



SOWAEUMED

FP7 ref. no. 245843

**Network in solid waste and water treatment between Europe and
Mediterranean countries**

Case Study I

**Monitoring of Water and Lake Sediment Quality
in Natural Environment**

Programme and Abstracts



**Plitvice Lakes National Park, Croatia
29 May – 1 June, 2011**

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Edited by:
Ines Krajcar Bronić
Bogomil Obelić



Ruđer Bošković Institute
Zagreb, Croatia
May 2011

Plitvice Lakes National Park

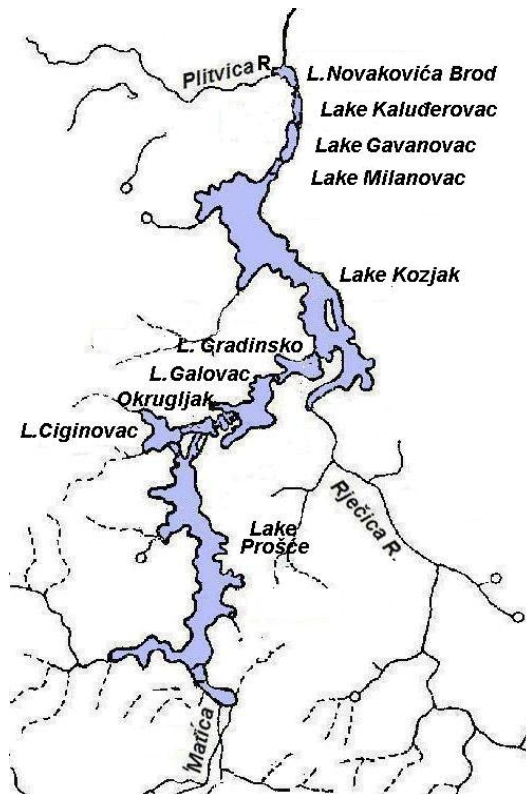
Croatia's first National Park established in 1949 covers 296.85 km² of breathtaking natural splendor becoming with it the largest among the eight national parks of the country, ranging in altitude from 367 m (Koranski most) to 1279 m (Seliški vrh) above sea level. The Park is situated at 44°51'N 15°37'E, 44.85°N 15.62°E, in central Croatia, in the eastern part of the mountainous region of Lika-Senj county. The National Park is also home to 4,000 inhabitants. The local economy is based on tourism and farming.



Plitvice Lakes are recognized as an astonishing natural monument for the benefit and enjoyment of the people now and for the generations to come. The park was inscribed on the UNESCO's World Heritage List in 1979, in recognition of its "outstanding natural beauty and undisturbed production of travertine (tufa) through chemical and biological action".

The central part of the Park consists of 16 lakes separated by tufa barriers, representing thus a unique phenomenon of karst hydrography. The origin and the evolution of the lakes is connected with intensive tufa formation process in which physico-chemical and biogenic factors play an active role.

The Park harbours a grand collection of waterfalls, gallery of lakes, forest and diversity of animal life. The lakes, separated into Upper and Lower Lakes, are renowned for their distinctive colors, ranging from azure to green, grey or blue. The colors change constantly depending on the quantity of minerals or organisms in the water and the angle of sunlight. About eight km of pathways and wooden walking trails around lakes are accessible to visitors. Trails are descending from an altitude of 636 m to 503 m a.s.l.



<http://www.np-plitvicka-jezera.hr/en/index.php>

SOWAEUMED project



Project SOWAEUMED – **Network in solid waste and water treatment between Europe and Mediterranean countries** – is a Coordination and support action (CSA) of the EU 7th Framework Programme (FP7), category CAPACITIES, which refers to strengthening the research potential of the Mediterranean countries, in order to enable them to collaborate in the future on scientific projects with research institutions of the EU on an equal footing basis. Its objectives are to establish a sustainable cooperation platform for forming strategic partnerships between scientists, scientific managers, policy makers, technology transfer and industrial experts between EU Member States (MS), Associated States (AS) and the Mediterranean Partner Countries (MPC), concerning the development and implementation of solid waste and water treatment technologies.

This 3-years project worth 880 000 € started on 1 December 2009. The project foresees the exchange of scientists, several scholarships for young associates, and acquisition of equipment necessary for future research in the Mediterranean countries. Together with three other projects of the 7th Framework Programme within the category CAPACITIES this project forms the **WASTE cluster** dedicated to treatment of solid and liquid waste. The first meeting of the cluster initiative was held in Marrakech (Morocco), from 13 to 15 January 2010, and the second one was held in Kalmar (Sweden), November 22 to 25, 2010. The cluster was also presented on the Week of Innovative Regions in Europe (WIRE), held in Granada (Spain) from 15 to 17 March, 2010.

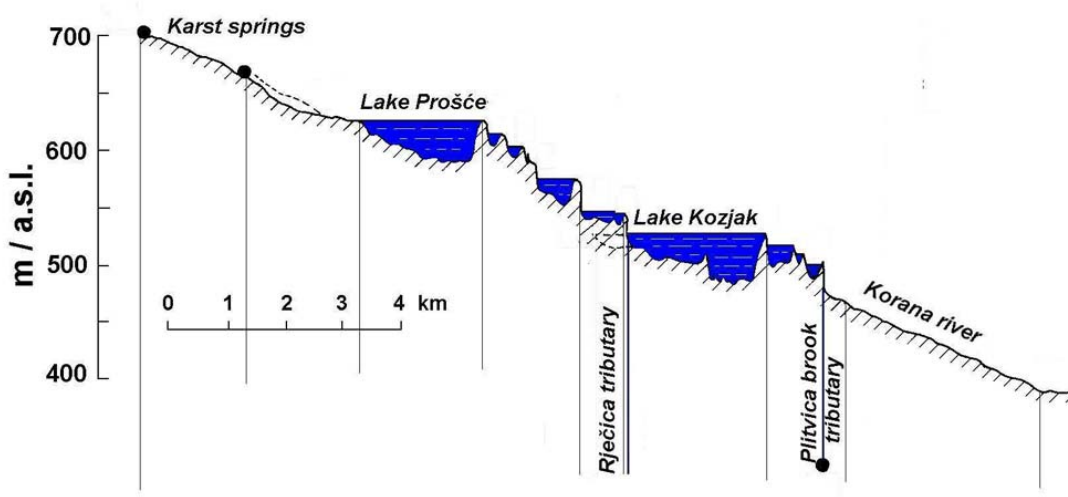
Unlike other participants in the Consortium, who generally treat the problem of pollution and the removal of solid and liquid waste from urban or industrial areas, co-workers of the Ruđer Bošković Institute focus their work on the protected karst areas where very low amounts of contaminants can irreversibly affect the ecological balance, so the presence of these contaminants should be constantly monitored.

