: Sodium chloride, iodine use, salt, Albania, iodometric titration

INTRODUCTION

Iodine is essential for healthy brain development in the fetus and young child. Iodine deficiency negatively affects the health of women, as well as economic productivity and quality of life. Most people need an additional source of iodine as it is found in relatively small amounts in the diet. Iodization is the process of fortifying salt for human consumption with iodine and is an effective strategy to increase iodine intake at the population level.
The public health goals of reducing salt and increasing iodine intake through salt iodization are compatible as the concentration of iodine in salt can be adjusted as needed. Monitoring the levels of iodine in salt and the iodine status of the population are critical for ensuring that the population's needs are met and not exceeded.

Measurement of iodine salt

The iodine salt content in the form of potassium iodate (KIO_3) reacts with the sulfuric acid (H2SO4, 1M) and potassium iodide (KI) for converting iodate (IO_3) to molecular iodine (I_2). It is then titrated with sodium thiosulfate ($Na_2S_2O_3$, 0.5 N) in the presence of starch as an indicator of completion of the reaction.
Samples of salt for assessing levels of iodine, were collected random from different points of the markets and from the factory of iodized salt production ENG-SALE, in Panaja, Vlora district. They were kept in plastic containers (about 40-50 grams) hermetically and transported to the IPH Laboratory for analysis.
The criteria used to evaluate the use of iodized salt are based on the cut-off points proposed for the classification of iodized salt (according the Law no. 9942, dated 26.06.2008, "On prevention of disorders caused by insufficient iodine in the human body "), as follows:

Non adequately iodized and Adequately iodized

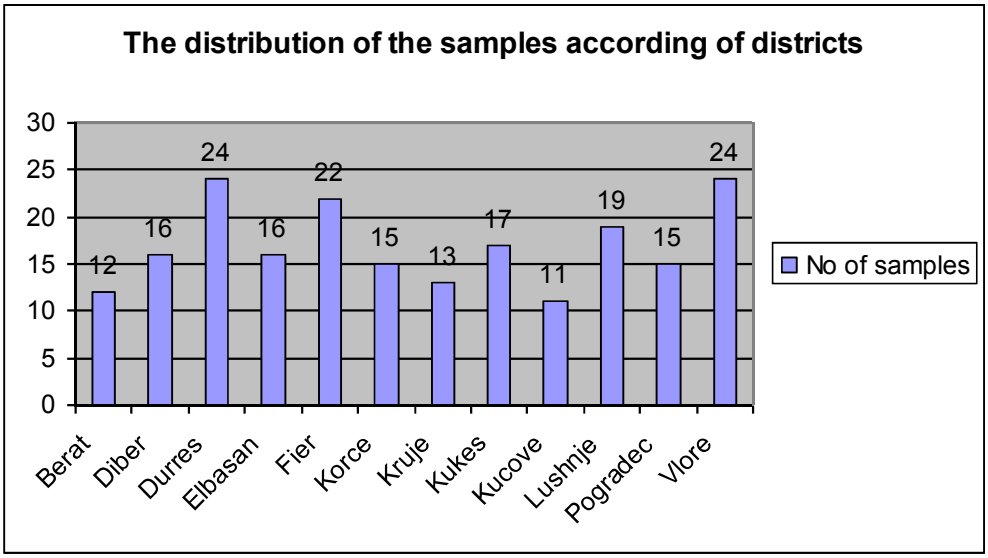
	The level of production	The level of marketing
Non adequately iodized	< 40 ppm	< 20 ppm
Adequately iodized	≥ 40 ppm	≥ 20 ppm

MATERIALS AND METHODS

The samples are collected in the districts: Berat, Diber, Durres, Elbasan, Fier, Korce, Kruje, Kukes, Kucove, Lushnje, Pogradec, Vlore. Totally we have collected 204 samples of salt with a distribution by districts as follows in:

Table 1. Represent the distribution of the samples according the districts

Districts	No. of sample
Berat	12
Diber	16
Durres	24
Elbasan	16
Fier	22
Korce	15
Kruje	13
Kukes	17
Kucove	11
Lushnje	19
Pogradec	15
Vlore	24
Total	204



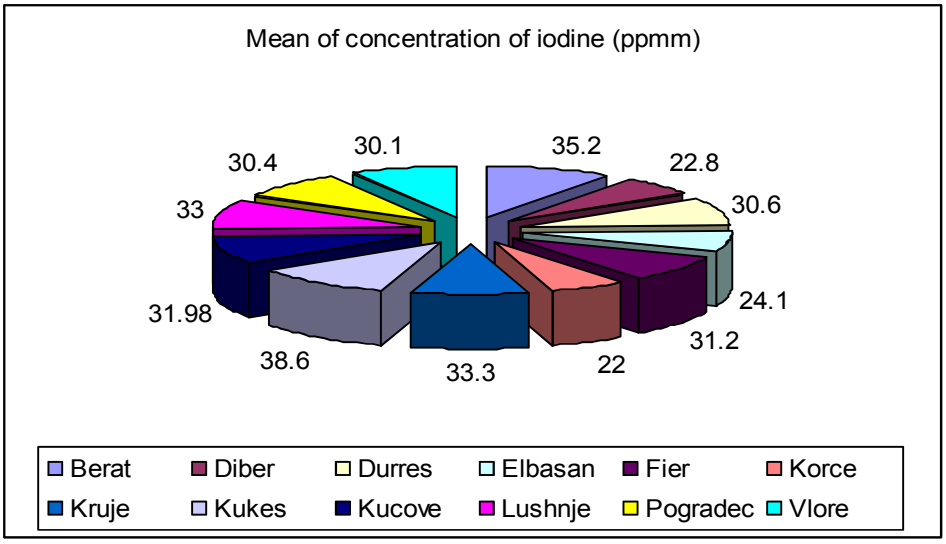
Graphic 1 The distribution of the samples according the districts

RESULTS

The national mean iodine concentration of the salt was 30.27mg/kg (ppm). The minimum value encountered was 0 mg iodine / kg salt, while the maximum value 68.8 mg iodine / kg salt (or ppm).

Table 2. Represent the values of mean of concentration iodine for any district of our study:

District	Mean of concentration of iodine (ppm)
Berat	35.2
Diber	22.8
Durres	30.6
Elbasan	24.1
Fier	31.2
Korce	22.0
Kruje	33.3
Kukes	28.6
Kucove	31.9
Lushnje	33.0
Pogradec	30.4
Vlore	30.1



Graphic 2 The values of mean of concentration iodine for all districts

It should be noted that median overall sample in every district in particular is within the normal value appropriate iodization of salt for human consummation (≥ 20 mg iodine / kg salt). The analysis of levels of iodine in samples collected showed that 81.4% of samples had ≥ 20ppm iodine content (according to parameters set by law), while 18.6% had no iodine or iodine content below 20ppm.

CONCLUSIONS

The lowest level of mean was in the salt samples taken in Korça region (22.0 mg iodine / kg salt) and higher values (35.2mg iodine / kg salt) was encountered in Berat. It should be noted that median overall sample, and every district in particular is within the normal value appropriate iodization of salt for human consumption (≥20 mg iodine / kg salt).

The analysis of levels of iodine in samples collected showed that 81.4% of samples had ≥ 20 ppm iodine content (according to parameters set by law), while 18.6% had no iodine or iodine content below 20 ppm.

REFERENCE

WHO, UNICEF, ICCIDD Indicators for assessing Iodine Defficiency Disorders and their control through salt iodization 1992.
Iodine status worldwide WHO Global Database on Iodine Deficiency 2004
Delange F. The disorders induced by iodine deficiency.*Thyroid*, 1994, 4:107–128
Bleichrodt N, Born MP. A meta-analysis of research on iodine and its relationship to cognitive development. In: Stanbury JB, ed. *The damaged brain of iodine deficiency*. New York, Cognizant Communication, 1994:195–200.
Stanbury JB. *The damaged brain of iodine deficiency*. New York, Cognizant Communication, 1994.
"Prevalence of iodine deficiency worldwide" Bruno de Benoist ,Maria Andersson, Bahi Takkouche , Ines Egli The Lancet, Volume 362, Issue 9398, Pages 1859 - 1860, 29 November 2003
"Iodine supplementation of pregnant women in Europe: a review and recommendations". M Zimmermann and F Delange. European Journal of Clinical Nutrition (2004) 58, 979–984.
Sustainable elemination of Iodine Deficiency: Progres since the 1990 World Summit fort children . UNICEF, 9-14.
WHO, UNICEF, ICCIDD. *Assessment of iodine defi ciency disorders and monitoring their elimination: A guide for programme managers.* Geneva, World Health Organization, 2001.
Indicators for assessing Iodine Deficiency Disorders and their control through salt iodisation. WHO-ICCIDD-UNICEF. Micronutrient series. 1995.
Assessment of iodine deficiency disorders and monitoring their eliminatioA guide for programme managers Third edition WHO 2007.
WHO, UNICEF, ICCIDD. *Recommended iodine levels in salt and guidelines for monitoring their adequacy and effectiveness*. Geneva, World Health Organization, 1996 (WHO/NUT/96.13).
Bürgi H, Schaffner T, Seiler JP. The toxicology of iodate: A review of the literature. *Thyroid*, 2001, 11:449–456.

PAPER 081

RESULTS OF ANALYSIS FROM DEA MODEL IN MEASURING AND IMPROVING THE EFFICIENCY OF LIVESTOCK FARMS IN THE REGIONS OF ALBANIA

Mariana Nikolla[1*], Silvana Mustafaj[2], Elfrida Dishmema[2], Jona Mulliri[2], Eris Zeqo[2], Blerta Kristo[2]

[1]Agriculture University of Tirana, Mathematics & Computer Science Department, Tirana- Albania.
[2]Agriculture University of Tirana, Mathematics & Computer Science Department, Tirana- Albania.
[2]Agriculture University of Tirana, Mathematics & Computer Science Department, Tirana- Albania.
[2]Agriculture University of Tirana, Mathematics & Computer Science Department, Tirana- Albania.

*E-mail: *mariana_nikolla@live.com*

ABSTRACT

In this study it is shown how to use a mathematical model to measure and improve the efficiency of livestock farms. The study refers to data collected from dairy farms of 12 regions of Albania in respect of incomes and expenses for processed dairy products in 2011. This analysis gave the answer to the question: what are efficient and inefficient farms under DEA model? (nonparametric model based on linear programming). Some of the results of the analysis are: Korca, Gjirokastra, Shkodra and Kukes result in 100% efficiency of DEA, while other regions are inefficient. The results of less efficient regions are: Lezha 24%, 28% Fier, Tirana 37.6% and Vlora 37.7%. In inefficient farms for processed dairy products, the DEA model shows the best possible weights use of inputs (food, veterinary services, medications, transportation, and others) in order to improve the DEA efficiency. The allocation of quantities of the inputs identified by the use of the model provides a minimum of the same income from livestock products but with less expenses.These and other conclusions are illustrated with pictures, which give a clear picture of the study conducted.

Key words: Mathematics model, efficiency, DEA model, livestock products, regions of Albania.

INTRODUCTION

Agriculture is one of the most important sectors of the economy of our country. Developments in this sector today are visible, measurable and progressive. Albanian Farm is gaining more and more commercial nature. It is being specialized altering the structure of the mode of production and trading. Financial instruments such as subsidy, credit easing, are used for the expansion of cultivated area, producing quality livestock, additional funds leaf, organic farming and agro-processing. Agricultural production accounts for about 17.3% of GDP from which livestock production accounts about 52% of it.

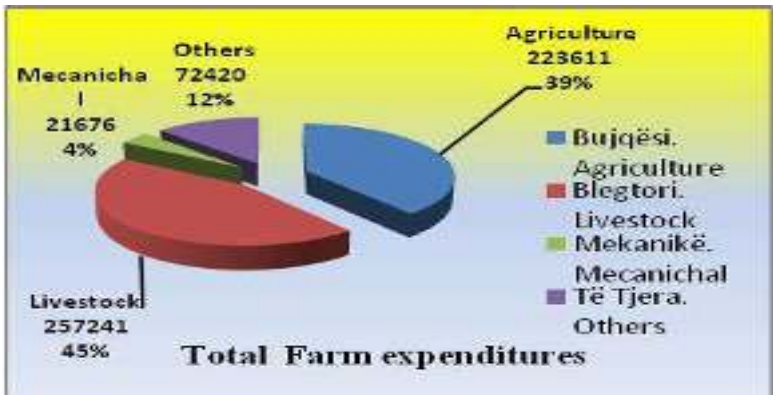


Fig.1 Information collected from Regional Directory Agriculture and Food(2011)

Source: Elaborated by the authors

Referring to the livestock development over the years it is shown that there is a stability in the number of heads, but also it is shown the increase in production of dairy products mainly in milk and meat that occupy a specific weight substantial income coming from agriculture. The livestock farms which have operated as mixed farms, each year more and more are headed to their specialization which has led to increasing the number of farms that breed a significant number of animals breed. In the production growth an important role has played the improvement race. This is reflected in the increased production of milk that comes from cattle (about 87%). In increasing milk production in cattle affected and increase the level of nutrition, improving breeding facilities, artificial insiminimit growth. Meat production accounts for about 46.6% of livestock production where the largest part is the meat product produced by cattle around 47.4%. Increased egg production is the result of investment by farmers in advanced technology. Animal genetic resources are the primary biological capital for livestock development, and are vital for food security and sustainable rural development. (Statistical Yearbook (2011)).

1.1. Meat and meat products

Meat production is dominated by cattle, which together comprise about half of the meat produced in the country. Production is still very fragmented, where the most cattle breeding farm / small rumin ants and pigs are small or very small. Across the country are 211,454 families who breed cattle (2011), mainly for milk production; and farms specializing in the production of meat are rare to nonexistent. There are also 55,339 farms with sheep, 24,494 farms with goats (2011), and about 15% have more than 50 sheep or goats, and the number of larger farms with small ruminants has seen a slight increase in recent years - in some regions, small ruminant farms are mainly devoted to the production of milk, in others there is a mixed balance between meat and milk production.

There are 41 manufacturers intensive poultry meat- broiler (more than 1000 head) and 19 over 10,000 such (2011), which supply the meat bird about 25% of domestic market needs.

Meat processing industry is the first sector of the agro-industry develop, modernize and consolidate. There are 63 registered meat processor, but five large factories dominate the industry. The meat industry is focused on the domestic market, and relies on imports of free frozen meat, which is provided by several major importer.

The export of meat is very low, while imports remained high and stable in recent years, recording about 40,000 tons / year, corresponding to more than 25% of domestic demand. In addition there is a growing import of livestock, especially pigs and cattle (in 2011 imported 81,400 pigs and 32,625 cattle), which are slaughtered in Albania and sold as "fresh country meat". Imports of beef is particularly high given the high price of meat in the country, which is very expensive for the processing industry. In addition to the small size of farms, a factor contributing to the high prices of meat is the high price of food. Investment sector is needed to meet safety standards and environmental regulations. There is a need for investment in slaughterhouses, but in the current uncertain enforcement of food safety laws would be a high-risk business, as traders prefer not to use meat slaughterhouses, if they are not legally obliged to do this.

Milk and dairy products

Domestic production of milk reached about 1.1 million mt in 2011, has marked an increase of 16% since 2000. Milk production is dominated by cow's milk (about 86%), while the rest is split equally between sheep and goat milk.

Milk produced by very small manufacturer specializing half and mixed farms that have less than 50 sheep or goats and farms that have less than 5 cows (most family farms have 1-2 cows and only less than 2 % of them have more than 5 cows). However there is a consolidation trend: the number of farms over 5 cows has tripled compared to 2005, while the number of farms with over 10 cows (1,317 in 2011) has increased five-fold compared to 2005. Currently there are 1,317 farms with 10 cows; 8347 farms with more than 50 sheep and 3504 farms with more than 50 goats. Cow's milk production comes mainly from the plain and hilly; small livestock farms (sheep & goats) are concentrated in the south, where specialized factories for the production of cheese from milk do not exist. Dairy processing industry is also highly fragmented and consists mainly of informal processing units. For every unit of formalized processing (about 334 in 2011) may have 2-3 maker informal.

Most actors filierws (especially small farms and processors) do not meet environmental and safety standards. Milk collection and transportation is one of the weakest points of this FILIERE / value chain. Collecting raw milk is organized mainly by milk processors and dairy from private collectors. In most cases no milk remains cool even on the farm or during transport to the line / processing factory.

In recent years, the import of milk reaches levels of approximately 8,500 tons per year, while the import of cheese around 1,200 tons per year. However, domestic production dominates; the import of dairy products cover less than 10% of domestic supply. There is a need for investment in farm and storage chain / collection and transportation, but

such investments are unlikely to be made until the whole system of quality control and safety will be improved. Support should be given to improving the packaging and labeling.

MATERIAL AND METHODS

In this paper is analyzed the efficiency of livestock farms of 12 regions of Albania in respect of income and expenses for processed dairy products. The study undertaken refers to data collected by:

Regional Directorates of Agriculture, Food and Consumer Protection (MAFCP)
Livestock specialists in the Regional Directorates of Agriculture.
Statistical Yearbook 2011
Different Scientific studies and research conducted on this issue.

In the picture 2 are shown the diagrams of income for the farms (in thousand ALL), for all regions of the country and for the Republic.