The Project Consortium is composed of partners from 6 institutions:

1. **Universitat Autònoma de Barcelona** (UAB), Barcelona (Spain)
2. **Royal Institute of Technology** (KTH), Stockholm (Sweden)
3. **Rudjer Bošković Institute** (RBI), Zagreb (Croatia)
4. **Université Cadi Ayyad** (UCAM), Marrakech (Morocco)
5. **NADREC S.A.** (NAD), Barcelona (Spain)
6. **Sousse University** (SOU), Sousse (Tunisia)

Case Study

The **Case Study I** entitled "**Monitoring of Water and Lake Sediment Quality in Natural Environment**" is organized at the Plitvice Lakes National Park from 29 May to 1 June 2011 by the **Laboratory for Measurements of Low-level Radioactivity** of the **Ruder Bošković Institute** (RBI) in Zagreb, Croatia. The RBI staff will present their recent research on monitoring quality of water and lake sediments in the natural environment, with the emphasis on the parameters controlling processes of carbonate precipitation from natural water and possible contaminants that may affect these processes. The **Case Study I** will include lectures by scientists from Croatia and neighbouring countries associated with their studies of the overall eco-system of lakes and the surrounding area, and lectures by the foreign partners on a project related to their research of environmental pollutants. Field trips with the aim to demonstrate *in situ* measurements and sampling of water and lake sediments are foreseen. For the purpose of monitoring changes in the lakes and in the surrounding environment in the past various geochemical and isotopic analyses have been used.



Cross section of the Plitvice Lakes system

Agenda

Time-table	Sunday 29 May, 2011	Monday 30 May, 2011	Tuesday 31 May, 2011	Wednesday 1 June, 2011
08:00 – 09:00	Free time in Zagreb	Breakfast	Breakfast	Breakfast
09:00 – 09:30		1-2 Opening (<i>M. Valiente, B. Obelić</i>)	10 (<i>M. Valiente</i>)	17 (<i>P. Vreča</i>)
09:30 – 10:00		3 (<i>M. Juračić</i>)	11 (<i>M. Muhammed</i>)	18 (<i>I. Bikit</i>)
10:00 – 10:30		4 (<i>B. Obelić</i>)	12 (<i>A. Uheida</i>)	19 (<i>M. Brenčić</i>)
10:30 – 11:00		5 (<i>J.L. Briansó</i>)	13 (<i>M. Seffen</i>)	Coffee break
11:00 – 11:30		Coffee break	Coffee break	20 Closing (<i>B. Obelić</i>)
11:30 – 12:00		6 (<i>J.L. Briansó</i>)	14 (<i>E. Capezzuoli</i>)	Free time in the National Park
12:00 – 12:30		7 (<i>M. Ahel</i>)	15 (<i>S. Zavadlav</i>)	
12:30 – 13:00		8 (<i>N. Horvatinčić</i>)	16 (<i>N. Džankić</i>)	
13:00 – 13:30		9 (<i>M. Vurnek</i>)	Lunch	
13:30 – 14:00		Lunch		
14:00 – 14:30		Visit to Plitvice Research Centre	Field trip to the Lower Lakes Boat, including ca 1.5 hours walk: Demonstration of sediment retrieving (<i>I. Sondi & lab. staff</i>)	Lunch
14:30 – 15:00				Departure to Zagreb (2.5 hours by bus)
15:00 – 16:00	Departure to Plitvice (2.5 hours by bus)	Field trip to the Upper Lakes Train, including ca 2 hours walk: Demonstration of <i>in situ</i> measurements (<i>N. Horvatinčić & lab. staff</i>)	Farewell dinner in Zagreb (SOWAEUMED partners only)	
16:00 – 17:00				
17:00 – 18:00				
18:00 – 19:00	Steering Committee meeting	Dinner	Dinner	
19:00 – 20:00				
20:00 – 21:00	Dinner	Dinner		

Lectures

No.	Name	Title of presentation
<i>Chairperson: B. Obelić</i>		
1	M. Valiente & B. Obelić	Opening and plan of Case Study (10 min)
2	Manuel Valiente	Presentation of SOWAEUMED and WASTE Cluster Initiative
3	Mladen Juračić & Igor Felja	Plitvice Lakes – a hydrogeologic phenomenon
4	Bogomil Obelić	Geochronological and paleoclimatological investigations at the Plitvice Lakes
5	Jose Luis Briansó	Project ANTHROPOL.PROT (FP5) – a success case
<i>Chairperson: M. Valiente</i>		
6	Jose Luis Briansó	Presentation of the project STRAVAL (FP7 People – IRSES)
7	Marijan Ahel	Chemical indicators of anthropogenic impacts in sediments of the Plitvice Lakes
8	Nada Horvatinčić	Chemical and isotopic measurements of water and recent sediments at the Plitvice Lakes
9	Maja Vurnek	Presentation of the Plitvice Research Centre "Ivo Pevalek"
<i>Chairperson: J.L. Briansó</i>		
10	Manuel Valiente	New materials for arsenic adsorption in polluted waters
11	Mamoun Muhammed	Potential of nanoparticles for environmental applications
12	Adbusalam Uheida	Application of nanoparticles in waste water treatment
13	Mongi Seffen	The use of adsorption and biosorption technique in treatment of industrial water
<i>Chairperson: N. Horvatinčić</i>		
14	Enrico Capezzuoli	Tufa from Tuscany (Italy): paleoclimatic and paleoenvironmental reconstructions
15	Saša Zavadlav & al	Recent tufa and lacustrine sediments of River Krka (Croatia): reflection of recent environmental change
16	Nejra Džankić & al	Natural and anthropogenic influence to water quality of Una River catchment area
<i>Chairperson: I. Krajcar Bronić</i>		
17	Polona Vreča & al	Sedimentary organic as record of natural and anthropogenic impacts - Case studies from Slovenian lakes
18	Ištván Bikit & al	Low-background spectrometry in radioecology
19	Mihael Brenčić	Landfill influences on Karstic aquifers - questions, problems and solutions
20	Bogomil Obelić	Closing session

Field work

Field trip to the Upper Lakes (Monday, 30 May, 2011, afternoon)

Taking the Plitvice panoramic train at the point **1** (*see next page*).

Stop at the Rječica Brook mouth (**2**) for the demonstration of *in situ* measurements in the water (pH, temperature, conductivity) and sampling of water for laboratory analyses.

Continuing by train to the end station Labudovac (**3**).

Walking along the Upper lakes (ca 2 hours easy walk).

Demonstration of *in situ* measurements in water of Gradinsko Lake (**4**).

Boarding the boat (**5**) and returning to the hotel (**6**).

Field trip to the Lower Lakes (Tuesday, 31 May, 2011, afternoon)

Boarding the boat at the dock **A** and driving to the point **B** at the Kozjak Lake.

Demonstration of sampling of undisturbed sediment cores using a gravity corer and measurements of physico-chemical parameters in sediments and vertical water profile.

Driving by boat to the point **C**, walking (ca 1.5 hours) along the Lower Lakes to the Big Waterfall (**D**). Walking to the train station Rapajinka (**E**) and returning to the hotel (**F**).