Figure 2. Diagram of the data collected on income for farm
Source: Elaborated by the authors

In order to achieve the purpose of the study it was used Dea mathematical model, which is based on linear programming method. (case 1 output, 5 inputs). As output were obtained the incomes from livestock products processed (000.leke) for 12 regions of the country. The inputs used in the model: food, veterinary services, medications, transportation etc. (R.Färe,S.Grosskopf,and C.A.K.Lovell).
According to the Dea model, the efficiency of each unit (region) is given by the following formula:

$$h(u,v) = \frac{\text{sum of the weighted outputs of the unit}}{\text{sum of weighted input unit}} = \frac{\sum_{n=1}^{s} y_n \times u_n}{\sum_{i=1}^{k} x_i \times v_i}$$

Where μ_n is the weight (ratio) of the output n (n = 1,2,3, ..., s) and v_i is the weight (ratio) of the input i (i = 1,2,3, ..., k). According to the model μ_n and v_i treated as unknown variables. DEA model assigns weights to the best possible group of outputs and inputs used, which are selected in order to maximize the coefficient "h". According to the model, which are more efficient units will have a DEA efficiency score of 100%. (WW Cooper, LM Seiford and Tone K, 2007).
The objective of this study is to maximize the outputs:

$$y_1 * \mu_1 + y_2 * \mu_2 + \cdots + y_s * \mu_s [max] \quad (1)$$

with condition: $\begin{cases} \sum_{n=1}^{s} y_n \mu_n - \sum_{i=1}^{k} x_i v_i \leq 0 \\ \sum_{i=1}^{k} x_i v_i = 1 \end{cases}$ (2)

the non-negative condition $\mu_n \geq 0 \; for \; n = 1 - s, v_i \geq 0 \; for \; i = 1 - k$ (3) (*Ragsdale C.T*, 2008).

Model Application- To evaluate the efficiency of the unit 1, which is represented by Tirana region, must solve the following LP problem. These constraints are set for all units of the study. (Mikulas Luptacik, (2009))

Max: $174681\mu_1$ output weight for unit 1. (1)

Constraints:

$$\begin{cases} 174681\mu_1 - 300022v_1 - 82030v_2 \; - 0\,72271v_3 \; - 199909v_4 \; - 16821v_5 \; \leq 0 \; efficiency\ constraint\ unit\ 1 \\ 257593\mu_1 - 303120v_1 - 82895v_2 \; 133929v_3 \; - \; 22525v_4 \; - 30139v_5 \; \leq 0 \; efficiency\ constraint\ unit\ 2 \\ \dots \\ \dots \qquad (2) \\ 194128\mu_1 - 208309v_1 - 15099v_2 \; - \; 18629v_3 \; - 8389v_4 \; - 6815v_5 \; \leq 0 \; efficiency\ constraint\ unit\ 12 \\ 300022v_1 + 82030v_2 \; + 0\,72271v_3 \; + 199909v_4 \; + 16821v_5 \; = 1 \quad inputs\ conditions\ for\ unit\ 1 \end{cases}$$

$\mu_1, v_1, v_2, v_3, v_4, v_5 \geq 0 \; non-negativity\ constraint$ (3)

This problem was elaborated by us with Excel (Solver Solution).

RESULTS

In the figure 3 is given the DEA efficiency analysis of Tirana region and other regions included in the study. It was found from Dea analysis that Tirana region has a 37.6% efficient result, that is inefficient under Dea's.

Full analysis of all municipalities in the study obtained by changing the contents of the cell "C18" manually in 2,3,4 to 12 and the Solver orders the efficiencies for each unit in the column Efficiency (figura3).

In this study Dea model is used not only to analyze the efficiency of the 12 counties of the Republic in respect of income from livestock products, but also to improve the efficiency of circuits inefficient. In the Figure 5 is shown the example of a composite unit which has a higher efficiency than the unit 1. To find the composition (composite unit) refer to the results of the sensitivity ratio (figure 4). The amount absolute shadow prices (Shadow Prices), the image in yellow columns are composed unit weights, which results in efficient unit in the study. Figure 4 gives the average weights 32.7% for unit 5 (Donegal), 32.1% of the added weight of the unit 10 (Gjirokastra) and 2.5% by weight of unit 12 (Kukes), which form the constituent unit. This unit produces at least the same output with that of unit 1, requiring smaller amounts or equal input 1. In the unit in Figure 6, is shown the improvement efficiency DEA to Tirana region, with weights found by Solveri. Results indicate that the region of Tirana (figure 6) is efficient according to DEA (100%). (Ragsdale, C.T. (2008), Fitzsimmons, J.A. and Fitzsimmons, M.J. (2006)).

Adjustable Cells

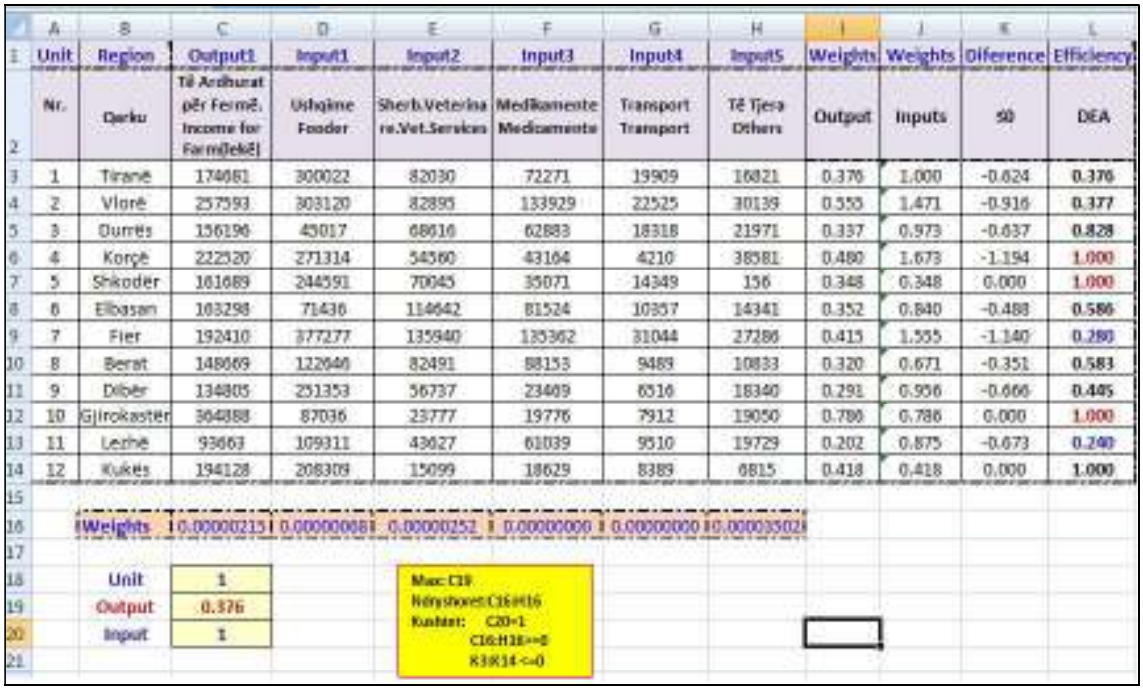
Cell	Name	Final Value	Reduced Cost	Objective Coefficient	Allowable Increase	Allowable Decrease
$C$16	Weights Income for Farm(leke)	0.00000215	0.00000000	174681	1E+30	174681
$D$16	Weights Fooder	0.00000068	0.00000000	0	3816.573796	2281.558919
$E$16	Weights Veterinary Services	0.00000252	0.00000000	0	22896.17661	571.1385353
$F$16	Weights Medicamente	0.00000000	-8946.31801895	0	8946.318019	1E+30
$G$16	Weights Transport	0.00000000	62.57247328	0	62.57247328	1E+30
$H$16	Weights Others	0.00003502	0.00000000	0	13790.4062	390.7229225

Constraints

Cell	Name	Final Value	Shadow Price	Constraint R.H. Side	Allowable Increase	Allowable Decrease
$C$20	Income for Farm(lekë)	1	0	1	1E+30	1
$K$3	Tirane ≤0	-0.624	0.000	0	1E+30	0.623565844
$K$4	Vlorë ≤0	-0.916	0.000	0	1E+30	0.915610066
$K$5	Durres ≤0	-0.637	0.000	0	1E+30	0.636621431
$K$6	Korçë ≤0	-1.194	0.000	0	1E+30	1.193735378
$K$7	Shkoder ≤0	0.000	0.327	0	0.176901344	0.56541232
$K$8	Elbasan ≤0	-0.488	0.000	0	1E+30	0.4881927
$K$9	Fier ≤0	1.140	0.000	0	1E+30	1.140410385
$K$10	Berat ≤0	-0.351	0.000	0	1E+30	0.3505289
$K$11	Diber ≤0	-0.666	0.000	0	1E+30	0.665797246
$K$12	Gjirokastër ≤0	0.000	0.321	0	0.433839746	0.234739488
$K$13	Lezhe ≤0	-0.073	0.000	0	1E+30	0.073492815
$K$14	Kukës ≤0	0.000	0.025	0	0.105481152	0.110609647

Sensitivity Report Tirane / Sensitivity Report Shkoder / Sensitivity Report Lezhe

Fig 3. DEA analysis results for the units in the study



Unit	Region	Output1	Input1	Input2	Input3	Input4	Input5	Weights	Weights	Difference	Efficiency
Nr.	Qarku	Të Ardhurat për Fermë. Income for Farm(lekë)	Ushqime Fooder	Sherb.Veterinare.Vet.Services	Medikamente Medicamente	Transport Transport	Të Tjera Others	Output	Inputs	SD	DEA
1	Tiranë	174681	300022	82030	72271	19909	16821	0.376	1.000	-0.624	0.376
2	Vlorë	257593	303120	82895	133929	22525	30139	0.555	1.471	-0.916	0.377
3	Durrës	156196	45017	68616	62883	18318	21971	0.337	0.973	-0.637	0.828
4	Korçë	222520	271314	54560	43164	4210	38581	0.480	1.673	-1.194	1.000
5	Shkodër	161689	244591	70045	35071	14349	156	0.348	0.348	0.000	1.000
6	Elbasan	163298	71436	114642	81524	10357	14341	0.352	0.840	-0.488	0.586
7	Fier	192410	377277	135940	135362	31044	27286	0.415	1.555	-1.140	0.280
8	Berat	148669	122646	82491	88153	9489	10833	0.320	0.671	-0.351	0.583
9	Dibër	134805	251353	56737	23469	6516	18340	0.291	0.956	-0.666	0.445
10	Gjirokastër	364888	87036	23777	19776	7912	19050	0.786	0.786	0.000	1.000
11	Lezhë	93663	109311	43627	61039	9510	19729	0.202	0.875	-0.673	0.240
12	Kukës	194128	208309	15099	18629	8389	6815	0.418	0.418	0.000	1.000
	Weights	0.00000215	0.00000081	0.00000252	0.00000000	0.00000000	0.00003502				

Unit 1
Output 0.376
Input 1

Max: C19
Nënshoret: C16:H16
Kushtet: C20=1
C16:H16>=0
B18:B14<=0

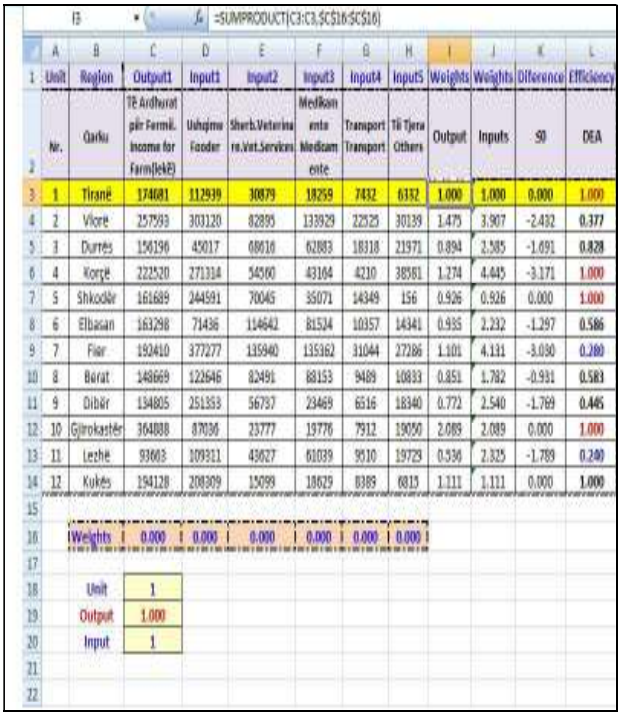
Fig 4. Sensitivity Report of Tirana's Region
Source: Elaborated by the authors

=SUMPRODUCT(C3:C14,$I$3:$I$14)

Unit	Region	Output1	Input1	Input2	Input3	Input4	Input5	Weights
Unit	Region	Income for Farm(lekë)	Fooder	Veterinary Services	Medicamente	Transport	Others	of Composition
1	Tiranë	174681	300022	82030	72271	19909	16821	0.000
2	Vlorë	257593	303120	82895	133929	22525	30139	0.000
3	Durrës	156196	45017	68616	62883	18318	21971	0.000
4	Korçë	222520	271314	54560	43164	4210	38581	0.000
5	Shkodër	161689	244591	70045	35071	14349	156	0.327
6	Elbasan	163298	71436	114642	81524	10357	14341	0.000
7	Fier	192410	377277	135940	135362	31044	27286	0.000
8	Berat	148669	122646	82491	88153	9489	10833	0.000
9	Dibër	134805	251353	56737	23469	6516	18340	0.000
10	Gjirokastër	364888	87036	23777	19776	7912	19050	0.321
11	Lezhë	93663	109311	43627	61039	9510	19729	0.000
12	Kukës	194128	208309	15099	18629	8389	6815	0.025
	Composition values	174681	112939	30879	18259	7432	6332	
	Additional inputs used	0	187083	51151	54012	12477	10489	

Cells	Formulas	Range of copying
C16	SUMPRODUCT(C3:C14,$I$3:$I$14)	D16:H16

Fig 5. The values of composition for unit1



=SUMPRODUCT(C3:C3,$C$16:$C$16)

Unit	Region	Output1	Input1	Input2	Input3	Input4	Input5	Weights	Weights	Difference	Efficiency
Nr.	Qarku	Të Ardhurat për Fermë. Income for Farm(lekë)	Ushqime Fooder	Sherb.Veterinare.Vet.Services	Medikamente Medicamente	Transport Transport	Të Tjera Others	Output	Inputs	SD	DEA
1	Tiranë	174681	112939	30879	18259	7432	6332	1.000	1.000	0.000	1.000
2	Vlorë	257593	303120	82895	133929	22525	30139	1.475	3.907	-2.432	0.377
3	Durrës	156196	45017	68616	62883	18318	21971	0.894	2.585	-1.691	0.828
4	Korçë	222520	271314	54560	43164	4210	38581	1.274	4.445	-3.171	1.000
5	Shkodër	161689	244591	70045	35071	14349	156	0.926	0.926	0.000	1.000
6	Elbasan	163298	71436	114642	81524	10357	14341	0.935	2.232	-1.297	0.586
7	Fier	192410	377277	135940	135362	31044	27286	1.101	4.131	-3.030	0.280
8	Berat	148669	122646	82491	88153	9489	10833	0.851	1.782	-0.931	0.583
9	Dibër	134805	251353	56737	23469	6516	18340	0.772	2.540	-1.769	0.445
10	Gjirokastër	364888	87036	23777	19776	7912	19050	2.089	2.089	0.000	1.000
11	Lezhë	93663	109311	43627	61039	9510	19729	0.536	2.325	-1.789	0.240
12	Kukës	194128	208309	15099	18629	8389	6815	1.111	1.111	0.000	1.000
	Weights	0.000	0.000	0.000	0.000	0.000	0.000				

Unit 1
Output 1.000
Input 1

Fig 6. Improvement of efficiency for unit1

Source: Elaborated by the authors

	The formulas used for solving the Dea problem	
Cell	Formula	The formula's rang
I3	SUMPRODUCT(C3:C3,$C$16:$C$16)	I3:I14
J3	SUMPRODUCT(D3:H3,$D$16:$H$16)	J3:J14
K3	I3-J3	K3:K14
C19	INDEX(I3:I14,C18,1)	
C20	INDEX(J3:J14,C18,1)	

CONCLUSION

Livestock Production Sector aims to analyze, identify and develop policies, sectoral strategies for the development of livestock, guide and support at the national level, local growth and more and better meeting the demands and needs of the market for livestock products through the rational use of resources and the introduction of new techniques and technologies in production. This study analyzes the efficiency of the country's livestock farms regarding processed dairy products. To solve the problem is used a non-parametric mathematical model Dea. The analysis showed that regions: Shkodra, Kukes, Gjirokastra and are efficient according to DEA (100%), while other units are less efficient. For the inefficient units, there is a linear combination of efficient units resulting a composite unit which produces at least the same output using the same or less input than inefficient unit. (For the non efficient unit, this model applies the possibilities of improvement by determining the best weights of inputs Taken Into Account, in order to Take at least the same output (Sucha either, Production and profit).
Specifically, the Tirana region, to receive the same income from livestock products processed should be reduced costs for food around 187,083 (thousand ALL), for veterinary services 51,151 (thousand ALL), for medications 54,012 (thousand ALL), for transport 12,477 (thousand ALL), and for other expenses 10,489 (thousand ALL). With this reduction of costs, resulting Tirana region Dea 100% efficiency. These conclusions are illustrated with figures implemented in a spreadsheet and solver giving a clear picture of the study undertaken. Such analysis can be used effectively in solving various problems of the economy and production.

REFERENCES

Mikulas Luptacik, (2009). Mathematical Optimization and Economic Analysis. Vol. 36, Issue 5, 136-184 .
Ragsdale, C.T. (2008). Spreadsheet Modeling and Decision Analysis, 5th Edition. South-Western, Thomson
Fitzsimmons, J.A. and Fitzsimmons, M.J. (2006). Service Management. Issuse 3, Supplement on DEA, McGraw Hill.
Statistical Yearbook (2011), 4-15.
W.W.Cooper, L.M.Seiford, and K.Tone, (2007).Data Envelopment Analysis:A Comprehensive Text with Models,Applications,References, and DEA- Solver Software, vol.2, Springer, New York.
K.J.Arrow,George Dantzing In the development of economic analysis, Discrete Optim.,5(2008), 159-167.
A.I.Ali,Computational aspects of Dea, in A. Charnes,W.W.Cooper, A.Lewin, and L.M.Seiford,eds.,Data Envelopment Analysis:Theory,Methodology and Applications, Kluwer Academic Publishers, Boston,1994,63-88.
R.Färe,S.Grosskopf,and C.A.K.Lovell, The Measurement of Efficiency of Production, Kluwer Academic Publishers,Boston,1985.
Sharma, K.R., Leung, P.S. and Zane, L. 1999. "Performance measurement of Hawaii state public libraries: an application of data envelopment analysis (DEA)," *Agricultural and Resource Economics Review, 28(2):*190-198.

PAPER 084

BIOMONITORING OF URBAN AIR POLLUTION OF TIRANA USING THE MOSS BAG TECHNIQUE

Ilva Gjikaj[1], Majlinda Vasjari[2], Majlinda Terpo[3]

[1]Chemistry Department, Faculty of Mathematical Engineering and Physical Engineering, Polytechnic University of Tirana, Albania;
[2]Chemistry Department, Faculty of Natural Sciences, University of Tirana, Albania;
[3]Biochemistry Department, Faculty of Natural Sciences, University "Eqrem Çabej", Gjirokastra, Albania;

E-Mail: ilva_gjika@yahoo.com

ABSTRACT

This study is focused on the evaluation of the heavy metal air pollution of urban area of Tirana, Albania using mosses as biominitors. Based on the fact that mosses obtain most of their nutrients directly from rain water and from the deposition of air-borne particulate material, the concentration of heavy metals in them directly reflects the air quality. In polluted urban areas where mosses are often absent the moss bag technique is used for air pollution survey. *Pseudoscleropodium purum* moss samples were collected during September-October 2010 at rural areas isolated from urban and industrial centers and then transplanted at seven monitoring sites located in Tirana for a period of five months. The concentrations of Zn, Fe, Mn were determined by flame AAS, the concentrations of K, Na were determined by flame AES and the concentrations of Cu, Cd, Pb were determined by graphite furnace AAS. Cluster Analysis of elements was used to define different pollution sources.

Keywords: air pollution, biomonitor, moss bag, heavy metals, AAS, AES, Cluster analysis

INTRODUCTION

Environmental pollution is known to be one of the most important problems in urban areas. Heavy metals are a major source of environmental pollution. The main sources of these pollutants in the atmosphere are stack and exhaust emissions in the form of particulate matter from industry, power stations, domestic heating systems, and motor vehicles (Karaca *et al.,* 2005; Nriagu and Pacyna, 1988). Heavy metal pollution represents an important environmental problem due to toxic effect of metals and their accumulation throughout the food chain leading to serious ecological and health problems. Studies on atmospheric contamination have frequently been limited by the high cost of classical analytical methods and difficulties in carrying out extensive monitoring in time and space. There has been increasing interest in the use of indirect monitoring methods, such as the use of organisms that act as bioaccumulators. Many studies have demonstrated the ability of moss to absorb and accumulate atmospheric pollutants in tissue. Root and cuticle absence makes them find their nutritive elements in wet and dry atmospheric deposition (Rühling and Tyler, 1968). Mosses have also been recognized as valuable biomonitors in the assessment of temporal trends in trace metal accumulation (Harmens et al., 2008), and also in spatial variations across national boundaries (Schröder et al., 2008). In urban areas, where mosses are often scarce or even absent, the ″moss bag technique″ (active biomonitoring) has been initiated and developed with the aim of spatial and/or temporal assessment of contaminant deposition in highly polluted areas (Goodman and Roberts, 1971; Martin and Coughthrey, 1982; Hynninen, 1986; Vasconcelos and Tavares, 1998; Fernandez et al., 2004; Culicov and Yurukova, 2006). In this technique, moss is collected from an unpolluted area and then moss samples held within mesh bags are exposed at the monitoring stations for a certain period of time, in order to monitor the presence of contaminants in the air. So, with this method the initial concentration of metals and exposure period are known.
The city of Tirana is considered as the most polluted one in Albania regarding to the air quality, which is a concerning problem for the health of people. The main sources of air pollution are the old vehicles, heavy traffic, the quality of petroleum, the constructions which do not follow the criteria to avoid pollution or the inappropriate burning of wastes. This was the first attempt to apply this technique in Tirana, the capital city of Albania. The atmospheric deposition of trace elements by means of the moss biomonitoring technique associated with analytical techniques were applied to study multielement atmospheric deposition. The aim of this study is the evaluation of the

urban air pollution of Tirana from heavy metals, identification of the most polluted areas and defining different pollution sources.

MATERIALS AND METHODS

Pseudoscleropodium purum moss sample was collected from a pristine wetland area, in Libohova, isolated from urban and industrial centers, during September-October 2010. The survey was carried out at seven monitoring stations. The moss bag samples were exposed for a period of five months at each monitoring station. Some unexposed moss sample were preserved as well, to be used further as background concentration level of the elements. After exposure moss bag samples together with unexposed sample were carefully cleaned from all dead material and attached litter and just the green and green-brown shoots were included. The unwashed samples were dried to constant weight at 40ºC and then homogenized to a fine powder. Nearly 0.5 g aliquots of each sample were placed in Teflon digestion vessels and 10 ml HNO_3 (9:1) were added. They were first left for 48h at room temperature, after that heated at 150-200^{0}C for 3h and then at 250^{0}C for 1h. After the vessels were cooled the digested materials were transfered quantitatively to 25 ml calibrated flasks and diluted to the mark with bidistilled water. The concentrations of Zn, Fe, Mn were determined by flame atomic absorption spectrometry (FAAS) (Varian, Spectra AA 10 Plus), the concentrations of K, Na were determined by flame atomic emission spectrometry (FAES) (Varian, Spectra AA 10 Plus) and the concentrations of Cu, Cd, Pb were determined by graphite furnace atomic absorption spectrometry (GFAAS) (Analytik jena, AA 400). The analysis of moss samples were performed at ″Analytical Chemistry Department, Faculty of Natural Sciences, University of Tirana, Albania″.

RESULTS

In Figure 1. is shown the map of the survey area with the monitoring stations and in Table 1. are given the locations of the monitoring stations in the urban area of Tirana where the moss bags where exposed.

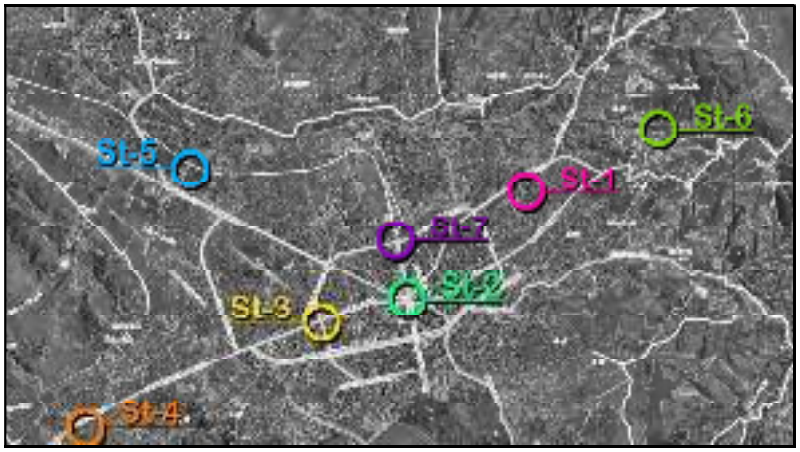


Figure 1. *Survey area of Tirana with the monitoring stations.*

Table 1. *The number and location of the monitoring stations.*

Station number	St–1	St–2	St–3	St–4	St–5	St–6	St–7
Station location	Spitali ″Nene Tereza″	Qender	21 Dhjetori	Kombinat	Laprake	Stacioni i teleferikut Dajt	Stacioni i trenit

Accumulation data were submitted to statistical analysis (cluster analysis) in order to detect the groups of analyzed elements with similar deposition rates. This method arranges the elements in different categories. The results of cluster analysis are ilustrated in the dendrogram in Figure 2. It is evident that the analysed elements are divided into three main groups, represented with three different colors.

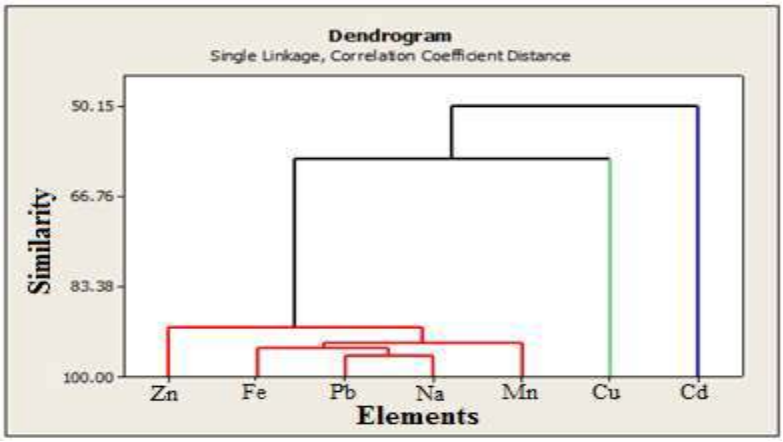


Figure 2. *Dendrogram according to the analysed elements.*

Group 1. In this group are the elements Zn, Fe, Pb, Na and Mn. The occurrence of the lithogenic elements such as Fe and Na in this group, shows that it is related to the windblown road dust, where the elements Pb, Mn and Zn released to the environment from anthropogenic activities were previously deposited. The anthropogenic origin of lead in urban areas is related to the burning of fuel and oil in vehicle's motors and with the consumption of their brakes. Also, manganese is released in urban areas as a result of fuel burning where MMT is found as additive. While the element zinc in urban areas is found mainly as a result of the consumption of vehicle's tires.
Group 2. In this group is found the element Cu, which in urban areas is related to the burning of fuel and the brake consumption of vehicles. The higher concentration of copper is found in station St-5 (Laprake). In the vicinity of Laprake is located Paskuqan. In the past, this area was completely covered with vineyards, where copper-based pesticides were used. As a result, in the area of Laprake is reflected the pollution from this element (Otvos, 2003).
Group 3. In this group is found the element Cd. Road traffic is a considerable source of cadmium in urban areas. The origin of cadmium in the exhaust gas is supposed to be related to its presence in the gasoline and to all kind of corrosion effects of the car, eg. coatings in the exhaust pipe. The presence in the fuel might be due to a result of a series of cracking of the heavier residues of the oil, contamination from storage tanks, additives to the gasoline etc.. Rubber tire wear is another additional source of cadmium in the environment. Products like batteries, coating and plating, pigments and plastics and synthetic products can be the origin of cadmium emissions when they are incinerated as waste. The highest level of cadmium is in the St-4 (Kombinat). The characteristic of this area is the fact that in its vicinity is the field of Sharra, where is found the only landfill of urban wastes of Tirana, in which wastes are burned continuously in uncontrolled conditions. Also, some small manufactories, located in Kombinat, carry out their activities in the ambiances of the former glas factory and production of silicate bricks, by using various fuels during their processes. This is the reason of the elevated concentration of cadmium in this area.

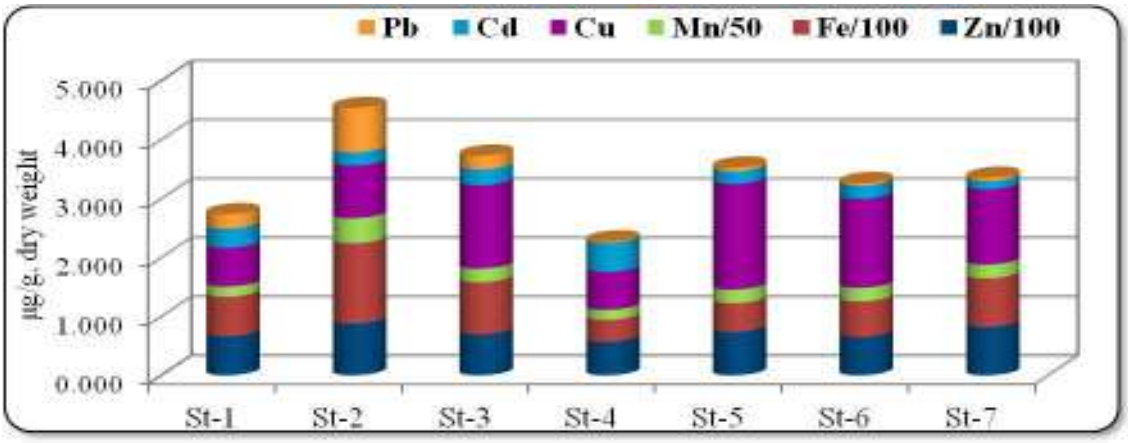


Figure 3. *Accumulation of elements according to the monitoring stations in urban area of Tirana.*

In Figure 3. is given the graphical presentation of the accumulation of elements in moss samples after exposure. It is clearly seen that Qender (St-2) is the station where most of the elements are accumulated, showing that here the urban air is more polluted with heavy metals.

CONCLUSIONS

This was the first study of this kind in our country. From the results of cluster analysis it is seen that the elements are divided into three main groups. In group 1 are the elements Zn, Fe, Pb, Na and Mn which are related to the windblown road dust where the elements Pb, Mn and Zn released to the environment from anthropogenic activities, like the burning of fuel and oil in vehicle's motors, burning of fuel where MMT is found as additive, the consumption of their brakes and tires, were previously deposited. In group 2 si the element Cu which in urban areas is related to the burning of fuel and the brake consumption of vehicles, but it is separated from other elements because of its higher concentration found in Laprake, in the vicinity of which is located Paskuqan where copper-based pesticides were previously used in the vineyards. In group 3 is the element Cd which in urban areas is related to road traffic (exhaust gas and rubber tire wear), but it is separated from other elements because of its higher concentration found in Kombinat in the vicinity of which is the landfill of Sharra, where wastes are burned continuously in uncontrolled conditions. Products like batteries, coating and plating, pigments and plastics and synthetic products can be the origin of cadmium emissions when they are incinerated as waste. Also, some small manufactories, located in Kombinat, carry out their activities in the ambiances of the former glas factory and production of silicate bricks, by using various fuels during their processes.

REFERENCES

Čeburnis, D., Valiulis, D., 1999. Investigation of absolute metal uptake efficiency from precipitation in moss. Sci. Total Environ. 226, 247–253.

Culicov, O.A., Yurukova, L., 2006. Comparison of element accumulation of different moss and lichen-bags, exposed in the city of Sofia (Bulgaria). Journal of Atmospheric Chemistry 55, 1–12.

Fernandez, J.A., Aboal, J.R., Carballeira, A., 2004. Identification of pollution sources by means of moss bags. Ecotoxicology and Environmental Safety 59, 76–83.

Goodman, G.T., Roberts, T.M., 1971. Plants and soils as indicators of metals in the air. Nature 231, 287–292.

Harmens, H., Norris, D.A., Koerber, G.R., Buse, A., Steinnes, E., Ruhling, A., 2008. Temporal trends (1990–2000) in the concentration of cadmium, lead and mercury in mosses across Europe. Environmental Pollution 151, 368–376.

Hynninen, V., 1986. Monitoring of airborne metal pollution with moss bags near an industrial source at Harjavalta, southwest Finland. Annales Botanici Fennici 23, 83–90.

Karaca, F., Alagha, O., and Ertürk, F. (2005). Statistical characterization of atmospheric PM10 and PM2.5 concentrations at a non-impacted suburban site of Istanbul, Turkey. *Chemosphere* 59, 1183–1190.

Martin, M.H., Coughthrey, P.J., 1982. Biological monitoring of heavy metal pollution. Land and Air. Applied Science Publishers, London, pp. 311-336.

Nriagu, J.O., and Pacyna, J.M. (1988). Quantitative assessment of world-wide contamination of air, water and soils by trace metals. *Nature* 333, 134–139.

Otvos, E., Pazmandi, T., Tuba, Z., (2003). First national survey of atmospheric heavy metal deposition in Hungary by the analysis of mosses. Sci. total. Environ., 309: 151-160.

Radenković, M., Joksić, J., 2008. Assessment of air quality in an urban area of Belgrade, Serbia. In: Güngör, B.Ö (Ed.), Environmental Technologies, New Developments, pp. 209–245.

Rühling, A., Tyler, G., 1968. An ecological approach to the lead problem. Botanisk Notiser 122, 248–342.

Schröder, W.; Pesch, R.; Englert, C.; Harmens, H.; Suchara, I.; Zechmeister, H. G.; Thöni, L.; Maňkovská, B.; Jeran, Z.; Grodzinska, K. & Alber, R. (2008). Metal accumulation in mosses across national boundaries: uncovering and ranking causes of spatial variation. *Environmental Pollution*, 151, 377-388, 0269-7491

Vasconcelos, M.T.S.D., Tavares, H.M.F., 1998. Atmospheric metal pollution (Cr, Cu, Fe, Mn, Ni, Pb and Zn) in Oporto city derived from results for low-volume aerosol samplers and for the moss Sphagnum auriculatum bioindicator. Science of the Total Environment 212, 11–20.

PAPER 085

GEOCHEMICAL NORMALIZATION METHOD IN BIOMONITORING OF HEAVY METAL AIR POLLUTION

Ilva Gjikaj[1], Majlinda Vasjari[2], Majlinda Terpo[3]

[1]Chemistry Department, Faculty of Mathematical Engineering and Physical Engineering, Polytechnic University of Tirana, Albania;
[2]Chemistry Department, Faculty of Natural Sciences, University of Tirana, Albania;
[3]Biochemistry Department, Faculty of Natural Sciences, University "Eqrem Çabej", Gjirokastra, Albania;

E-Mail: ilva_gjika@yahoo.com

ABSTRACT

A biomonitoring survey involving the moss *Hypnum cupressiforme* was carried out in three regions of Albania (Tirane, Durres and Lezhe) to evaluate the atmospheric deposition of trace elements. Moss samples were collected at 13 sites during October-September 2010, following the guidelines of UNECE ICP Vegetation. The content of elements in moss samples were determined using the ICP-AES technique. In order to differentiate between the natural and anthropogenic origin of trace elements, the data obtained from chemical analysis were normalized to element Li as a typical element of earth crust. With the data obtained from chemical analysis and the data after the normalization to Li, the Descriptive Statistic were perfomed and the chart of elements were constructed. After the normalization it was seen that the elements like Cr, Ni, Cu, Pb, Cd show anthropogenic origin.

Keywords: air pollution, biomonitor, moss, trace element, normalization, ICP-AES.