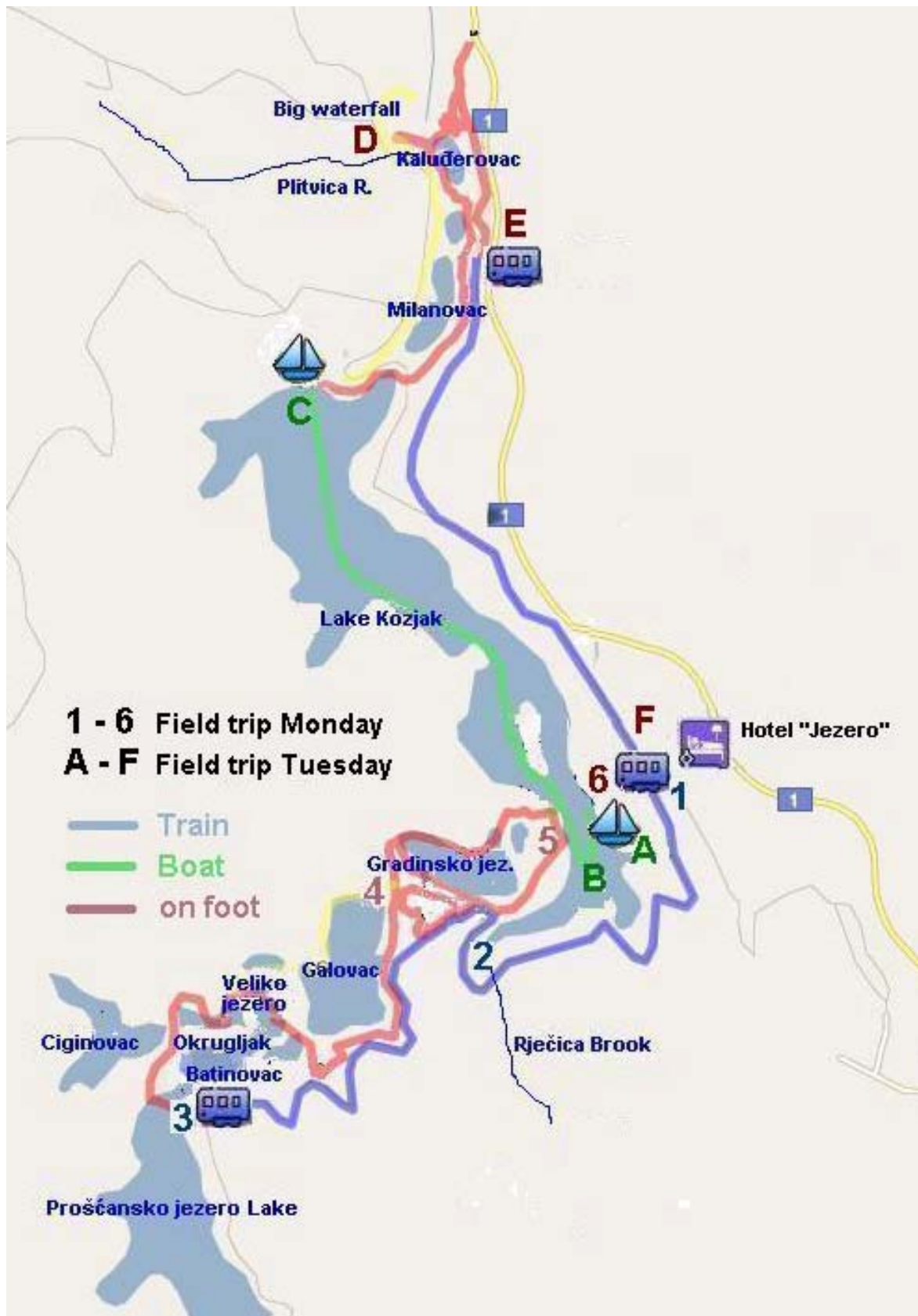


Physico-chemical measurements *in situ*



Retrieving of lake sediment cores

Map of the field work



Abstracts

Plitvice Lakes – a hydrogeologic phenomenon

Mladen Juračić and Igor Felja

Department of Geology, Faculty of Science, University of Zagreb,
Horvatovac 102a, Zagreb, Croatia

In the presentation an explanation for the existence of freshwater Plitvice Lakes in Dinaric karst will be presented. Formerly the existence of the Plitvice Lakes was considered a "miracle" due to the fact that generally in the high karst region underground water flow prevails. The area where Plitvice Lakes are located is built of carbonate rocks of Mesozoic age. There is a thick series of dolomite and limestone rocks (3500 – 4000 m) that were deposited from Upper Triassic (T_3 "Hauptdolomit") to Upper Cretaceous (K_2 rudist limestone and marly (clayey) limestone). In the upper part (below the Upper Lakes) this Triassic dolomite covers older impermeable clastic rocks, and the formation of surface flow is easily explained. However, the Lower Lakes are formed in the Upper Cretaceous well karstified limestone with a number of caves in the canyon flanks. The only plausible explanation is that a series of marly (clayey) limestone of Turonian age (K_2^2) represents a barrier for underground flow. Therefore, the lithology could explain the existence of the surface water flow. The existence of the lakes is, however, the consequence of intense deposition of calc tufa within the water flow. Mechanisms, chemistry and biogeochemistry of calc tufa deposition are important topic of the ongoing research in the world.

Geochronological and paleoclimatological investigations at the Plitvice Lakes

Bogomil Obelić

Ruđer Bošković Institute, Zagreb, Croatia

The group of scientists from Radiocarbon and Tritium Laboratory of the Ruđer Bošković Institute in Zagreb started investigation at the Plitvice Lakes National Park in 1976, when first radiocarbon dating of tufa was performed. Since that time the scientists continued systematic and comprehensive investigation encompassing both conditions required for calcite precipitation and age determination of tufa and lake sediments.

Tufa is created from carbon partly of biogenic origin, and therefore its age can be determined by radiocarbon (^{14}C) dating method. However, there are several factors that affect the accuracy and reliability of ^{14}C dating of carbonates: (i) since tufa represents a very porous material, there exists a great possibility for contamination with allochthonous calcareous deposits; (ii) there is a possibility of carbon isotope exchange during the aging of the deposits. (iii) It is also necessary to know the initial ^{14}C activity at the time of carbonate deposition (so called reservoir effect). It was determined by measurements of ^{14}C activity in dissolved inorganic carbon (DIC) and showed a continuous increase along the Plitvice watercourse from 65% to 85% as the consequence of influence of atmospheric CO_2 and respiration of water plants.

More than 500 samples of tufa were collected from the whole area of the National Park, both from active tufa barriers located along the present-day water flows and from the remnants of old tufa deposits outside them. Results of ^{14}C dating showed that tufa at active barriers was formed within last 7000 years, i.e. during Holocene.

The age of old barriers was determined by $^{230}\text{Th}/^{234}\text{U}$ method, since it exceeds the maximum age that could be measured by ^{14}C method. The results showed that majority of these barriers were formed in interglacial periods: from 90 000 to 130 000 years (Riss-Würm), as well as in the period between 250 000 and 300 000 years (Mindel-Riss). These results verify also that the tufa precipitation process was associated with warmer climatic periods.

Retrieving of sediments from two bigger lakes (Kozjak and Prošće) with total depth up to 12 m, enabled numerous analyses which contributed to the knowledge of geochronology of Plitvice Lakes. ^{14}C measurements showed the beginning of sedimentation in Lake Prošće about 7000 years ago and in Lake Kozjak about 6500 years before present. These measurements indicated that the sediment, like the tufa barriers, was deposited also in warmer geologic periods. Comparative dating of sediment layers by ^{14}C method and distribution of characteristic non-arboreal pollen indication of density of settlement in the wider area of National Park in the past was obtained. Age determination of peat found in the same area showed that peat-bogs were formed in Holocene period, i.e. during last 7000 years.

Project ANTHROPOL.PROT (FP5) – a success case

José Luis Briansó

Universitat Autònoma de Barcelona, Barcelona, Spain

The objective of this EU-FP5 project was the assessment of anthropogenic pollution after the war events and its consequences to the karst ecosystem in a border zone between Croatia and Bosnia-Herzegovina promoting the scientific-technical co-operation between these countries and some Member Countries of the European Union. The activities were focused on the hydrogeologically connected areas of the Plitvice Lakes National Park, including karstic fields (poljes) Koreničko, Lapačko and Krbavsko, from the Croatian side, and the Una River catchment area in the Bihać region, Bosnia and Herzegovina. The project was oriented towards the end users: local authorities, enterprises, national parks and non-governmental organizations in the area. Therefore, three specific case studies were chosen: on a tourist domain (National Park Plitvice Lakes), a municipality domain and an industry domain (Bihać area).