INTRODUCTION

Airborne particulate matter, which is composed of a broad class of chemically and physically diverse substances are variable in size, chemical composition, formation, origin and concentration, and is variable across space and time. Health effects associated with particulate matter (PM) are linked to respiratory, cardiovascular problems and premature mortality (Callen et al., 2009). The particulates may include a broad range of chemical species, ranging from metals to organic and inorganic compounds (Tsai and Cheng, 2004; Park and Kim, 2005). Among the inorganic compounds, most important ones are the trace metals, which are emitted by various natural and anthropogenic sources such as crustal materials, road dust, mines, construction activities, motor vehicles, coal and oil combustion, incineration and other industrial activities (Watson et al., 2002; Quiterio et al., 2004).
Concerns about the accumulation of metals in ecosystems increased during the 1980s. Mosses are used to monitor metal bioaccumulation (Markert et al. 2003). Their use as passive, i.e. in situ biomonitors for atmospheric metal accumulation in terrestrial ecosystems goes back to Rühling and Tylor (1971). Metal accumulation surveys have been performed in at least 21 European states at 5-year intervals since 1990. The technique of moss analysis provides a time-integrated measure of the spatial patterns of metal accumulation in terrestrial ecosystems. It can be used as a surrogate for deposition measurements which is easier and cheaper than conventional precipitation analysis. Further, the spatial density of the network encompassing almost 7,000 sampling sites in 28 European countries is much higher than could ever be achieved by monitoring stations of atmospheric deposition.
Since particulate matter from natural and anthropogenic sources accumulate together in moss, it can be difficult to determine what proportion of the elements load is natural and what proportion is anthropogenic. Normalization of the data is an attempt to compensate for the natural variability of trace metals in mosses, so that any anthropogenic metal contributions may be detected and quantified (Loring, 1991). Several methods of normalization are possible, ranging from the use of simple metal/normalizer ratios to more complex methods based on regression analysis (Rowlatt and Lovell, 1994).
In this study, a normalizing procedure of element content in each sample to the corresponding Li content in the sample was applied to reduce the influence of the predominant crust component. For that purpose, ratios of X_n/Li_n were calculated, where X_n is the concentration of element X in sample number n and Li_n is the Li concentration in

sample number *n*. Lithium has been shown to serve as a better normalizing element because it is a typical component of earth crust and is generally not contributed by anthropogenic activity (Loring, 1990). For the first time this technique has been applied to a systematic study of air pollution with heavy metals. This study is only a part of the survey that covers all the territory of Albania. With this survey Albania attended for the first time the *European moss survey* in 2010/11, through the *UNECE ICP Vegetation Programme*. The aim of this study was the monitoring of air pollution at three regions in Albania and defining different pollution sources.

MATERIALS AND METHODS

Hypnum cupressiforme moss samples were collected at three regions of Albania (Tirane, Durres and Lezhe), following the guidelines of the UNECE ICP Vegetation. The moss samples were collected during September-October 2010 at 13 locations. In the laboratory, after manual removal of all adhering material (plant remains, soil particles, etc.), only the green–brown moss shoots were subjected to analysis as they correspond approximately to the deposition over the last three years. Then the moss samples were dried to constant weight at 30–40°C for 48 h and homogenized to a fine powder in agate mill.

Moss samples were digested by using of Microwave digestion system (Marsx, CEM, USA). All of the reagents used for this study were with analytical grade: nitric acid, trace pure (Merck, Germany), hydrogen peroxide, p.a. (Merck, Germany), and redistilled water. About 0.5 g of moss material was placed in a Teflon vessel and treated with 7 ml of concentrated nitric acid (HNO_3) and 2 ml hydrogen peroxide (H_2O_2) overnight. The procedure was continued with full digestion of moss material in microwave digestion system (Mars, CEM, USA). Digests were filtrated and quantitatively transferred to 25 ml calibrated flasks.

The content of elements in the moss samples were determined by inductively coupled plasma – atomic emission spectrometric (ICP-AES) method performed at the *"Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia"*. The certified M2 and M3 moss samples were used for quality control of ICP-AES analysis. These certified moss samples were prepared within the monitoring program "The European Moss Survey".

RESULTS

With the results obtained from the chemical analysis of moss samples with the ICP-AES method, the Descriptive Statistic was performed. The statistical data are given in Table 1. and ilustrated in Figure 1. where it is shown the distribution trend of elements according to the increasing order of their concentration values. Then, the concentration values of elements analysed in moss samples are normalized with element Li via the ratio C_X/C_{Li}, where C_X is the concentration value of the element X in a moss sample and C_{Li} is the concentration value of Li at the same moss sample. With the results obtained after the normalisation, the Descriptive Statistic was performed again. The statistical data are given in Table 2. and ilustrated in Figure 2. where it is shown the distribution trend of elements after the normalization with Li.

Table 1. *Descriptive Statistic data before the normalization with Li (μg/g, dry weight).*

Elements	As	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V	Zn
Mean	0.29	7015	0.13	5.30	6.72	1539	2431	65.7	6.01	2.46	4.25	16.6
Median	0.19	7147	0.11	4.42	5.75	1351	2208	56.5	3.85	2.37	2.91	15.9
Minimum	0.08	5316	0.05	2.40	2.96	469	1563	22.4	2.21	1.48	1.15	2.08
Maximum	0.68	10504	0.37	11.7	15.55	3538	3836	166	13.0	3.76	16.9	46.9

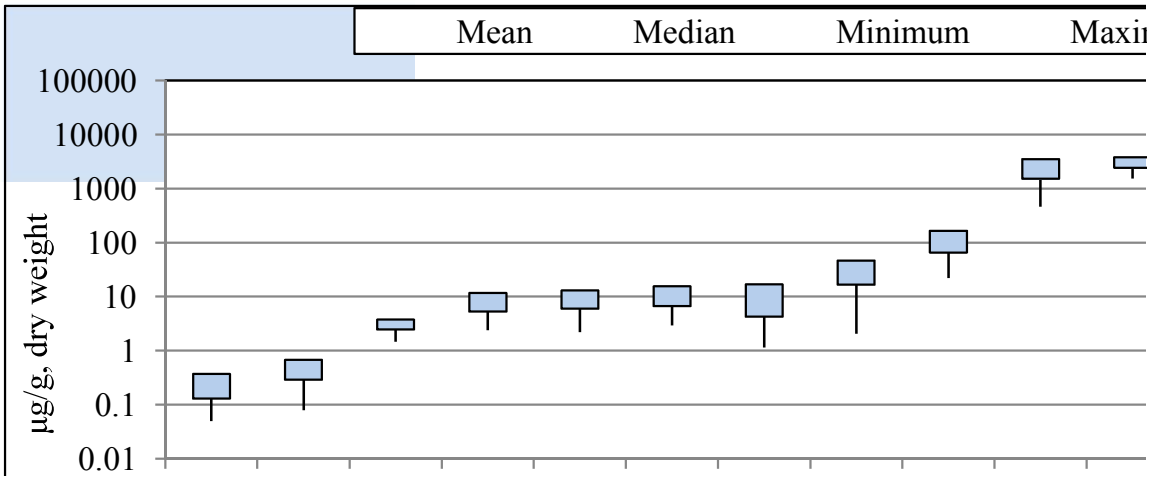


Figure 1. *The distribution trend of elements before the normalization with Li.*

As it is seen in Figure 1. the distribution trend of elements before the normalization with Li is: Cd < As < Pb < Cr < Ni < Cu < V< Zn < Mn < Fe < Mg < Ca. For the elements Ca, Mg it is seen that the rate of change as a max/min ratio of their concentration values is smaller than that of the other elements, which indicates that Ca, Mg are typical elements of earth crust. For elements Zn, V, As, Fe, Cd the max/min ratio of their concentration values is bigger, indicating that they have double origin, natural and anthropogenic.

After the normalization of the concentration values of elements with Li, the distribution trend of elements changes and as it is seen in Figure 2. it becomes: Cd < As < Pb < V < Cr < Ni < Cu < Zn < Mn < Fe < Mg < Ca. After the normalization the elements Cr, Ni, Cu are shifted, crossing the element V, indicating that the elements Cr, Ni, Cu are related to natural and anthropogenic sources. Also, after the normalization it is seen that for the elements Pb, Cu, Cd the rate of change as a max/min ratio of their concentration values increases, indicating that these elements have also anthropogenic origin.

Also, from the Correlation Analysis it is found that elements Fe, Ni, Cu, V, Cr have considerable correlation coefficients with the element Li, indicating for their geogenic origin, whereas the low correlation coefficients of elements Pb, As with the element Li indicate that they are of double origin, geogenic and anthropogenic. The elements Zn, Cd have high correlation coefficient between them, but do not show any correlation with the geogenic elements, indicating that they are mainly of anthropogenic origin, which is related to the road traffic in general (tire debris) and also with the burning of tires, coal, petroleum products and by-products, different plastics, etc. particularly in lime kilns. Considerable correlation coefficients exist also between elements Pb, Cu, Cd indicating their anthropogenic origin from road traffic, burning of different combustible materials and processing of copper ores containing Pb and Cu as their secondary minerals.

Table 2. *Descriptive Statistic data after the normalization with Li (µg/g, dry weight).*

Elements	As	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V	Zn
Mean	0.25	7598	0.13	4.71	6.58	1259	2490	63.5	5.12	2.55	3.25	16.10
Median	0.19	5988	0.11	4.57	5.62	1276	1917	46.8	4.11	2.07	3.02	12.11
Minimum	0.09	2393	0.04	2.53	2.10	1026	1344	24.7	2.95	1.24	2.18	2.80
Maximum	0.60	19112	0.42	8.42	16.38	1646	7879	211	12.48	6.14	7.42	55.84

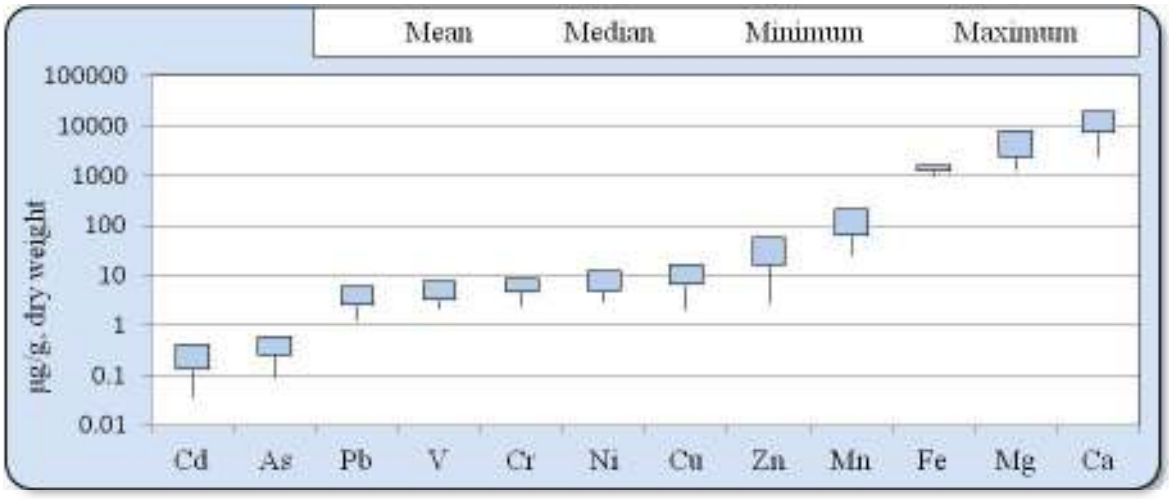


Figure 2. *The distribution trend of elements after the normalization with Li.*

CONCLUSIONS

This was the first study of the atmospheric environment within the Republic of Albania.
The distribution trend of elements before the normalization with Li is: Cd < As < Pb < Cr < Ni < Cu < V< Zn < Mn < Fe < Mg < Ca. After the normalization of the concentration values of elements with Li, the distribution trend of elements changes and the elements Cr, Ni, Cu are shifted, crossing the element V, indicating that they are related to natural and anthropogenic sources. Also, the rate of change as a max/min ratio of the concentration values of the elements Pb, Cu, Cd increases, indicating that these elements have also anthropogenic origin. From the Correlation Analysis, based on the correlation coefficients, we can say that Fe, Ni, Cu, V, Cr have mainly geogenic origin, elements Zn, Cd are mainly of anthropogenic origin.

Acknowledgements: The authors gratefully acknowledge Prof. Trajçe Stafillov of Sts. Cyril and Methodius University, Skopje, Macedonia for his collaboration.

REFERENCES

Arditsoglou, A., Samara, C., 2005. Levels of total suspended particulate matter and major trace elements in Kosovo: a source identification and apportionment study. *Chemosphere* 59, 669-678.
Callen, M.S., de la Cruz, M.T., Lopez, J.M., Navarro, M.V., Mastral, A.M., 2009. Comparison of receptor models for source apportionment of the PM10 in Zaragoza (Spain). *Chemosphere* 76, 1120-1129.
Loring, D.H., 1990. Lithium - a new approach for the granulometric normalization of trace metal data. Mar. Chem. 29, 155-168.
Loring, D. H. (1991) Normalization of heavy-metal data from estuarine and coastal sediments. *ICES J. Mar. Sci*. 48, 101–115.
Miris, Castello.(2007): A Comparison Between Two Moss Species Used as Transplants for Airborne Trace Element Biomonitoring in NE Italy. Environ Monit Assess 133:267–2
Markert, B., Breure, A., & Zechmeister, H. G. (Eds.) (2003). Bioindicators, biomonitors. Amsterdam, The Netherlands: Elsevier.
Park, S.S., Kim, Y.J., 2005. Source contributions to fine particulate matter in an urban atmosphere. *Chemosphere* 59, 217-226.
Quiterio, S.L., da Silva, C.R.S., Arbilla, G., Escaleira, V., 2004. Metals in airborne particulate matter in the industrial district of Santa Cruz, Rio de Janeiro, in an annual period. *Atmospheric Environment* 38, 321-331.
Rowlatt, S. M. and Lovell, D. R. (1994) Lead, Zinc and Chromium in Sediments around England and Wales. Marine Pollution Bulletin 28, 324±329.

Rühling, A., & Tylor, G. (1971). Regional differences in the deposition of heavy metals over Scandinavia. Journal of Applied Ecology, 8, 497–507.
Shah, M.H., Shaheen, N., Jaffar, M., Khalique, A., Tariq, S.R., Manzoor, S., 2006. Spatial variations in selected metal contents and particle size distribution in an urban and rural atmosphere of Islamabad, Pakistan. *Journal of Environmental Management* 78, 128-137.
Shah, M.H., Shaheen, N., 2010. Seasonal behaviours in elemental composition of atmospheric aerosols collected in Islamabad, Pakistan. *Atmospheric Research* 95, 210-223.
Tsai, Y.I., Cheng, M.T., 2004. Characterization of chemical species in atmospheric aerosols in a metropolitan basin. *Chemosphere* 54, 1171-1181.
Watson, J.G., Zhu, T., Chow, J.C., Engelbrecht, J., Fujita, E.M., Wilson, W.E., 2002. Receptor modeling application framework for particle source apportionment. *Chemosphere* 49, 1093-1136.

PAPER 087

ECONOMIC EFFICIENCY ON PRODUCTION OF THE VINE IN KOSOVO

Isuf Lushi

"Public University of Prizren "Ukshin Hoti" , Kosovo;

Email: isuf.lushi@uni-prizren.com

ABSTRACT

Vine is known as the agro-culture product that is gained by the processing of the grape, which has of nutrition, protection and heals values for the people. The aim of this paper is to research the relevant factors which impact on the development of the vine sector in Kosovo. In general the factors that deeply impact on the economical effects at the production industry of the vines are multi-dimensional, like: sort of the adequate varieties for vine, educational factors of the production, grape vine feeding, checking of the sickness and the damagers, marketing, data record, equipment for storage of the vine, etc. For the raise of the vine production benefit are required to have reduced fixed expenses for the production unit (labor force, facilities); Enhancement of the nutrition base by the quality aspect and the production costs; improvement of the grape cultivators for white and red vines; Vertical integration of the vines and findings of the new alternatives of the incomes that will impact on the profit raise which is also the aim of each business. Assigning the human capacities, with the aim of development the sector as well as including the advisory services regarding enforcement of the innovations of best practices in production, professional education and training of the new staff in the area of Oenology.

Key-words: Vine, production, varieties, economic evaluation

INTRODUCTION

Archeological researches show the first Vineyards about 2000 ago. The tradition of the cultivation and grape production has been continuing to date.
The best agro-ecological conditions, love and readiness to produce and manufacture the grape into the vine and brandy was the main factor in this tradition. The Vineyards also had raising and falling. The most considerable damages of the vineyards appeared the damager of the grape filoksera, during the period of 1913-1923 which was destroyed. After this period, the new vineyards have been worked out with grafted seedling resistant to the filoksera.
The most successful period was that one of the 1980, when Kosova had about 9.000 vineyards. The capacities of the grape manufacturing were more than 100 million liter per annum.
On its peak, the export of the vine from Kosova was 40 million liter; mainly to Germany and former republics of the Yugoslavia. During the war the fields with vineyards reduced in drastic way.
Vineyards of the SOE like "Mirusha" in Malisheva and "Vreshtaria" in Prizren, as well as "Dubrava" in Istog were destroyed completely.

MATERIALS AND METHODS

For this research have been used the resources of the information like: data by the relevant institutions (the Agency of the Vineyards, and Wineries 2013). Other data from studies. Data by the scientific literature. In this research have been apllied the contemporary research methods wit the aim of determining the most objective of the competitive capabilities of the farms to producing the vines in Rahovec. Regarding realization of this method have been used the data of the information's for the farms of the vines production, as follows: Production, market, grape varieties, sorts of the vines, manner of nutrition, expenses and benefits/loses, the engaged labor force in the farms (active and part time), qualified structure, gender and the age of the farmers, farm assets, farmers comments, etc. This method we used to treat the quality aspect, knowledge genuine, the former studies and the used practices in this field of the studying. By this method we did a comparison of the common features and differences between the farms in the level of the country and comparison with farms of the region countries as well as those from the EU. Also through

this method has been done the comparison of the incomings and expenses according to the farms. One of the basic method used was the statistical method.