Project was executed by 6 partners coming from 2 Member States (Spain and Germany) and 2 Western Balkan countries (Croatia and Bosnia-Herzegovina). *Universitat Autònoma de Barcelona*, was the co-ordinator of the Project and responsible for Project organization and co-ordination. They performed measurements of cations in water and trace elements in water and sediments, as well as qualitative and semiquantitative X-ray diffraction analyses of the sediment samples. *Institut für Geowissenschaftliche Gemeinschaftsaufgaben, Hannover*, was partly responsible for the hydrogeological recognition of the area. They measured anthropogenic and natural radionuclides; stable isotopes in surface and spring waters, in sediments, noble gases and chlorofluorocarbons and SF₆ in water. *Ruđer Bošković Institute, Zagreb*, was responsible for sampling and helped the co-ordinator in contacts with Croatian and Bosnian partners. They performed *in situ* measurements at the Plitvice Lakes National Park and partly at Una River, measurements of organic and inorganic carbon, anions, cations, tritium in precipitation and spring waters, polycyclic aromatic hydrocarbons. *Geological Institute, Zagreb*, was responsible for elaboration of the Geographic Information System and hydrogeological modeling. *Geological Institute of BH, Sarajevo*, was responsible partly for hydrogeological recognition and partly for investigation of industrial influence to water quality and water supply capacities of the Bihać area. *Biotechnical Faculty, University of Bihać*, was responsible for sampling and laboratory analyses at the Una River area, and partly for investigation of industrial influence to water quality and water supply capacities of the Bihać area. They performed *in situ* physico-chemical measurements and sampling of spring and surface waters in the Una River area for stable isotope and tritium analyses.

The main result of the project was the conclusion that in general no anthropogenic contamination exists in the region of the National Park Plitvice Lakes. However, some kind of control monitoring should be applied by the authorities of the National Park. On the other hand, in the Bihać region (Bosnia and Herzegovina) we found many environmental problems, mainly as the consequence of war activities 1992-1995. The proposed Rehabilitation measures are listed in the Consolidated Scientific Report.

Presentation of the project STRAVAL (FP7 People – IRSES)

José Luis Briansó

Universitat Autònoma de Barcelona, Barcelona, Spain

The title of the project is "Studies, Training, Socioeconomical valorization and management of natural, cultural and monumental property for the promotion of the local societies of Latin America (Argentina, Brazil and Mexico)".

Project summary: When a natural or monumental site is declared as a protected area such as World Cultural Site, National Historic Monument, Biosphere Reserve, Natural Space, a strong impact undergoes in the region. This declaration involves a large public and private investment which often affects only the site itself or immediate surroundings. The direct impact is reduced by marginalization of more distant areas, which in many cases, present unquestionable heritage values, susceptible of being valorised and recovered in order to further generate financial resources to promote economic, social and regional development. The protected sites act as a powerful magnet promoting economic and social bookmarking of remote places, if that marginal area is valorised properly. Such valorisation generates knowledge and good practices that can be transferred to natural or monumental sites that have received some form of protection either at national or international level in Latin America in order to avoid the marginalization of surrounding areas. To overcome the reduced impact and promote future economic and social progress derived from such declarations, the STRAVAL main purpose is to make non-interventional studies on the conservation of these sites in LA in order to valorise the selected sites. Such studies will be performed from an architecture, environment, geo & bio-diversity, history and conservation/alteration of building materials point of view. It will complemented by the identification of existing economic potentials around these sites and a social study of the neighbouring populations. As a result of the performed studies, education and training programs shorter training courses and open day sessions addressed to students in Higher Education Institutions, civilian population at large and to professionals in the tourism sector will be one of the outputs of the project. A Valorisation, Business and Action Plans will become the other important output of STRAVAL.

Within the Project several case studies will be performed:

In Mexico the selected site is the Cuitzeo Lake (Volcanic and Monumental area). The main proposed activities, close to Morelia, are: a) A section of Route 2010 (Cuitzeo lake area), which means the roads, history, landscape, biota (flora and fauna) geo-resources (minerals and rocks), volcanic geo-morphology etc. (Route of Bicentenary 1810-2010), and b) Joining the Augustinian monasteries (XVI and XVII centuries) which were the origin of this route. In almost each small village around the lake one church was build during the colonial period.

In Argentina the Selected site will be the surroundings of Luján area (Religious pole of attraction). The Basilica "Nuestra Señora de Luján" and Enrique Udaondo Museographic Complex are declared a historical heritage of the Argentine Republic.

In Brazil the selected site will be the Ambient Protection Area for the southern right whale: in the center-south coast of the State of Santa Catarina. The protection area includes the coves of bigger concentration of southern right whales with younglings, and important terrestrial areas, dunes, bathed, lagoons and many archeological sites (Guananies).

Chemical indicators of anthropogenic impacts in sediments of the Plitvice Lakes

I. Mikac¹, Ž. Fiket¹, S. Terzić¹, J. Barešić², N. Mikac¹, M. Ahel¹

¹Division for Marine and Environmental Research, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia

²Division of Experimental Physics, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia

The anthropogenic impact on the Plitvice Lakes was investigated using a combination of inorganic and organic constituents, including major elements (Al, K, Fe), trace metals (Li, Ag, Cd, Sn, Pb, Bi, Cr, Co, Ni, Cu, Zn and Sb), polycyclic aromatic hydrocarbons (PAHs) and anionic surfactants of linear alkylbenzene sulfonate (LAS) type. Dated cores of recent sediments from the two largest lakes, Lake Prošće and Lake Kozjak, were analysed for the selected contaminants using highly specific methods, including inductively coupled plasma mass spectrometry (ICP/MS), gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/tandem mass spectrometry (LC/MS/MS). The distribution of inorganic constituents reflected primarily the geological background of the area. The concentration of all elements was significantly higher in the Lake Prošće, which was due to the comparatively higher terrigenous input into that lake. The concentration of toxic metals was relatively low in both lakes, except for Cd ($>1 \text{ mg kg}^{-1}$) and Pb (up to 40 mg kg^{-1}). The vertical profiles of these metals suggested that elevated concentrations of Cd were of natural origin, while Pb was predominately of recent anthropogenic origin. A similar distribution pattern like for Pb was observed for pyrolytic polycyclic aromatic hydrocarbons (PAHs), suggesting the same prevailing mechanism of input. The characteristic diagnostic PAH ratios revealed that higher PAHs prevalingly originated from the combustion of biomass and fossil fuels. LAS were found in rather high concentrations in the recent sediment layers (up to 4.7 mg kg^{-1}), suggesting that contaminated household and hotel wastewaters reach the Lakes, very probably by leaking through the porous karst rocks.

Chemical and isotopic measurement of water and recent sediments at the Plitvice Lakes

Nada Horvatinčić

Ruđer Bošković Institute, Zagreb, Croatia

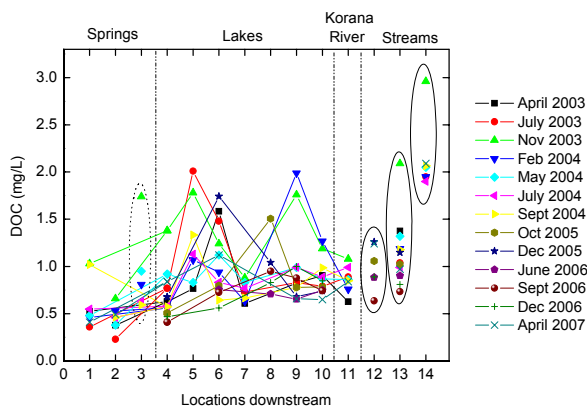
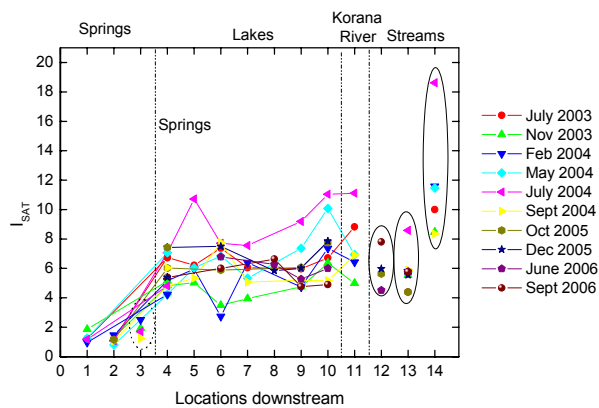
Tufa is formed by calcium carbonate precipitation from surface water by a combination of physico-chemical and biological processes. In the Plitvice Lakes the process of tufa formation is very intensive, forming a series of tufa waterfalls and barriers. At the same time the precipitation of lake sediment at the bottom of the lakes is also occurring. Calcium carbonate precipitation in form of tufa or lake sediment is a very sensitive process and any pollution of water and/or changes in the lake environment can disturb the equilibrium conditions of calcite precipitation.

To study the physico-chemical conditions of tufa precipitation in the lake waters, the environmental conditions in the Plitvice Lakes and possible anthropogenic influence on the system the following investigations were performed:

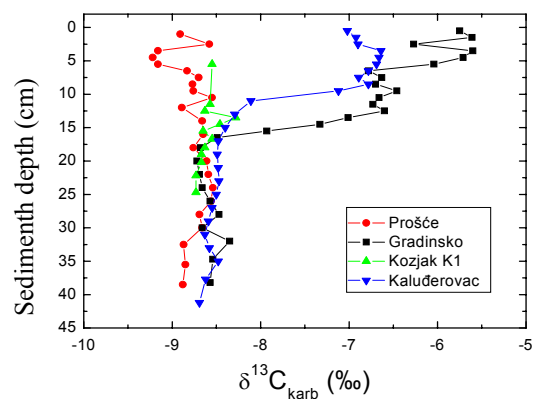
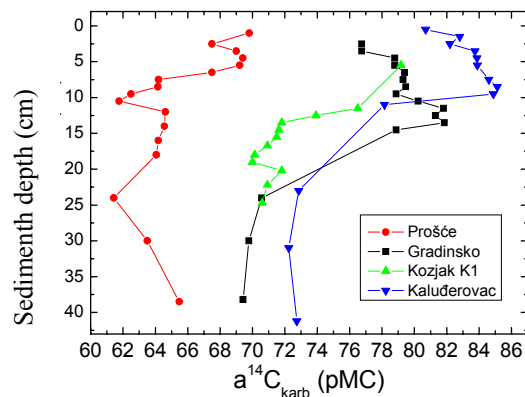
- Physico-chemical conditions for calcite precipitation. Water samples were collected in different seasons at 18 sampling points including springs, lakes, tributaries and Korana River which outflows from the Plitvice Lakes (total distance ~12 km). Some of the sampling points are characterized by the process of eutrophication in the form of intense plant growth in the lakes. Temperature, pH values, conductivity and concentration of dissolved oxygen were measured *in situ* and in the laboratory alkalinity, CO₂, dissolved organic carbon (DOC), kations Ca²⁺, Mg²⁺, Na⁺, K⁺, Sr²⁺, anions Cl⁻, F⁻ and SO₄²⁻, and nutrients (ammonium, nitrates). Physico-chemical conditions for calcite precipitation showed that calcite precipitated in lake waters oversaturated with respect to CaCO₃ (I_{sat} values 4-10). The present status of the water quality was compared with the parameters measured at the same locations in the period 1982-1985. Most of the parameters did not change significantly. Regarding to all of the water analyses we can conclude that the Plitvice Lakes waters are very clean and oligotrophic with low primary productivity. Local anthropogenic pollution has not been observed; however, some influence of global climate change has been noticed.
- Recent sediments, five short cores (top 40 - 45 cm of sediment) from four lakes of the Plitvice Lakes system were measured for ²¹⁰Pb, ¹³⁷Cs, a¹⁴C, δ¹³C, δ¹⁸O to study the influence of environmental changes on the sediment system in small and large lakes. Lake sediments consisted mainly of autochthonous carbonates with higher sedimentation rate in small lakes. Sediments from the two large lakes, Prošće and Kozjak, showed constant stable isotope profiles for the carbonate fraction and full agreement between the ¹³⁷Cs and ²¹⁰Pb chronologies. Sediments from the two small lakes, Gradinsko and Kaluđerovac, showed synchronous increases in ¹⁴C and δ¹³C and disturbed ¹³⁷Cs records. All lakes showed an increase in a¹⁴C in the carbonate sediments above the first occurrence of ¹³⁷Cs which was interpreted as a damped and decades-delayed

consequence of the bomb-induced increase in $a^{14}\text{C}$ in atmospheric CO_2 . For the small lakes, increased $\delta^{13}\text{C}$ in the last two decades and part of the $a^{14}\text{C}$ increase is probably due to an increase in primary productivity that enhanced biologically-induced calcite precipitation with concomitant changes in the carbon isotopic composition of carbonate sediments.

- Recent sediments in Lake Kozjak were used to study the impact of the material delivered to the lake sediment via Rječica Brook. Distribution of organic matter, C/N values, $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ in sediment profiles showed strong influence of terrestrial organic and carbonate fraction run-off via Rječica Brook which decreased rapidly in the direction of the open lake. The sedimentation rate as well as the ratio of allogenic and authigenic fraction in sediments was estimated. The steady decrease of the $\delta^{13}\text{C}_{\text{org}}$ with decreasing depth in all sediment profiles might be a consequence of the increase in algal productivity, but might also be a consequence of the change of $\delta^{13}\text{C}$ of atmospheric CO_2 on the global scale due to enhanced fossil fuel combustion during last century.



Saturation index, I_{sat} , and dissolved organic carbon, DOC, in the Plitvice Lakes system (springs, lakes and stream waters)



Distribution of ^{14}C activity and $\delta^{13}\text{C}$ values in the carbonate fraction of the lake sediments from 4 lakes.

New materials for arsenic adsorption in polluted waters

Manuel Valiente

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Arsenic is a widely distributed element in the environment, being As(V) the most common species present in surface waters. There is a great concern on the study of new adsorbent materials for either the removal or fixation of arsenic species because of their high toxicity and the health problems associated with such substances.

In this concern, we will present for discussion at the Case Study meeting of Plitvice (Croatia), some results obtained in the study of different adsorbing materials for arsenic species in aqueous solution. These materials include ion exchange resins, open cellulose sponges and different nano-structured materials. Both basic and applied aspects have been object of study. Both adsorption capacity and the rate of adsorption have been emphasized for applications purposes.