RESULTS

Data from the vineyards cadastre for the period of 2013 show that actually the vineyards surfaces are 3220 ha. (Agency VW 2013). The surfaces of the vineyards are situated in eight vinery zones, where only the vinery zone of Rahovec and Suharekë compounds of 90 % of the area with vineyards of the wineries in all area of the Republic of Kosova.

In the Table below number 1, are shown the details upon area in hectares, participation in percentage %, number of the Vineyards and number of the Farmers.

Table 1. The Vineyards Zone, area, participation i perncetage % , number of the vineyards and number of the farmers.

Vineyard Zone	Area [ha]	Percentage [%]	No. Of Vineyards	No of Farmers
Gjakova	55.70	1.73	129	117
Istogu	0.11	0.03	2	2
Klina	7.80	0.24	13	11
Malisheva	35.24	1,09	220	234
Peja	6.00	0.18	30	30
Prizren	208.70	6.45	865	793
Rahovec	2243.94	69.69	4945	2630
Suhareka	663.14	20.6	1371	1148
Amount	3220.63	100	7575	4965

From the data provide by vineyards cadastre in 2013, we are providing a overview more detailed as it belongs to the vineyards farm organizations (Resource: Agency for Vineyards and Winneries in Rahovec.).

More than 40 grape varieties are cultivated in Kosovo, for different purposes. A considerable number of the varieties are disregarded as it belongs to the area.

Last year for the first time are cultivated also two new varieties like Crimson Seedless and Red Glob in a area of 6 ha.

Table 2. Grape varieties of the vine manufactured.

Varieties	Destination	Total area in ha
White Burgundez	Vine	5
Black Burgundez	Vine	157
Frankofkë	Vine	31.82
Inked Range	Vine	49.99
Simple Range	Vine	317.47
Mixed Grape	Vine	0.79
Kaberne Frank	Vine	30.6
Kaberne Sovinjon	Vine	86.78

Melnik	Vine	11.62
Merlo	Vine	27.72
Without Varieties	Vine	6.19
Pllovdinë	Vine	20.12
Prokupë	Vine	380.59
Rizling Italian	Vine	247.97
Rizling Rajne	Vine	69.05
Rrkacitel	Vine	19.88
Rubini	Vine	2.06
Semion	Vine	3.32
Shardone	Vine	118.59
Shasla	Vine	5.5.
Smederevë	Vine	391.98
Syrah	Vine	3.94
Vranac	Vine	396.37
Zhametë	Vine	109.56
Zhillavkë	Vine	4.62
Zhuplanka	Vine	24.34
		2517.37

In table 2, its shown the variety of Vranc which is in the biggest area, this variety recently has been growing with area especially was spread out in the zone of Rahovec vineyards and very less in the other zones with vineyards, also with big areas of the variety Prokupë are present to date. Simple range, Smederevë, all these with tendency of minimizing the areas, especially the variety of Prokupë which shows the oldest variety for its age, 70 % of this variety is older than 30 years. The manufacturing of the vine begins with grape selection and ends up to the filling of the vine bottles. The manufacturing of the vine can be divided in two general categories: production of none carbonated vine and production of the carbonated vine (CO_2). After picking, the grape will be crushed and will be allowed to get fermented. The red vine is manufactured by the must (plume) of the red grape or black grape that goes through fermentation together with grape peel, while the white vine usually is manufactured with fermentation of the liquid that comes from the kernel of the white grape by pressure but also can be manufactured by the extracted must of the red grape by minimal contact of the grape peel. Rose vines are manufactured by the black grape where the extracted liquid is allowed to become in contact with the peel as long as will get the bright red color (rose).After the primary fermentation, which usually lasts from one to two weeks , yeast makes the most part of the sugar by the grape liquid in ethanol (alcohol). After primary fermentation, the liquid is transformed to the reservoir for secondary fermentation the remained sugar slowly is becoming in alcohol and the vine becomes clear.

After this the vine is allowed to stay in the wooden tank before the bottles will be filled, by which the vine gets a extra aroma while other will be filled immediately.

Many vines with comparable quality are produced by using similar manufacturing methods or different ones. Recently it came out to the quality movement of the vine production; the new manufactures are appearing with modern approach and contemporary equipment.

The tendecy of the vine production by the regional autochtone varietes that in the future will expected to produce the vines with better quality. Actually in the Republic of Kosova are operating 15 licenced companies by the Ministry of

Agriculture Spatial Planning and Rural Develpoment that are dealing with grape manufacturing and other grape products as well as the vine:

" Stone Castle Vineyards&Winery" LLC – Rahovec.
NTP " Haxhijaha"– Rahovec.
NTP " Muja" – Rahovec.
LLC " Rahoveci" – Rahovec.
LLC "Dea" – Gjakovë.
"Biopak" Shpk – Rahovec.
NTP " Agro-alf" – Rahovec.
NTP " Rahvera" – Rahovec.
NTP " Daka" – Rahovec.
P.T.P "Boemi" - Bërnicë e Poshtme
N.T.SH. "BAHHA" - Rahovec
"Agrokosova – Holding" Sh.p.k. – Suharekë.
NTP " Sefa" – Rahovec.
NTP " JIDO" – Prilluzhë.
NTP " Albatros" Prizren.

Also in the Republic of Kosova are operating 33 companies that are realizing the import of vine and other products from grape and vine. As it belongs to the structure of the vine manufactures, are dominating four big manufacturers that are followed by 11 vine production companies.

After privatization the companies vine producers and other products from grape and vine step by step are stabilized and have created their profiles.

Have realized basic investment starting by the location of grape collection, digital ferment, stabilized facilities of the vine up to the modern lines of vine filling. Many manufacturing companies have created also their labs to conduct the chemical-physical analyses on vine, that reflect with enhancement of the quality control of the produced vine.The main types of the vine produced in 2012 are: red vines: Pinot Noir, Vranac & Game, Merlot, Cabernet Sauvignon. General production was 5,3 million liter vine only 35% of production is subject to the official declaration. With the price of the producer that goes around from 1,30 to 2,50 €/liter of the red vine. White vine: Rizling Italian, Shardone, Rizling Rajne. The price of the producer is about 1, 30 to 2,00 €/liter of the white vine. To produce a liter of vine is required about 1,55 kg grape.

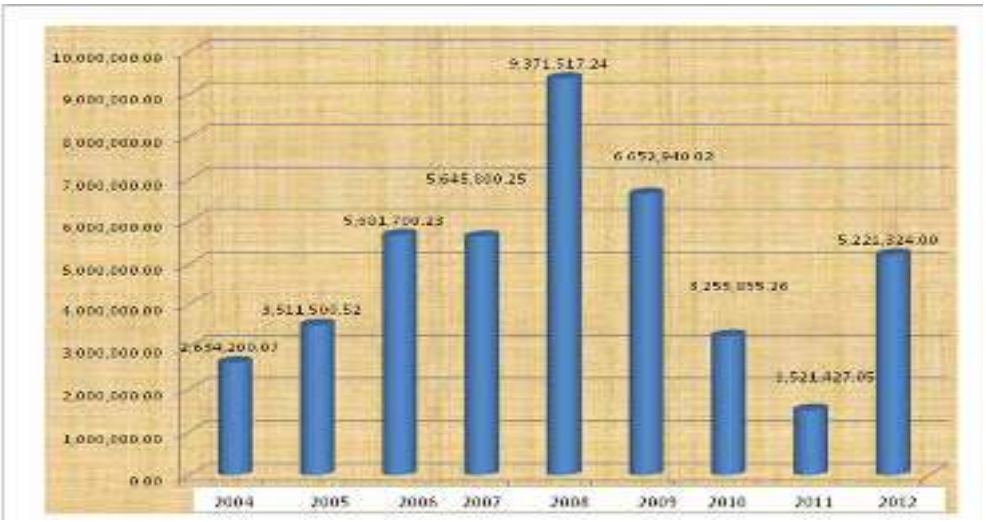


Figure 1. Manufacture of the vine for the years of 2004 – 2012.

Figure 1. Shows the production from 2004 to 2012,as it can be seen by the figures in 2008 the vine was manufactured more. The production after the war and herein after of this cannot at all be stabilized: There is a big difference between the productivity projected and that one officially declared.

There is a big difference between the projected productivity and that one officially declared. The total production is not included through the official channels of the controlling. Approximately 60% of the production by the grape

varieties for vine are subject to other forms of trading like: table grape, alcohol production, usage for conservation, grape liquid, and other forms of manufacturing.
Republic of Kosovo from 2007 to 2012 has realized export to 24 countries. The biggest export took place in these countries:
Serbia --------8,698.662 liter
Germany – 6,113.984 liter
Croatia ----- 5,329.027 liter
Macedonia – 2,759.126 liter
Slovenia —-- 1,975.890 liter, etc

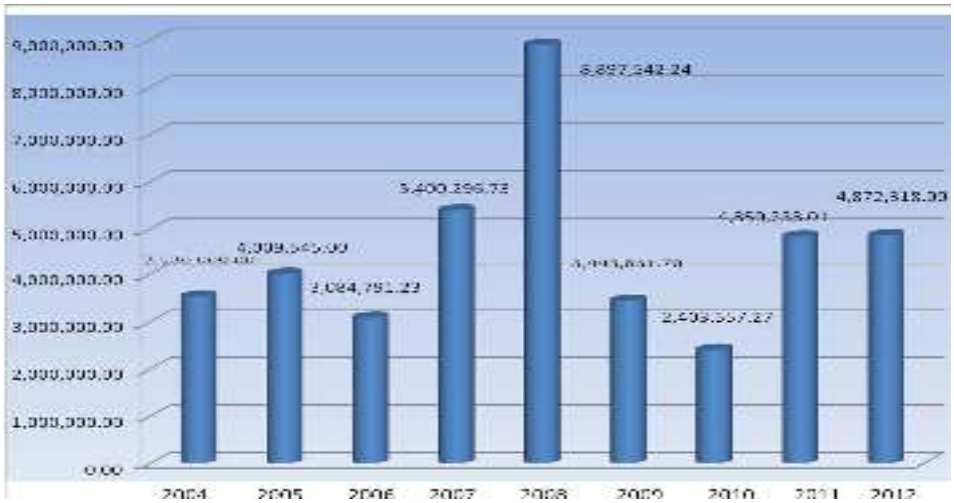


Figure 2. Export of the vine in 2004 -2012

Republic of Kosova from 2007 to 2012 has realized import to 27 Countries.
The biggest import took place at these countries:
Monte Negro — 1,114.708 liter
Macedonia – 399.837 liter
Italy ----------300.684 liter
Serbia ---------110,185 liter etc.

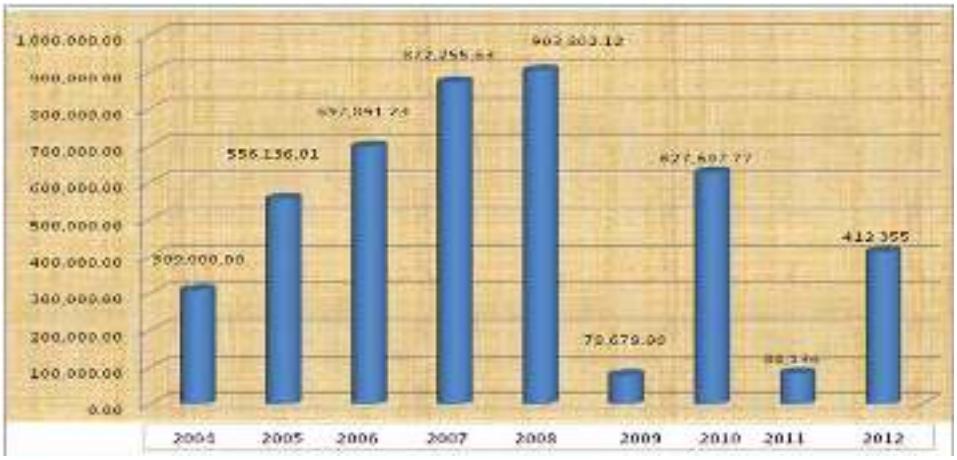


Figure 3. Vine Import in 2004 -2012

CONCLUSION

Providing training and possibilities for advises for manufacturers- enhancement of the general technical knowledge's, through advisory services. For increase of the profit and the vine production, are required reducing of the fix expenses for production unit (labor force, compounds); Improvement of the nutrition base by the quality aspect and the production costs; Improvement of the grave cultivators for white vines and red vines; vertical integration of the farms and finding a new alternatives of the incomes, that will impact on raise of the profit, which is the aim of every business. Enforcement of the quality assurance system and the security rules of the food. Enhancement of the production in industry, and technology of the assortment raise, as well as the building of the capacities of technologist. Improvement of the production conditions and trading with export advantages.Regionalisation of the vine sector in the aspect of political drafting (Sectro of agro-food expresses the regional consudearble differences which require to be reflected during gthe political drafting. Improvement of the macroeconomical environment incleding taxation, trade, and interest.

REFERENCE

CÓMO DEGUSTAR LOS VINOS: MANUAL DEL CATADOR. Renato AÑO 2011.
Lushi, I. (2013). Authorized Lectures" Introduction to Horticulture", Prizren..
TRATADO DE VITICULTURA GENERAL. Authors: José Hidalgo Togores y Luis
Kongol.R." Production of the table vine in the domestic conditions, 2006,Tirana.
Agency of Vineyards and Winery in Rahovec.
Kongol,R." Direction of the Quality in Agro Food Industry,2010.Tirana.
Zigori, V., Sotiri, P., Kongoli, R. – studying of the current situation of the Vineyards and
Vine Industry and the optimal ways to improvement of the autochthones cultivators and vines manufactured by them, 2001.
MEST-DANIDA, 2011, Prishtina.

PAPER 091

BEHAVIOUR OF SOME APPLE CULTIVARS ON PAJAM 2 ROOTSTOCK IN DIBRA REGION

Telat Spahiu*, Fadil Thomaj, Endrit Kullaj****

*ADAD; Dibra;
**Agricultural University of Tirana, Department of Horticulture and Landscape Architecture

ABSTRACT

Progressive dissemination of new apple rootstocks in Europe and broader has made immediate the study of their behaviour under certain pedological and climatic conditions as well as their combination with certain cultivars. The present research was conducted in Dibra region aiming at studying Pajam 2 apple rootstock on vegetative and reproductive characteristics of cvs. 'Red Chief', 'Grany Smith', 'Golden Delicious' and 'Starking' . The experimental plot was planted in 2011 with distances 3.5 x 1.5m. During three consecutive years (2011 – 2013), at the end of the vegetative growth, we measured the volume of the canopy, trunk circumference at 20 cm above the grafting point, elements of the canopy architecture, yield and production efficiency. Data show that trees of cv. 'Red Chief'had the highest volume of the canopy and trunk and those of cv. 'Starking' the lowest values, although the latest achieved the highest efficiency (kg/cm2 of trunk circumference). The highest yield was collected from trees of cv. 'Granny Smith' while the efficiency was almost similar to 'Starking'. Significant changes have been found in the elements of canopy architecture, with cv. 'Golden Delicious' had highest percentages of vegetative shoots.

Key words: cultivar, rootstock, canopy architecture, production per tree

INTRODUCTION

An increasing competitive and globalised apple market demands by producers to increase yields, improve quality and reduce production costs. These objectives are achieved only by harmonising the knowledge on the biology of the crop with innovative experiences in choosing and implementing the agronomic techniques (Massetani et al. 2006;Sansavini et al. 2003). Of primary importance for the success or failure of an orchard is the choice of the appropriate cultivar and rootstock for a certain location and for a certain training system (Kosina 2010;Perry et al. 2008;Spahiu et al. 2013).
Rootstock plays an important role in determining the training system and orchard performance (Ikinci et al. 2014;Karlidag et al. 2014). Its effects are easily visible in reducing the dimensions of the canopy, branching type and structure. Such changes determine canopy architecture, orchard density and the level of intensification in the orchard(Autio et al. 2002;Domi et al 2012;Gjamovski et al. 2011;Hooijdonk et al. 2011;Lauri et al.2005, 2006; Tarrahi et al. 2010).To fulfil the above requirements, often there is a use of an interstock taken from a rootstock with a dwarf (weak) rootstock (Di Vaio et al. 2009;Karlidag et al. 2014). Although the use of clonal rootstocks dates back 170 years ago, it is dominated by M9 rootstock as the best adapted to different environment (Webster 1995). However, M9 rootstock has shown some drawbacks related to disease and cold resistance. Such phenomena have incentivised a wide selection work and since two decades there are other rootstocks tested and found more resistant to unfavourable biotic and abiotic factors (Autio et al. 2011;Barrit et al.2012, Blanco et al. 2008;Fischer 2012;Gjamovski et al. 2011; Guerra et al. 2011;Kosina 2010;Tabakov et al. 2005).
The clonal rootstocks under the Albanian conditions are relatively new and especially Pajam 2 rootstock,which is found in other regions of Europe (Gjamovski et al. 2011;Losciale et al. 2012;Szczygielet et al. 2002). This research aimed at testing the behaviour of four apple cultivars under the environmental conditions of Dibra region.