Toxicity of arsenic compounds is known to follow the order: AsH_3 (arsine) > As(III) > As(V) > organic As compounds.

In this concern, some other features including specific adsorption of most abundant As species, i.e., arsenate and arsenite, as well as most common anionic interferences have been evaluated for some of the studied materials. To this purpose, materials loaded with different forms of Fe have played a major role.

Application of Nanoparticles in Waste Water Treatment

Abdusalam Uheida

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Recently, nanomaterials have gained considerable attention for applications in environment due to their small size and large surface area. Nanomaterials exhibit different physical, chemical, and biological properties that may not be predictable from observations on larger-sized material. Nanotechnology hold great promise for creating new means of detecting pollutants, cleaning polluted waste streams, recovering materials before they become wastes, and expanding available resources. Like all emerging technologies with great promise, the nanotechnology industry will present new challenges in ensuring that environmental risks are properly managed.

Rapid industrialization and societal development have led to elevated releases of toxic substances into the environment. The pollutants seriously influence the metabolism of living organisms and cause permanent threats. The continuously increasing quantities of contaminants released into the environment, as a result of industrial activities, represent a potential hazard to the ecosystem. High environmental standards have made the removal of contaminates such as heavy metals, arsenic and other toxic substances from water bodies an important issue for environmental engineering.

This presentation aims at providing a brief review on the application of nanoparticles in environmental clean-up including waste water treatment and specifically the treatment of industrial effluents.

The use of adsorption and biosorption technique in treatment of industrial water

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In the last decade, a large number of papers have been devoted to model adsorption and biosorption process involved in the removal of pollutants from contaminated waters. It has been found that like activated carbons (ACs), in many instances biomass can be used for water treatment purposes.

Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid. The term *sorption* encompasses both processes, while *desorption* is the reverse of adsorption. It is a *surface phenomenon*.

When the adsorbent is a natural biomass or biological material like hazelnut shell, sugar beet pulp, rice husk, waste tea, bagasse fly ash, chitosan, posidonia oceanic, Agave fibers, the technique is called biosorption. Biosorption is a physicochemical process that occurs naturally in natural support or waste which allows it to passively concentrate and bind contaminants onto its cellular structure. Though using biomass in environmental clean-up has been in practice for a while, scientists and engineers are hoping this phenomenon will provide an economical alternative for removing pollutants like dyes and toxic heavy metals from industrial wastewater and aid in environmental remediation.

In Tunisia, the textile sector is very important. However, this industry produces a large pollution due to the use of dyes and other chemicals. Dyes even in very low concentrations affect the aquatic life and food chain. Hence, the removal of dye from process or waste effluents becomes environmentally important. Because of the high degree of organic compounds present in these molecules and the stability of modern dyes, conventional physicochemical and biological treatment methods are ineffective for their removal. This led to the study of other effective methods.

In our research biosorption of several industrial reactive and direct dyes such as Sumifixe Supra Red and Alpacelle Limiere Gray etc. onto *Stipa tenacissima* (L.) leaves, *Posidonia oceanica*; *Agave Americana* fibers was carried out in batch system. The influence of various parameters such as pH, temperature, and mass of biomass, initial concentration and contact time were investigated. The isotherm, describing the retention of a substance on a solid at various concentrations at a constant temperature is a major tool to predict the efficiency of a sorbent to remove a given pollutant from polluted waters. The isotherm data are traditionally fitted with either the Langmuir isotherm (LI) or the Freundlich isotherm (FI). The Redlich–Peterson isotherm (RPI) tending to the two previous isotherms at low and high value of solute concentration, respectively, has been used as well with some success. Biosorption data were fitted to both pseudo-first-order and pseudo-second-order kinetic models.

Tufa from Tuscany (Italy): paleoclimatic and paleoenvironmental reconstructions

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Travertine and calcareous tufa comprise a widespread group of terrestrial carbonates which petrologic and geochemical proprieties reflect genetic conditions of deposition.

Described in many works under the general term "travertine", they are today separated into travertines (thermal, crystalline and mainly abiotic) and calcareous tufa (ambient temperature, microcrystalline and fossiliferous) on the basis of their constructional, petrological, geochemical and isotopic characteristics. Each of these characteristics closely reflects the genetic relationships with the physico-chemical conditions of the parent waters, the associated microbial processes and the geo/tectonic and morphological context of the depositing environments.

The sedimentological-petrologic study of the calcareous tufa allows to establish its genetic depositional microenvironments and to define the depositional processes of the different lithofacies, in order to reconstruct the respective parent depositional systems and the paleogeographic frame. Definition of fabrics and of their genetic connexions with the sedimentary facies will help in the facies analyses and finally will lead to the restoration of the depositional systems which produced the diverse calcareous bodies.

Being very sensitive to environmental conditions, calcareous tufa are accurate proxy-indicators of environmental change and, in some circumstance, of anthropogenic influences for the most recent ones. Several case histories are described for important Holocene environmental human impacts, but natural events are even reported, as supported by paleoclimate reconstructions available from many Mediterranean examples.

This enhance the role of tufa precipitation processes as recorder of past environmental changes and as sensible, prompt warning for preservation and protection of karst environment.

Recent tufa and lacustrine sediments of River Krka (Croatia): reflection of recent environmental change

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The Krka River is a groundwater-fed karstic river, draining mostly carbonate terrains in Dalmatian Karst area. Along 49 km long freshwater section of the river only few surface tributaries occur, which usually dry out in summer. Continuous groundwater recharge and geomorphological conditions of the river canyon create ideal conditions for tufa formation. Common features of tufa deposits are large barrages and waterfalls, behind which few lakes were formed. Continuous sedimentary processes of barrage tufa and lacustrine sediment formation reflect fluvio-lacustrine dynamics of sedimentation in the Krka River, thus presenting an opportunity to study sedimentation processes in freshwater environment.

The aim of this study is to constrain sedimentary processes in the Krka River by elemental and stable isotope distribution in water and sediments. Lacustrine and riverine sediment cores (up to 45 cm long) were collected manually by scuba diving. Sediment cores were sectioned into 2 or 4 cm segments in a glove bag with N₂ atmosphere. Pore water was extracted from sediment cores by centrifugation and additionally filtered through 0.20 µm membrane filtration. In the pore water, Ca and Mg concentrations and stable isotope composition of dissolved inorganic carbon and oxygen were analysed. The sediments were oven dried, crushed and analysed for organic carbon and nitrogen concentration and their stable isotope composition. Surface water and particulate organic matter samples were also collected.

Concentrations of sediment organic matter (SOM) generally decrease with depth. A significant shift toward lower values in the depth segment corresponding to the time sequence of 1990 – 2000 was observed. Organic matter in lacustrine sediments originates mostly from C₃ terrestrial plants debris. A somewhat lower C/N values of SOM are observed in sediments from smaller lake, implying mixing of autochthonous (plankton organisms) and allochthonous (terrigenous) material. The concentrations of dissolved inorganic carbon and its stable carbon isotope composition in pore water increase with increasing depth. This is due to methane production during microbial degradation of organic matter and sediment diagenesis. Primary source of the carbonate in the lacustrine sediment is the in-situ precipitation of calcium carbonate from river water, since $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of carbonate in lacustrine sediments resemble to those observed in tufa. Consistent increase of stable carbon isotope composition in carbonate sediment and organic matter indicates interaction between inorganic and organic carbon pool.