MATERIALSAND METHODS

The orchard was planted in 2011 in the village Shimcan, Kastriot commune of Peshkopi, Albania (Fig. 1) (Wikipedia). It is located at an altitude of about 680m above the sea level, with a south – west orientation. The area is characterised by a cool climate, typical for apple growing. The maximum temperature reaches +39^{o}C during July while the minimum decreases to -18^{o}C, and in special cases up to -20^{o}C. January is the coldest month, with an

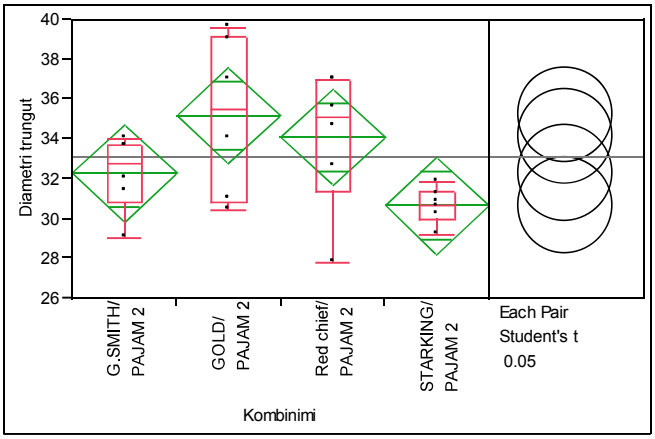
average temperature -2 to -3°C, while the hottest month is August with an average temperature of 21°C.The first frosts start in the first days of November and continue until the middle of March. The soil is medium sub-clayey.
For each cultivar, a total of 15 plants divided into three repetitions. The planting distances were 3.5x1.4m, with a theoretical density of about 2040 plants/ha. Trees were trained following the French axe training system.A drip irrigation system was supplying water to the trees.
During the years of the study (2011 – 2014)the following series of measurements were taken on thetrunk diameter at 20 cm above the grafting point, following the tree line. This value was used to calculate the trunk cross-section area (Autio et al. 2011; Gjamovsiki et al. 2011;Sassella et al. 2007). In year 2014, with a regular production, the fruits were harvested and we calculated the average production per tree as well as the production efficiency (kg/cm2 trunk; TCA)at the end of the vegetation period of each year. Before pruning intervention, we measured various elements of canopy architecture, namely the number of shoots, number of fruit shoots (spur and bourse), number of vegetative shoots; tree height (m), canopy diameter at the base and calculation of canopy volume. Data processing and statistical analyses were performed using JMP software.

Figure 1.Location of experimental plot

RESULTS

Vigour and productivity

Data on the increase of trunk diameter until the fourth year of orchard show that the highest diameter was found in cv. 'Golden Delicious' and 'Redchief', followed by 'Granny Smith'. The smallest diameter was found in cv. 'Starking'(Figure 2). Changes found were simply due to rootstock/scion interaction, because at planting, all the selected saplings were selected with the same diameter. Fischer et al. (2004) relates such changes to the hydraulic conductance of the root and the hydraulic architecture of the scion. Other authors (DiVaio et al. 2009) state that different rootstocks may reduce the vigour of certain cultivars up to 8 per cent.



Level			Mean
GOLD/P2	A		35.166667
Red chief/P2	A		34.100000
G.SMITH/P 2	A	B	32.266667
STARKING/P 2		B	30.633333

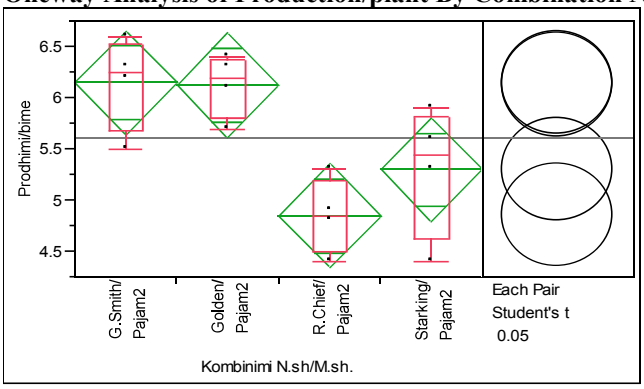
Oneway Analysis of Diametri trungut By Combination

Figure 2.The level of differences in vigour (TCA mm).

Calculation of the trunk cross–sectional areas show that cv. 'Redchief', although belongs to 'spur' group, when grown under Pajam 2 shows a more vigorous growth than the other cultivars under study, while cv. 'Starking' has the lowest growth. This demonstrates a weak compatibility of cv. 'Starking' with Pajam 2 rootstock (seeTable 1). Significant changes in growth were reflected also in the production of plants, with cv. 'Grany Smith'and 'Golden Delicious' have the highest yields, while cv. 'Redchief'and'Starking' the lowest yields forming two similar statistical groups (Figure 3).

Table 1.Data on the trunk cross-sectional area, yield and production efficiency (kg/cm2)

Oneway Analysis of Production/plant By Combination N.sh/M.sh.



Level		Mean
G.Smith/Pajam2	A	6.1500000
Golden/Pajam2	A	6.1250000
Starking/Pajam2	B	5.3000000
R.Chief/Pajam2	B	4.8500000

Figure3.The level of differences for yields.

As far as regards the production efficiency of the plants of each cultivar, it was found that cv. 'Golden'and'Starking' have the highest efficiency (kg/cm2), while the lower efficiency was found in cv. Redchief', the latest having the highest vegetative growth.This demonstrates an inverse relationship between growth and production which is confirmed by other authors (Barrit et al. 2008; Gjamovski et al. 2011; Iknici et al. 2014).

Elements of canopy architecture

Data on the structure of various branches formed during the years of study shows that the highest number of branches was found in cv. 'Redchief', while the smallest number belongs to cv. 'Starking'. Cv. 'Golden'is ranked second whilst cv. 'Granny Smith' is third. It is interesting to notice the structure of various types of shoots forming the canopy architecture. Data of Table 2 show that the ratio between shoots of different types does not depend only on the genetic characteristics of the cultivarbut also the influence that the rootstock has on the scion. Thus, we may say that while cv. 'Golden'is distinguished for the formation of thin shoots, but in our study, the highest number was in cv. 'Redchief' and less in cv. 'Granny Smith'and'Golden'. Moreover, fruiting shoots were more numerous in cv. 'Starking'and'GrannySmith'and less in the other two cultivars (Table 2;Figure 4). In general, it is accepted that reduction of growth in height forms more fruiting shoots while growth toward the apex reduces their development (Lauri et al. 2005, 2006)

Table 2.Data on the indicators of canopy architecture

Cultivar/rootstock	Surf. cm2	Yields kg/plants	kg/cm2
R.Chief/Pajam 2	9.6	4.8_b	0.5
G.Smith/Pajam2	9.1	6.3_a	0.69
Golden/Pajam2	8.03	6.1_a	0.76
Starking/Pajam2	7.06	5.3_b	0.75

Similar letters show non – significant changes (P<0.05)

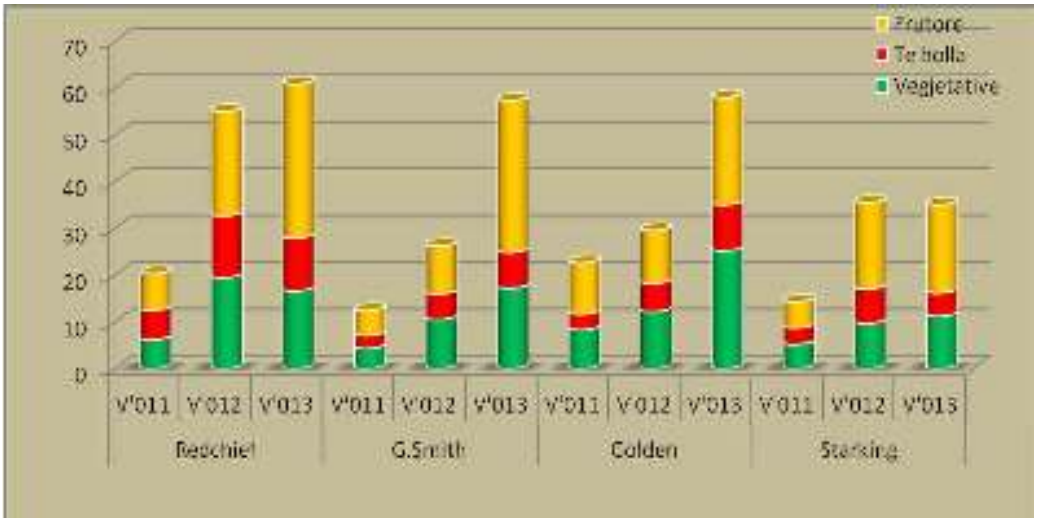
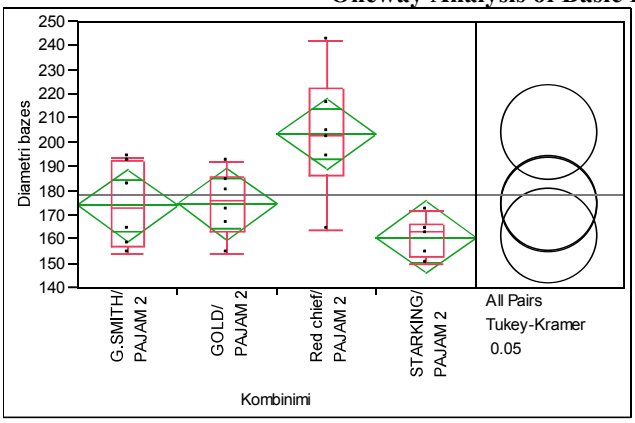


Figure 4.Structure of canopy elements during the years of study

'Redchief' cultivar, from the very first year, gives a priority to canopy elements and preserves that even in the fourth year. On the contrary, cv. 'Starking'in the first two years has almost no difference, which demonstrates a strong effect of the rootstock on slowing the growth in the first years. This stimulates an earlier bearing ad formation of trees with a small canopy (Table 2;Figure 5, 6). In this case, Pajam 2 rootstock, although grouped in semi–dwarf rootstocks behaves as a dwarf rootstock forming the smallest canopy and giving the highest yields in the first years. 'Redchief'forms the highest and widest canopy with the widest volume. This favours it to increase production in forthcoming years while cv. 'Starking'has a strong stunt of growth but also production.

Fit Y by X Group

Oneway Analysis of Basic Diameter ByCombination

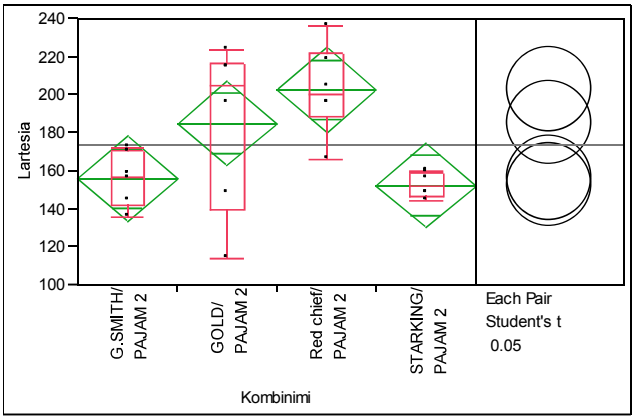


Level		Mean
Red chief/PAJAM 2	A	203.66667
GOLD/PAJAM 2	B	174.66667
G.SMITH/PAJAM 2	B	174.00000
STARKING/PAJAM 2	B	161.00000

Figure5.Leveo of differences in canopy diameter

Oneway Analysis of Canopy Height ByCombination

Cultivar/rootstock	Vegetative%	Thin %	Fruiting%	Canopy height	Diameter at the base of canopy (cm)	Canopy volume m3
R.Chief/Pajam 2	31.3	22.4	46.3		203.6	2.2a
G.Smith/Pajam2	33.2	16.6	50.1		174.6	1.2b
Golden/Pajam2	41.6	17.2	41.1		174.0	1.4b
Starking/Pajam2	31.2	18.6	50.2		161.0	1b



Level				Mean
Red chief/PAJAM 2	A			202.66667
GOLD/PAJAM 2	A	B		185.00000
G.SMITH/PAJAM 2		B	C	156.00000
STARKING/PAJAM 2			C	152.50000

Figure 6.Level of differences for tree height

CONCLUSIONS

Rootstock has a strong influence on forming vegetative and productive organs.
Pajam 2 rootstock under Dibra region gives good results in combination with cv. 'Granny Smith', 'Golden'and'Redchief'. Grafted with cv.'Starking' gives a weak growth and can be used only in the case of establishing superintensive orchards.

REFERENCE

Autio W.R., Krupa J.S., Clements J.M., Cowgill W.P., Magron R. 2011. Comparing strains of B.9, M.26, and M.9, P.14, and three pillnitz rootstocks: 2002 NC-140 apple rootstock trial in Massachusetts and New Jersey *(Fruit notes, vol.76. 6-10)*

Autio W., Robinson T., Archbold D., Cowgill W., Hampson Ch., Quezada R.P ., Wolfe D.2002. "Gala" apple trees on Supporter 4, P.14, and different strains of B.9, M.9 and M.26 rootstocks: Final 10-Year Report on the 2002 NC-140 Apple Rootstock (J. Amer. Pomol. Society 67:62-71).

Barritt B.H., Konishi B.S., Dilley M.A. 2012. Tree size, yield and biennal bearing relationships with 40 apple rootstocks and three sion cultivars. *(ISHS Acta Horticulturae 451: VI Int. Sym.Int. Canopy, Rootstock, Environmental Physiology in Orchard Systems*

Blanco A., Mata P.A., A. Lasaosa A., Val J. 2008. The P16 rootstock inhibits the growth but enhances the fruit quality of 'Jonagored' apples when grown under warm summer conditions. *(Spanish Journal of Agricultural Research 6(3), 412-421)*

Di Vaio C., Cirillo Ch., Buccheri M., Francesco Limongelli F. 2009. Effect of interstock (M.9 and M.27) on vegetative growth and yield of apple trees (cv ''Annurca'')*(Scientia Horticulturae vol 119 (3)*

Domi H., Spahiu T., Kullaj E., Thomaj F. 2012. Rootstock influence on apple canopy architecture under high radiation and temperature *(Agroznanje, vol. 13, (4): 527-533)*

Fischer M.2012. Pillnitzer Supporter 4(Pi80)- a semi - dwarf apple rootstock from dresden-pillnitz. *(Acta Hort.((ISHS) 451: 99-104)*

Fisher J.B., Machado K., Woodruff D., Jones T. 2004. Leaf photosynthetic traits scale with hydraulic conductivity and wood density in Panamanian forest canopy trees (Oecologia, 140: 543-550)

Guerra W., Höller I. (2011). Portinnesti del melo: M9 non sarà l'unico, molti i nuovi arrivi. *(L'Informatore Agrario 43/2011, 2-4)*

Hooijdonk B., David Woolley D., Warrington I.2011. Rootstocks Modify Scion Architecture, Endogenous hormones, and root growth of newly grafted "Royal Gala" apple trees.*(J.Amer. Soc. Hort. Sci. 136(2); 93-102)*

Ikinci A,. Bolat I., Sezai Ercisli S., Kodad O. 2014. Influence of rootstocks on growth, yield, fruit quality and leaf mineral element contents of pear cv. 'Santa Maria' in semi-arid conditions *(Biological Research , 47:71)*

Karlidag H., Aslantas R., Esitken A. 2014. Effects of Interstock (M9) Length Grafted onto MM106 Rootstock on Sylleptic Shoot Formation, Growth and Yield in Some Apple Cultivars. *(Journal of Agricultural Sciences 20; 331-336)*

Kosina J. 2010. Effect of dwarfing and semi dwarfing apple rootstocks on growth and productivity of selected apple cultivars (Hort. Sci. Vol. 37 (4): 121–126)

Lauri P.E., Maguylo K., Trottier C. 2006. Architecture and size relations: an essay on the apple (Malus x Domestica, Rosacae) tree. *(American Journal of Botany 93(3): 357–368*
Lauri P., Lauren F. 2005.Architectural types in apple (malus x domestica borkh) ‘’Crops: Growth, Quality and Biotechnology’’, pp. 1300-1313.
Losciale P., Manfrini L., Morandi B., Pierpaoli E, Zibordi M., Muzzi E., L. Grappadelli L.C. 2012.
Massetani F., Neri D., Colombo R.2006. Forme di allevamento e sistemi di impianto del meleto (*www.researchgate.net/)*
Perry R.L., Hull J. 2008.Apple scion/rootstock selection and planning for Michigan (Int. Symp.precision agricultural for fruit and vegetables, Orlando, FL)
Sansavini S., Pellegrino S.,Stainer R. 2003. Alle porte una nuova rivoluzione genetica? (Frutticoltura ; 12:20-30)
Sassella A., Monney Ph. 2007. Comportement agronomique et qualité du fruit de sept clones de M9 avec Golden Delicious (R. suisse Vitic. Arboric. Hortic. Vol. 39(4): 245-250).
Spahiu T., Thomaj F., Domi H. 2013. Behavior of the “Golden Delicious” cultivar on some clonal rootstocks, in the conditions of Dibra region. *(Albanian j. agric. sci. 12 (1): 495-501)*
Spahiu T., Thomaj F., Kullaj E., Domi H. 2013 The Behaviour of Some Apple Cultivars Grafted on M9 in Two Different Ecological Areas: Korça and Lushnja (J. Int. Environmental Application & *Science*, Vol. 8(4): 580-584)
Szczygiel A., Czynczyk A. 2002. Suitability of some semidwarf and dwarf rootstocks to three apple cultivars in the sub-Carpathian region. (J.Fruit&Ornamental Plant Vol.10:85-93)
Tabakov S., Dobrevska G. 2005. Influence of the clonal rootstocks MAC9, M9,M26 and MM106 upon growth and reproductive behaviour of the Golden resistant cultivar. *(Journal of Central European Agriculture Vol (3):353-360)*
Tarrahi,Tabrizi SH., Hajnajari, H. 2010. Morphological and tree architecture investigations on 30 apple commercial cultivars for specific Orchard Management*(Proceedings I. Sci. Conf. Samokhvalovichy: 43-47)*
Tombesi S., Johnson R.S,.Kevin R. Day K.R., DeJongTH.M. 2010. Interactions between rootstock, inter-stem and scion xylem vessel characteristics of peach trees growing on rootstocks with contrasting size-controlling characteristics *(AoB Plants).*
Webster T., Tobutt K., Kate Evans K. 2000.Breeding and evaluation of new rootstocks for apple,pear and sweet cherry *(The compact fruit tree , Vol 33(4): 100-104)*
Webster A.D.1995 .Rootstock and interstock effects on deciduous fruit tree vigour, precocity, and yield productivity*(New Zealand J. Hort.Sci., Vol. 23: 373-382)*

PAPER 092

INVESTIGATION OF ISOTHERMAL PARAMETERS OF DYE ADSORPTION ONTO ACTIVE CARBON

Ahmet SELÇUK[2], Ali Ender KUYUCU[1], Ali Rıza KUL[1], Gülen ÖNAL[2]

[1]Yuzuncu Yıl University Faculty of Sciences, Van, Turkey;
[2]Yuzuncu Yıl University, Faculty of Educational Van, Turkey;

E-mail : aselcuk@yyu.edu.tr

ABSTRACT

The fact that active carbon adsorps colourants and heavy metals has been known for a long time and thus it is used as adsorbant in removal of such pollutants. In this study, the capacity of active carbon in removal of colourant was investigated. As active carbon, Zivzik pomegranate from Siirt district of TURKEY was used and removal of colourants of Methylene Blue and Crystal Violet was studied. Active carbon was prepared with ZnCl2 by chemical activation. BET surface area, total surface volume and surface area of active carbon were measured by hte istrument called BET. In our study, adsorptions Methylene Blue and Crystal Violet colourants to active carbon at 45°C were evaluated for four different initial colourant concentrations of 200, 400, 600 and 800 mg/L graphically.