Natural and anthropogenic influence to water quality of Una River catchment area

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The protection of the quality of the water in the catchment area of the Una River has special significance because the basin (and all sources) is located mainly in the karst area with very complex hydrogeological relations and large surface areas that have impact on water quality, particularly the quality of water sources. In the biggest part of the catchment area of the Una River the typical karst hydrography was developed. Due to the relatively rapid underground water flow the underground water treatment options are poor and pollution increased. The changes in the water quality arise due to natural and anthropogenic influence

The assessment of water quality was based on determination of physico-chemical properties of water. The main pollutants in the waters of the investigated area are organic substances, ammonia, nitrites and increased saturation of water with oxygen, above 100% (so called super saturation of oxygen), as a result of increased photosynthetic processes caused by the presence of the nutrients (nitrogen and phosphorus). Other parameters of water quality were satisfactory.

In the Una River, 78.3 km from the spring, reduced rate of flow of the river leads to deposition of fine sand and silt, and suspended particulate matter (inorganic or organic). In this way the sediments in the water were created, known as bottom sediments, whose characteristics depend on the characteristics of the catchment area and potential anthropogenic impacts on the water or sediment.

It was found that the sediments are contaminated with organic matters, nutrients (nitrogen and phosphorus) and heavy metals. The type and proportion of metals in the sediment is an important indicator of pollution that is specific to a particular locality. By knowing the lithological properties of parent material of the Una River basin from the obtained data on the content of heavy metals in sediments, the conclusions can be drawn about the natural and anthropogenic origin of the metals.

Sedimentary organic matter as record of natural and anthropogenic impacts – Case studies from Slovenian lakes

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Future environmental changes large enough to disrupt the world's economy and health are difficult to predict therefore, it is necessary to know the past and present behaviour of the Earth-surface system. Stable isotopes of light elements proved to be useful tracers and can provide valuable information about past and present environmental conditions and elemental cycles.

Lakes represent a very sensitive ecosystems and interesting sedimentation environments. The biggest concern related to lakes is induced eutrophication caused by anthropogenic activities. Despite 20th century advances in understanding eutrophication, it remains one of the foremost problems in protecting freshwater ecosystems. It is now well known that anthropogenic nutrient loading to aquatic ecosystems from both point and nonpoint sources typically results in rapid increase in the rate of biological production and significant reduction in water column transparency and can create a wide range of undesirable water quality changes in freshwater ecosystems. In temperate latitudes lakes are especially sensitive and the two of the most consistent eutrophication effects are a shift in algal species composition and an increase in the frequency and intensity of nuisance algal blooms. In addition, lakes are especially sensitive to environmental changes in temperate latitudes because their seasonal stratification and primary production respond strongly to annual cycles. Furthermore, nutrient enrichment typically results in significant alterations in biogeochemical cycling over space and time.

Organic matter, produced in the surface water is exposed to degradation during sinking to the bottom of the lake. Much of the organic matter, produced in the surface water, is remineralized during sinking through the water column. Organic matter that reaches the lake bottom can be either incorporated into the sediment where it is exposed to diagenetic processes. During remineralization of organic matter nutrients are released into the water and this process affects quality of lake waters and the geochemistry of sedimentary deposits. Within this complex biogeochemical environment, mixtures of lipid "biomarkers" are biosynthesized. Many of these biomarkers provide unique insight into the sources, diagenetic alteration, deposition and preservation of organic matter in lacustrine environments.

Important historical information on environmental changes in C and N cycles that occurred within a lake and its surrounding catchment are recorded in the lake sediments as distinctive differences in the composition, also in isotopic composition, of the sediment. Unfortunately, induced eutrophication is observed also in remote and protected areas like Triglav National Park (Slovenia).

A review of results obtained during more than ten years of investigations on isotopic composition of carbon and nitrogen in sediments of oligotrophic, mesotrophic and eutrophic lakes on carbonate terrains in Slovenia will be presented.

Low background spectrometry in radioecology

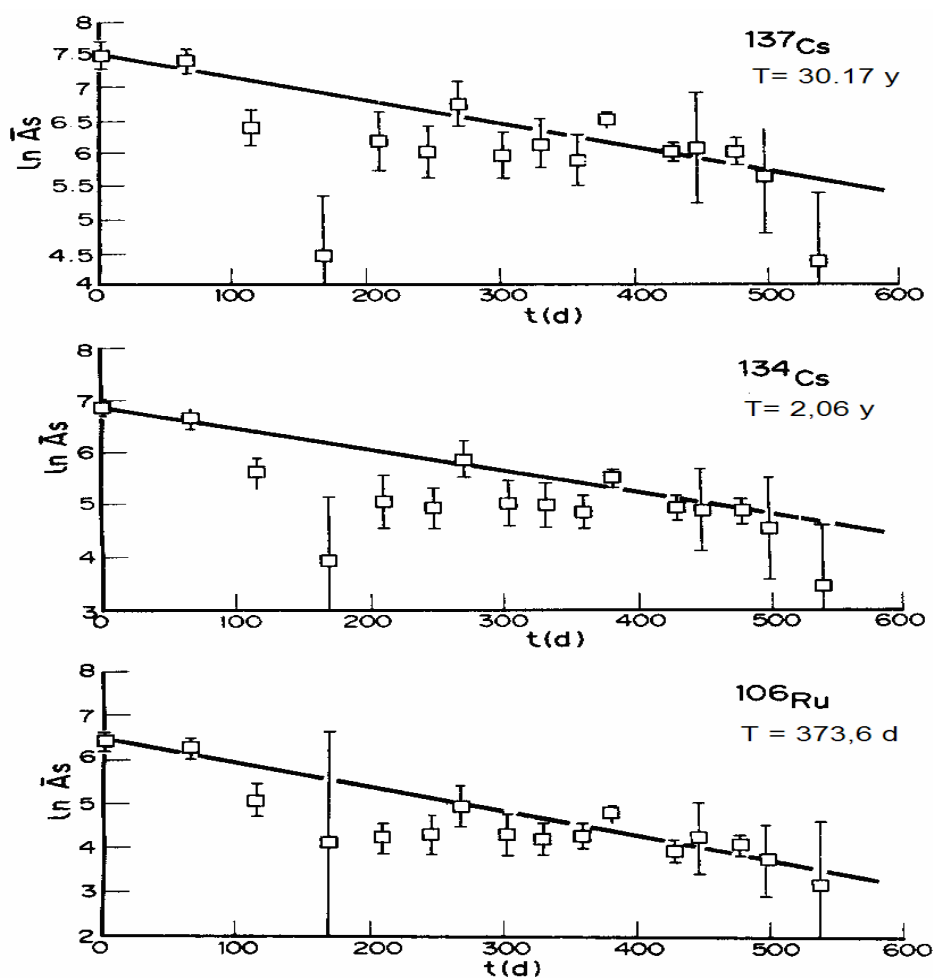
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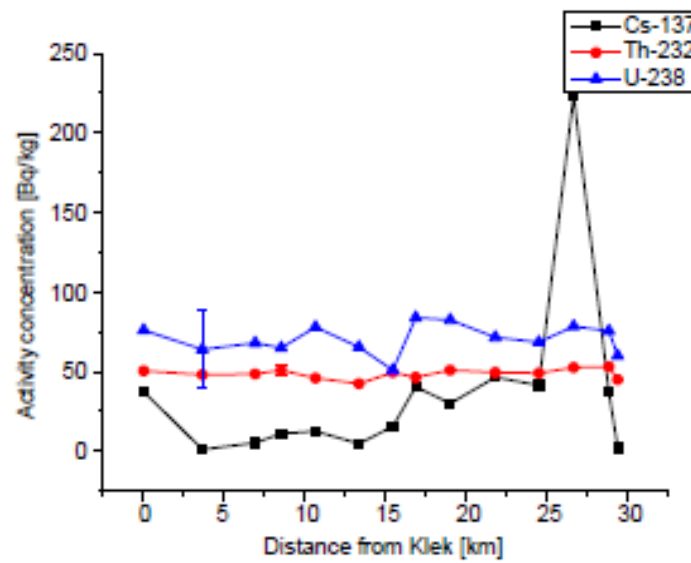
The basic principles of low level gamma spectroscopy by HPGe semiconductor spectrometers are presented. Various passive shielding methods with iron and lead realized in the Novi Sad Laboratory are described. The active shielding built in that Laboratory is also described.