Key words: Dye, Clay, Adsorption, Isotherm

INTRODUCTION

Equilibrium of adsorption is expressed by equations of adsorption isotherms. Adsorption isotherms is very important for design of adsorption systems. Adsorption isotherms, in general, explain how the adsorbant and adsorbat interact. Four different adsorption isotherm equations (Langmuir, Freundlich, Dubinin–Radushkevich and Temkin) were used for colourant adsorption.
Langmuir equation is given by;

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$$

where q_e (mg/g) is concentration of adsorbat which is adsorbed by adsorbant in eqüilibrium and C_e (mg/L)) is concentration of adsorbant for a solution in equilibrium. K_L (L/mg) and q_{max} (mg/g) are Langmuir constants. K_L expresses adsorpability of adsorbat q_{max} defines single layer capacity of adsorbant. Unitless seperation factor of R_L can be found by Langmuir isotherm data:

$$R_L = \frac{1}{1 + K_L C_0}$$

Here C_0 (mg/L) is maximum initial colourant concentration and K_L (L/mg) is defined as Langmuir isotherm constant.

Freundlich equation is in the form of $q_e = K_F C_e^{1/n}$ *where* K_F (L/g) and n (unitless) are Freundlich constants which are called as adsorbant capacity and heterogeneity factor, respectively (Kuyucu A.E. , 2013).
Temkin izoterm denklemi;

$$q_e = \frac{RT}{b} lnA + \frac{RT}{b} lnC_e$$

şeklindedir. Burada; R : Gaz sabiti (J $mol^{-1}K^{-1}$) ve T : Ortamın K cinsinden sıcaklığıdır (Temkin ve Pyzhev, 1940).
Temkin isotherm equation is

$$q_e = \frac{RT}{b} lnA + \frac{RT}{b} lnC_e$$

where R (J $mol^{-1}K^{-1}$) *is gas constant* and *T (K) istemperature of medium* (Temkin ve Pyzhev, 1940).

Dubinin-Radushkevich isotherm equation is in the form of $ln\ q_e = ln\ q_m - B_D\ \varepsilon^2$. Here q_m (mg/g) is Dubinin-Radushkevich single layer capacity, B_D (mg^2/J^2) is a constant about adsorption energy and ε is polony constant which is related to equilibrium concentration. B_D (mg^2/J^2) constant helps to find out adsorption energy (E). Adsorption energy provide information about whether adsorption mechanism is of physical or chemical character.

Value of E can be calculated (Dubinin ve Radushkevich, 1947) as following: $E = \frac{1}{\sqrt{2B_D}}$

MATERIAL AND METHODS

Preparation of materials

Two dyes were used in the study. The dyes, Methylene Blue (MB) (Chemical Formula = $C_{16}H_{18}N_3SCl$, MW = 319.85 g/mol, λ_{max} = 660 nm) and Crystal Violet (CV) (Chemical Formula = $C_{25}N_3H_{30}Cl$, MW = 407.979 g/ mol, λ_{max} = 594 nm) were supplied by Merck. One thousand milligrams per liter of stock solution was prepared by dissolving the required amount of dye in double distilled water. Working solutions of the desired concentrations were obtained by successive dilutions. (Önal, 2006)

Preparation of activated carbon

Zivzik Pomegranate supplied by Siirt pomegranate plant were dried under labaratory conditions and then dried again at 100 ^{0}C. Zivzik Pomegranate was mixed with $ZnCl_2$ at the $ZnCl_2$ initial weight ratio of 1:1 and the mixture was kneaded with adding distilled water. The sample was placed on a quartz dish and heated at the rate of 10 ^{0}C min^{-1} up to activation temperature (500 ^{0}C) under N_2 flow and held at the activation temperature for 1 h. After activation, the sample was cooled down under N_2 flow and 0,5N HCl was added on to activated sample. Activated sample was washed sequentially several times with hot distilled water to remove residual chemicals until it did not anymore give chloride reaction with $AgNO_3$. The washed sample was dried at 110 ^{0}C to prepare activated carbon (Selçuk , 2014).

Characterization of the prepared activated carbon

Activated carbon surface measurements were made by BET device. Its total surface area, total surface volume and BET surface area were measured as 429,044 m^2/g, 0,59232 cm^3/g and 1513,05 m^2/g, respectively (Selçuk A.,2014).

Instrumentation

A Tri Star 3000 (Micromeritics, USA) surface analyzer was used to measure nitrogen adsorption isotherm at 77 K in the range of relative pressure 10^{-6} to 1. Before measurement, the sample was degassed at 300 ºC for 2 h. The BET surface area, total surface area and volume of the total surface were measured by the surface analyzer. The spectrophotometric determination of dyes was done on a Boeco UV – vis spectrophotometer (model UV – S22, Germany).

Adsorption experiments

To monitor the adsorption process at 45 ^{0}C batch techniques were employed. Four different initial dye concentrations (200,400,600 and 800 mg/L) were used in this process. This concentrations were prepared in 1000 mL conical flask containing 500 mL solution of each concentration. A known amount of 0.1 g activated carbon was then added into the solution and conical flask was stirred with thermostatic bath operating at 400 rpm. And then samples taken about 1, 3, 5, 7, 9, 13, 17, 23, 30, 40, 50, 60 and 70 minutes time period (Selçuk A., 2014) .

RESULTS

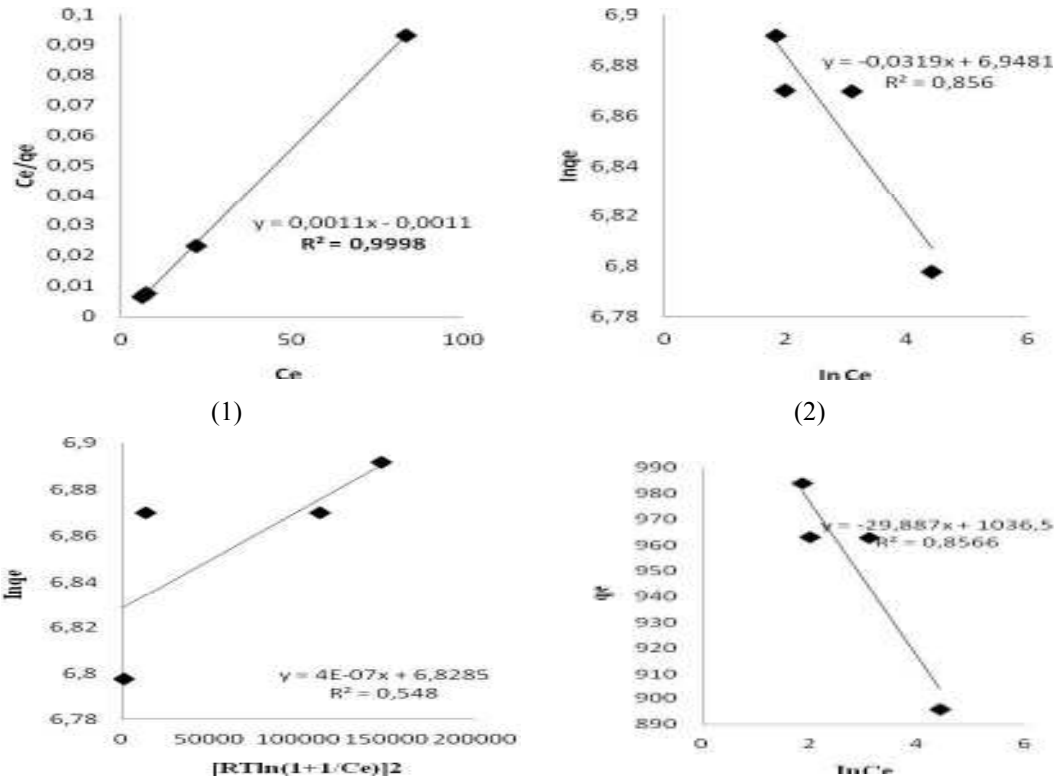
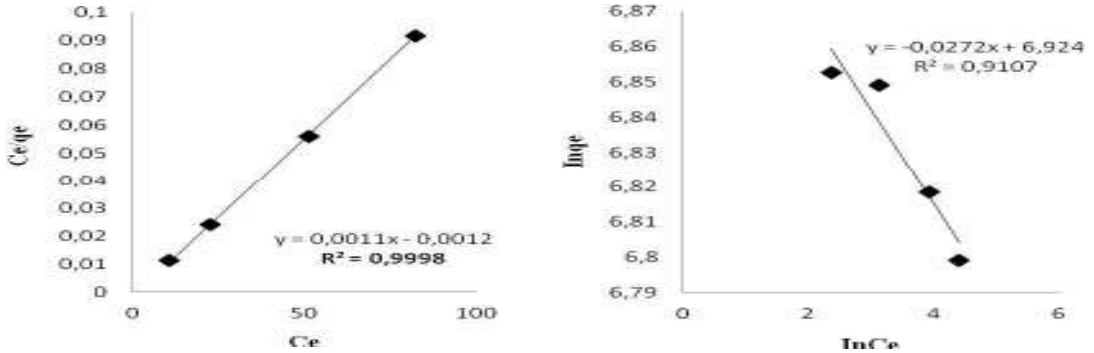
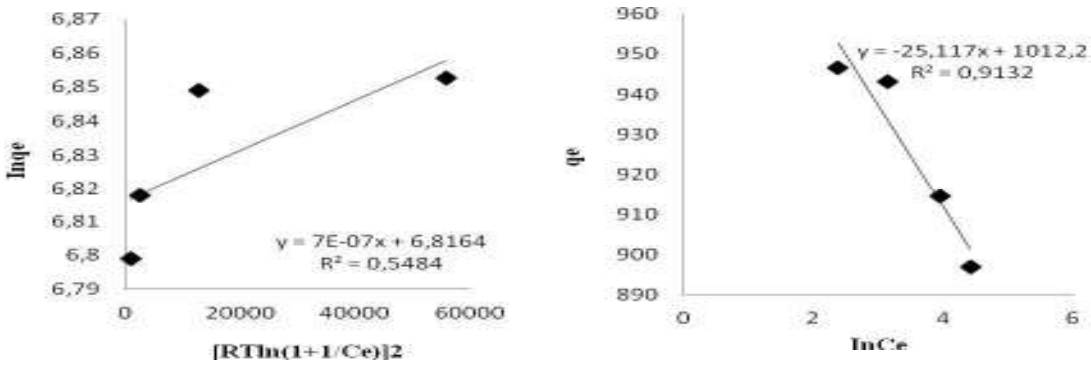


Figure 1:1-Langmuir, 2-Freundlich, 3-Dubinin-Radushkevich and 4-Temkin isotherm graphs of active carbon treated Methylene Blue

Table 1 : Isotherm contants of active carbon treated Methylene Blue

Langmuir		Freundlich		Dubinin- Radushkevich		Temkin	
q_{max} (mg/g)	909.091	n	-31.347	q_m (mg/g)	923.804	B_T	-29.887
K_L (L/mg)	-1	K_f	1041.16	B_D (mg^2/J^2)	-4.10^{-7}	A_T (L/mg)	$8.677.10^{-16}$
R_L	-0.0012			E (kj/mol)	1.118		
R^2	0.99	R^2	0.85	R^2	0.54	R^2	0.85





(3) (4)

Figure 2 : 1-Langmuir, 2-Freundlich, 3-Dubinin-Radushkevich and 4-Temkin isotherm graphs of active carbon treated Crystal Violet

Table 2 : Isotherm contants of active carbon treated Crystal Violet

Langmuir		Freundlich		Dubinin- Radushkevich		Temkin	
q_{max} (mg/g)	909.091	n	-36.764	q_m (mg/g)	912.693	B_T	-25.117
K_L (L/mg)	-1.09	K_f	1016.37	B_D (mg^2/J^2)	-7.10^{-7}	A_T (L/mg)	$3.149.10^{-18}$
R_L	0.0011			E (kj/mol)	8.174		
R^2	0.99	R^2	0.91	R^2	0.54	R^2	0.91

CONCLUSIONS

When corelation constants(R^2) in the table were examined, it is seen that for the adsorption of both colourants Langmuir equation is in better agreement than the others. Value of unitless seperation constant of R_L, that is calculated by using a Langmuir parameter (K_L), was calculated as 0.001. This result shows that adsorption process is efficient. The value of corelation constant for Crystal Violet colourant was found as 0.91 in Freundlich and Temkin equations and it is a satisfying reslt too (Kuyucu , 2013). According to Dubinin-Radushkevich isotherm, if value of E is in the range of 8–16 kJ/mol, then adsorption mechanism is the exchange of chemical ions. For values smaller than 8 kJ/mol adsorption process is physical (Tunalı ve ark., 2006). Values of E calculated from Dubinin-Radushkevich isotherm equations are 1.118 kJ/mol for Methylene Blue and 8.474 kJ/mol for Crystal Violet colourants. Thus, it can be stated that both adsorption processes are physical.S_{BET} , V_t and S_t values were measured as 1513,05 m^2/g, 0,59 cm^3/g and 429,044 m^2/g, respectivly. This shows that active carbon contains moicropores and mesopores..Adsorption capacity of both colourants increased for increasing temperature. It was understood that the active carbon studied in this work can be used for removal of colourants from waste textile water.

REFERENCES

Ma, X., Li, L., Yang, L., Su, C., Wang, K., Yuan, S., Zhou, J., 2012. Adsorption of heavymetal ions using hierarchical $CaCO_3$–maltose meso/macroporous hybridmaterials: Adsorption isotherms and kinetic studies. Journal of Hazardous Materials, 209– 210: 467–477;

Kuyucu A.E. , 2013. Zivzik Narı (SİİRT)'ndan Elde Edilen Aktif Karbonun Karakterizasyonu ve Boyar Madde Adsorpsiyonu (Yüksek Lisans Tezi). Yüzüncü Yıl Üniversitesi, Fen Bilimleri Enstitüsü, İlköğretim Anabilim Dalı, Van;

Temkin, M.J., Pyzhev, V., 1940. Acta Pysiochim. USSR Journal, 12: 217;

Dubinin, M.M., Radushkevich, L.V., 1947. Equation of the characteristic curve of activated charcoal. *Chemisches Zentralblatt* 1: 871;

Önal, Y., 2006. Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot. Journal of Hazardous Materials B137, 1719-1728;

Selçuk A., Kuyucu A. E., Kul A.R. , Ocak S., 2014. Adsorption of Dye on to Activated Carbon obtained from Zivzik Pomagranate. International Environmental Sciences Symposium of Van;

Tunalı, S., Akar, T., Özcan, A.S., Kıran, İ., Özcan, A., 2006. Equilibrium and kinetics of biosorption of lead(II) from aqueous solutions by Cephalosporium aphidicola. Separation and Purification Technology, 47: 105-112;

PAPER 093

INVESTIGATION OF THERMODYNAMIC PARAMETERS OF DYE ADSORPTION ONTO NATURAL AND COMMERCIAL CLAY

Ahmet SELÇUK[1], Ali Ender KUYUCU[2], Gülen ÖNAL[1], Ali Rıza KUL[2]

[1]*Yuzuncu Yıl University, Faculty of Educational Van, TURKEY*
[2]*Yuzuncu Yıl University Faculty of Sciences, Van, TURKEY*

ABSTRACT

It is known for a long time that clays adsorb organic and inorganic materials and thus are being used as adsorbants for removing such pollutants in recent years. In this study, possibility of using clays in removing colourants was studied.
The fact that clays are cheap and easily provided makes them economically attractive for using removal of colourants. Thus, two types of clays, which are natural clay from Derik-Mardin and montmorillonite clay from Southern Clay Products, were used as absorbant for investigating adsorpability of Methilene Blue colourant in this study. Since measurement of surface area determines amount of colourant it can remove, surface areas of clay samples were measured by BET (Önal, 2013).
In our study, adsorptions of Methylene Blue onto natural and commercial clays at three different temperatures of 25°C, 35°C and 45°C was evaluated as a function of initial colourant concentration of 50 mg/L graphically and thermodynamic parameters were investigated.

INTRODUCTION

Reactive and acid colourants are two important classes of textile dyes. Cheap, easy-to- use and non-pollutant new treatment methods have been gaining importance for removal of colourants from drain water since the physical and chemical technics such as adsorption, coalugation-floculation, filtration, oxidation, ozonization, electrochemical claeaning are expansive and have high investment and operating costs, also, they produce new pollutions (Doğan , 1989; Selçuk,2014).

Thermodynamics determines internal energy, enthalpy, entropy and free energy of a system during a physical or chemical change and investigates how these variables depend on conditions of reaction. Examining thermal events accompanying chemical reactions and themal properties of reactants, especially entropy and enthalpy, provides us with producing general criteria about reactions and having information on equilibrium.

Some thermodynamic parameters like ΔG°, ΔH° and ΔS° are determined *by equations below:*

$$K_C = \frac{C_A}{C_S}$$

$$\Delta G° = -RT \ln K_C$$

$$\Delta G° = \Delta H° - T\Delta S°$$

Making equation linear one can get:

$$\ln K_C = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$

Here K_C is equilibrium constant, C_A is amount of absorbed colourant in equilibrium and C_S is amount of residue (unabsorbed) colourant in equilibrium (C_A and C_S, were fonud by using experimental values.). ΔG°, ΔH° and ΔS° are defned as:

ΔG°: Change in free energy (kJ/mol)
ΔH°: Change in enthalpy (kJ/mol)
ΔS°: Change in entropy (J $mol^{-1}K^{-1}$)

Graph of $\ln K_c$ versus 1/T is drawn, then ΔH° and ΔS° are calculated from slope and shift in graph.

MATERIAL AND METHODS

In this study, natural clay from Derik, district of Mardin-TURKEY, and commercial clay (Na-montmorillonite) were used as adsorbent and methylene blue ($C_{16}H^{18}N_3SCl$) was chosen as adsorbate.

Charactarization of Clays

Natural clay of Derik-Mardin and commercial clay of known chemical content, Na-montmorilonite, have been used in our study. Percentages of components and chemical analysis of natural clay are %3.043 Fe_2O_3 , % 4.459 MgO, % 8.461Al_2O_3, %46.49 SiO_2, %4.27 K_2O, %17.09 CaO, % 0.6489 TiO_2 and %15.22 $CaCO_3$ according to XRF analysis results. Type of this clay mineral is bentonite. The natural clay has 1.3879 m^2/g micro and 10.921 m^2/g meso pore surface area and an average pore size distribution of 6.4283 nm according to BET analysis results.

Adsorption experiments

Clays of this study were treated thermally at 110 ^{0}C for 48 hours for removing its moisture before using in experiments and then were sieved by 400 mesh grid. 1000 ppm concentration Methilene Blue was prepared and then solutions of 50, 100, 150, 200, 250, 300 and 350 ppm concentrations were produced from that solution. For determining thermodynamic properties, 100 ml was taken from each of these solutions and treated to 1 g raw and 1 g commercial clays in a water bath with stirrer for 40 minutes at temperatures of 298K, 308K ve 318K. Then the samples were centrifuged and colourant concentrations in the filtrate were measured by UV-spectrometry at 660 nm wavelength.

RESULT

Using thermodynamic equations given above, ΔG°, ΔH° and ΔS° parameters (Table1) were calculated for adsorbed colourants onto surfaces of natural (Figüre 1) and commercial clays (Figüre 2).

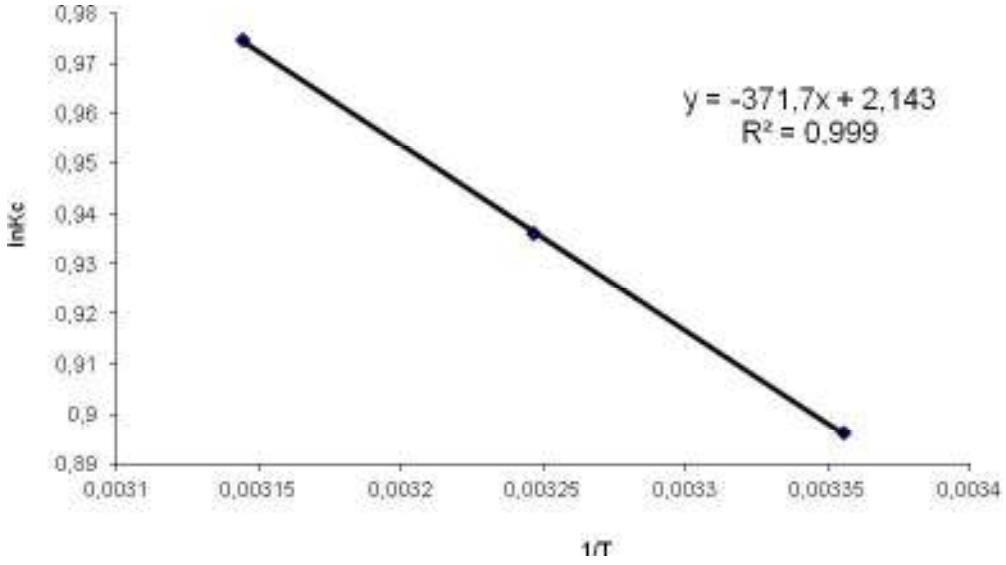


Fig. 1 : Graph of thermodynamic parameters for Methylene Blue which is treated by natural clay

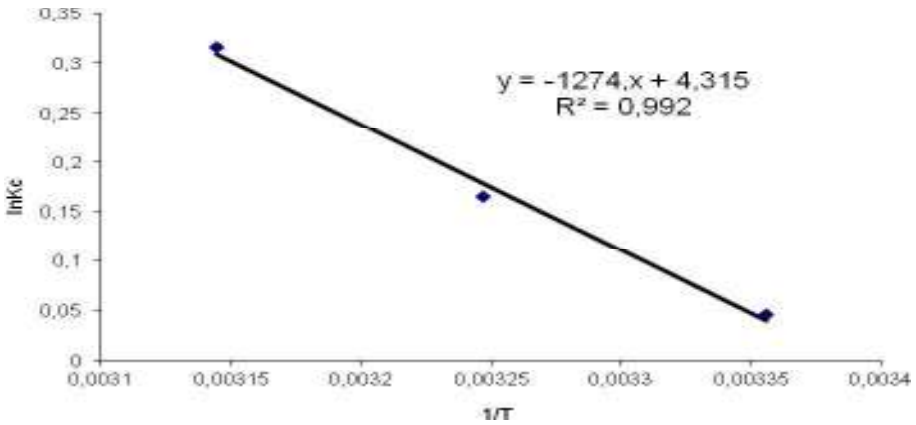


Fig. 2 : Graph of thermodynamic parameters for Methylene Blue which is treated by commercial clay

Table 1. Thermodynamic parameters for Methylene Blue adsorption which is treated by natural and commercial clays

KİLLER T (K)	ΔG^o (k j mol^{-1})	ΔH^O (k j K^{-1} mol^{-1})	ΔS^O (J $K^{-1}mol^{-1}$)	DENKLEM
HAM KİL (298K)	-2.2	3.090	17.816	y= -371.7x + 2.143
HAM KİL (308K)	-2.3			
HAM KİL (318K)	-2.5			
TİCARİ KİL(298K)	-0.1	10.592	35.874	y= -1274.0 x + 4.315
TİCARİ KİL(308K)	-0.4			
TİCARİ KİL (318K)	-0.8			

When Table 1 is examined, it is observed that free enthalpy values (ΔG^o) are negative for commercial and raw clays at temperatures of 298 K, 308 K and 318 K. That shows spontaneity of adsorption process and positive enthalpy values (ΔH^o) means adortion is endothermic (Önal , 2013;Selçuk,2014).

CONCLUSIONS

Pozitive $\Delta S°$ value shows increase in randomness at solid/solution interface and attraction power of absorbant for mentioned colourants (Kuyucu , 2013).
Increase in adsoption capacity has been observed by increasing temperature for both colourants.
It was understood that both of clays used in our study can be used in cleaning colourants from waste water.

REFERENCES

Önal G. , 2013. *Ham Kil ve Ticari Kil ile Sulu Çözeltiden Boyar madde Uzaklaştırılması* (Yüksek Lisans Tezi). Yüzüncü Yıl Üniversitesi, Fen Bilimleri Enstitüsü, İlköğretim Anabilim Dalı, Van.
Doğan, A., 1989. *Bir Pamuklu Tekstil Fabrikası Atık Suyunun Adsorpsiyon Yöntemiyle Arıtılabilirliğinin İncelenmesi* (Yüksek Lisans Tezi). Anadolu Üniversitesi, Fen Bilimleri Enstitüsü, Kimya Mühendisliği Anabilim Dalı, Eskişehir.
Kuyucu A.E. , 2013. *Zivzik Narı (SİİRT)'ndan Elde Edilen Aktif Karbonun Karakterizasyonu ve Boyar Madde Adsorpsiyonu* (Yüksek Lisans Tezi). Yüzüncü Yıl Üniversitesi, Fen Bilimleri Enstitüsü, İlköğretim Anabilim Dalı, Van.
Selçuk A. , Kuyucu A.E. , Kul A. R. , Ocak S. , 2014. *Adsorption of Dye on to Activated carbon obatained from Zivzik Pomagranate.* International Environmental Sciences Symposium of Van.
Selçuk A. , Kul A. R. , Kuyucu A.E. , Ocak S. , 2014. *Dye Removal from Waste water Using Natural Clay (Bentonite).* International Environmental Sciences Symposium of Van.

PAPER 094

INVESTIGATION OF THERMODYNAMIC PARAMETERS OF DYE ADSORPTION ONTO ACTIVE CARBON

Ali Ender KUYUCU[1], Ahmet SELÇUK[2], Ali Rıza KUL[1], Gülen ÖNAL[2]

[1]Yuzuncu Yıl University Faculty of Sciences, Van, TURKEY;
[2]Yuzuncu Yıl University, Faculty of Educational Van, TURKEY;

E-mail : aselcuk@yyu.edu.tr

ABSTRACT

In this study, active carbon, which was obtained from Zivzik pomegranate from Siirt district of TURKEY, as absorbant. Active carbon was prepared with ZnCl2 by chemical activation. Since measurement of surface area determines amount of colourant it can remove, surface area was measured by BET and removals of Methylene Blue and Crystal Violet were investigated.
In our study, adsorptions to active carbon at three different temperatures of 25°C, 35°C and 45°C for the colourants of Methylene Blue and Crystal Violet were evaluated as a function of initial colourant concentration of 800 mg/L graphically.

INTRODUCTION

Reactive and acid colourants are two important classes of textile dyes. Cheap, easy-to- use and non-pollutant new treatment methods have been gaining importance for removal of colourants from drain water since the physical and chemical technics such as adsorption, coalugation-floculation, filtration, oxidation, ozonization, electrochemical claeaning are expansive and have high investment and operating costs, also, they produce new pollutions (Doğan A., 1989).
Active carbon is a material which is frequently used for removal of colourants from environment owing to its properties like having vide surface area, containing micro, meso and macro pores. (Tatlı, İ. A., 2003)
Thermodynamics determines internal energy, enthalpy, entropy and free energy of a system during a physical or chemical change and investigates how these variables depend on conditions of reaction. Examining thermal events accompanying chemical reactions and themal properties of reactants, especially entropy and enthalpy, provides us with producing general criteria about reactions and having information on equilibrium.
Some thermodynamic parameters like ΔG°, ΔH° and ΔS° are determined *by equations below:*

$$K_C = \frac{C_A}{C_S}$$

$$\Delta G° = -RT \ln K_C$$

$$\Delta G° = \Delta H° - T\Delta S°$$

Making equation linear one can get:

$$\ln K_C = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$

Here K_C is equilibrium constant, C_A is amount of absorbed colourant in equilibrium and C_S is amount of residue (unabsorbed) colourant in equilibrium (C_A and C_S, were fonud by using experimental values.). ΔG°, ΔH° and ΔS° are defned as:
ΔG°: Change in free energy (kJ/mol)
ΔH°: Change in enthalpy (kJ/mol)
ΔS°: Change in entropy (J $mol^{-1}K^{-1}$)
Graph of $\ln K_c$ versus 1/T is drawn, then ΔH° and ΔS° are calculated from slope and shift in graph.

MATERIAL AND METHODS

Preparation of materials

Two dyes were used in the study. The dyes, Methylene Blue (MB) (Chemical Formula = $C_{16}H_{18}N_3SCl$, MW = 319.85 g/mol, λ_{max} = 660 nm) and Crystal Violet (CV) (Chemical Formula = $C_{25}N_3H_{30}Cl$, MW = 407.979 g/ mol, λ_{max} = 594 nm) were supplied by Merck. One thousand milligrams per liter of stock solution was prepared by dissolving required amount of dye in double distilled water. Working solutions of the desired concentrations were obtained by successive dilutions. (Önal, Y., 2006)

Preparation of activated carbon

Zivzik Pomegranate supplied by Siirt pomegranate plant were dried firstly under labaratory conditions and then dried again at 100 ^{0}C. Zivzik Pomegranate was mixed with $ZnCl_2$ at the $ZnCl_2$ initial weight ratio of 1:1 and the mixture was kneaded with adding distilled water. The sample was placed on a quartz dish and heated at the rate of 10 ^{0}C min^{-1} up to activation temperature (500 ^{0}C) under N_2 flow and held at the activation temperature1 h. After activation, the sample was cooled down under N_2 flow and 0,5N HCl was added on to activated sample. Activated sample was washed sequentially several times with hot distilled water to remove residual chemicals until it did not anymore give chloride reaction with $AgNO_3$. The washed sample was dried at 110 ^{0}C to prepare activated carbon (Selçuk A., 2014).

Characterization of the prepared activated carbon

Activated carbon surface measurements were made by BET device. Its total surface area, total surface volume and BET surface area were measured as 429,044 m^2/g, 0,59232 cm^3/g and 1513,05 m^2/g, respectively (Selçuk A., 2014).

Instrumentation

A Tri Star 3000 (Micromeritics, USA) surface analyzer was used to measure nitrogen adsorption isotherm at 77 K in the range of relative pressure 10^{-6} to 1. Before measurement, the sample was degassed at 300 ºC for 2 h. The BET surface area, total surface area and volume of the total surface were measured by the surface analyzer. The spectrophotometric determination of dyes was done on a Boeco UV – vis spectrophotometer (model UV – S22, Germany).

Adsorption experiments

To monitor the adsorption process at three different temperatures (25,35,45 ^{0}C) batch techniques were employed. Only one initial dye concentration (800 mg/L) was used in this process. This concentrations was prepared in 1000 mL conical flask containing 500 mL solution of each concentration. A known amount of 0.1 g activated carbon is then added into the solution and conical flask is stirred with thermostatic bath operating at 400 rpm. And then samples taken about 1, 3, 5, 7, 9, 13, 17, 23, 30, 40, 50, 60 and 70 minutes time period (Selçuk , 2014).

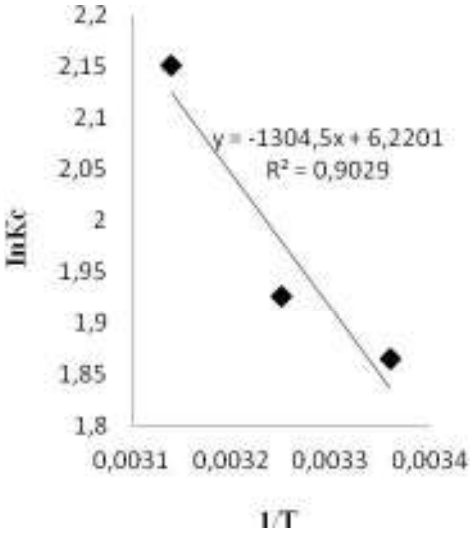


Fig. 1 : Thermodynamic parameter graphs of active carbon treated Methylene Blue

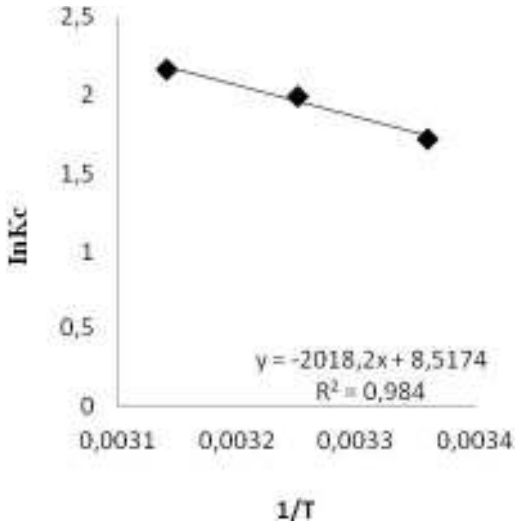


Fig. 2 : Thermodynamic parameter graphs of active carbon treated Crystal Violet

Table 1 : Table of thermodynamic parameter of active carbon treated Methylene Blue

T(K)	InKc	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
298	1,864	-4,565		
308	1,926	-5,082	10,846	51,717
318	2,151	-5,600		

Table 2 : Table of thermodynamic parameter of active carbon treated Crsytal Violet

T(K)	InKc	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
298	1,720	-4,323		
308	1,991	-5,031	16,780	70,817
318	2,164	-5,739		

RESULTS

When corelation constants in the tables were examined, it is seen that ΔH‘ is positive for both colourants which shows endothermic property of adsorption. Negative ΔG° value means adsorption is spontaneous thermodynamically and decrease in ΔG° value as temperature increases implies that adsorption is beter applicable at high temperatures. Pozitive ΔS° value shows increase in randomness at the solid/solution interface ve attraction power of adsorbent for stated colourants (Kuyucu A.E. , 2013).
S_{BET} , V_t and S_t values were measured as 1513,05 m^2/g, 0,59 cm^3/g and 429,044 m^2/g, respectivly. This shows that active carbon contains moicropores and mesopores..

CONCLUSIONS

Adsorption capacity of both colourants increased for increasing temperature. It was understood that the active carbon studied in this work can be used for removal of colourants from waste textile water.

REFERENCES

Doğan, A., 1989. *Bir Pamuklu Tekstil Fabrikası Atık Suyunun Adsorpsiyon Yöntemiyle Arıtılabilirliğinin İncelenmesi* (Yüksek Lisans Tezi). Anadolu Üniversitesi, Fen Bilimleri Enstitüsü, Kimya Mühendisliği Anabilim Dalı, Eskişehir.
Tatlı, İ. A., 2003. *Çeşitli Tekstil Boyarmaddelerin Adsorpsiyon/Biyosorpsiyonunun Karşılaştırılmalı Olarak Kesikli Sistemde İncelenmesi* (Yüksek Lisans Tezi). Hacettepe Üniversitesi, Fen Bilimleri Enstitüsü, Kimya Mühendisliği Anabilim Dalı, Ankara.
Önal, Y., 2006. *Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot.* Journal of Hazardous Materials B137, 1719-1728.
Selçuk A., Kuyucu A. E., Kul A.R. , Ocak S., 2014. *Adsorption of Dye on to Activated Carbon obtained from Zivzik Pomagranate.* International Environmental Sciences Symposium of Van.
Kuyucu A.E. , 2013. *Zivzik Narı (SİİRT)'ndan Elde Edilen Aktif Karbonun Karakterizasyonu ve Boyar Madde Adsorpsiyonu* (Yüksek Lisans Tezi). Yüzüncü Yıl Üniversitesi, Fen Bilimleri Enstitüsü, İlköğretim Anabilim Dalı, Van.