The heavily shielded spectrometers have been used for lot of radiological investigations:

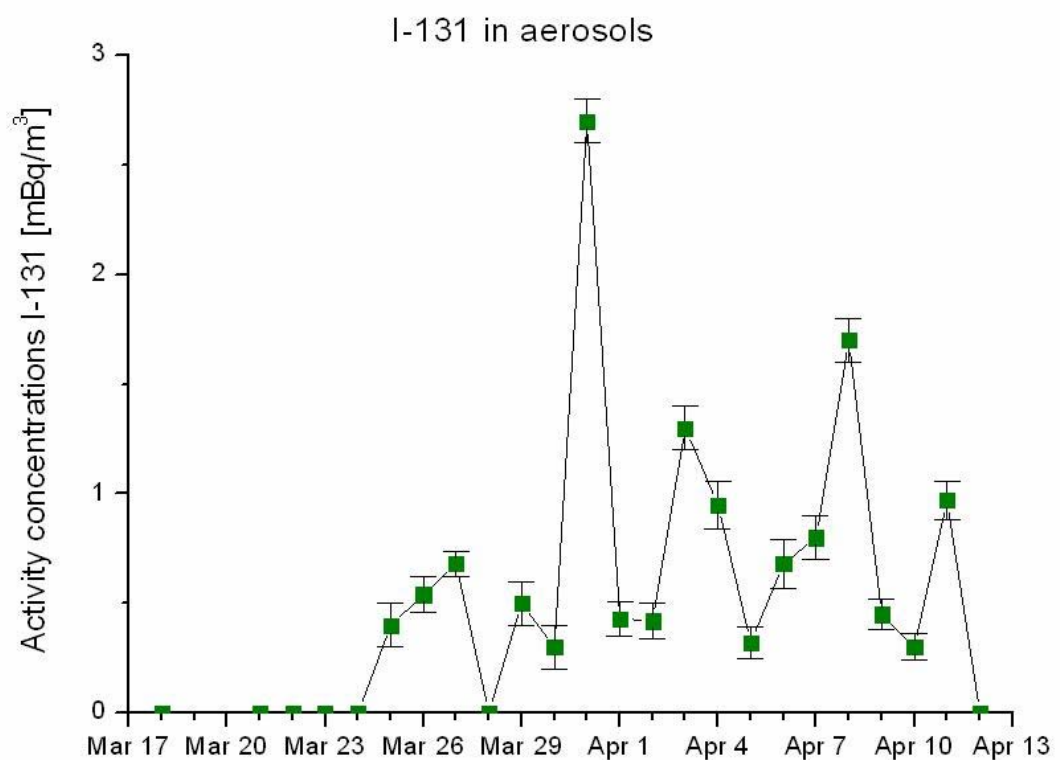
1. The elimination of the post-Chernobyl ^{137}Cs , ^{134}Cs i ^{106}Ru from the Danube sediment



2. The search for TENORM sources in the Bega river



3. The appearance of ^{131}I in aerosols after the Fukushima accident



Landfill influences on Karstic aquifers - questions, problems and solutions

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During past decades land filling practice has changed and evolved toward more sustainable way. Material flow to landfills has been diminished and engineering constructions on landfills improved profoundly. However, waste stream, existing and abandoned landfills in Karstic areas remains problematic. During spatial planning and engineering design of landfill recent practices are trying to avoid these conflicts with the different success. In areas where Karstic land presents large part of the total area conflict between waste dumping and natural vulnerability can rarely be avoided. In spite of many legislation demands and requirements, better planning and engineering practice problems with wastes are still on the agenda of communities positioned on Karstic areas.

Problems with landfills and old abandoned rubbish dumps are also very much related to cultural tradition and past waste dump practices. In ancient times when waste was predominantly of organic origin resulting from simple agricultural activities in rural areas caves and potholes were convenient places where these wastes were cast away. Even today such practices can be detected through the names of these caves (e.g. Goat cave, Horse cave, Rubbish cave etc.) and, what is more problematical, there are old waste dumps where caves are filled with thousands of cubic meters of old rubbish from bottom to the top. Today these places are understood as a past burdens and just recently they are more seriously recognised on the state level as a problem to achieving good surface and ground water bodies status based on the demands of European Water Framework directive.

In spite of the recognised problems and strict legislation requirements for abandoning and rehabilitation of old waste sites some old official landfills positioned above Karstic aquifers are still in operation. Some of them are so old that at the start of dampening no engineering barriers were constructed and waste leakages and other fluids originating from the waste are freely flowing to the groundwater. Contrary to some efforts detecting real and possible influences of these processes on on-site groundwater pollution mechanisms are

purely known. Karstic aquifers are very large and highly heterogeneous therefore, landfill influences on groundwater can not be detected as a sole influence but are integrated in the whole chemical status of groundwater and consequently these influences are not properly recognised.

Operational groundwater monitoring of landfills on Karstic aquifers is based on same paradigms as in alluvial intergranular aquifers where observation boreholes must be positioned in up and down gradient. Due to Karstic heterogeneity and thick unsaturated zone these requirements are difficult to achieve. Based on the recognition of natural conditions and problems new Karstic groundwater monitoring paradigms are needed. They must be based on the water balance approach. At the same time planning and designing process of waste removal and site rehabilitation must start. Sanitation activities can be also a challenge for profession as well as for the business. Old landfills are potential sources of some valuable materials.

The review of experiences, questions, problems and possible solutions related to landfills on Karstic areas of Slovenia will be presented and discussed.

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Laboratory for Measurements of Low-level Radioactivities

Laboratory for Measurements of Low-level Radioactivities (^{14}C and ^3H Laboratory; in Croatian: *LNA - Laboratorij za mjerenje niskih radioaktivnosti*) at the Rudjer Bošković Institute, Zagreb, Croatia, is a part of the Division for Experimental Physics. Main activities of the staff are radiocarbon (^{14}C) dating of archaeological, geological and paleontological samples and tritium (^3H) activity measurements of natural waters (precipitation, surface and groundwater). Natural radioactive (^3H , ^{14}C) and stable isotopes (^2H , ^{13}C , ^{18}O) are used in hydrogeological studies (protection of water resources, especially in karst areas), application of isotopic and geochemical analyses in paleoclimatological and ecological studies, as well as study of physico-chemical conditions necessary for formation of secondary carbonates (tufa, speleothems) in karst regions.

Laboratory is also continuously involved in development and modernizing of techniques for ^3H and ^{14}C measurements. Recently, the Laboratory introduced the chemical technique for graphite preparation of milligram-sized samples for ^{14}C measurement by accelerator mass spectrometry (AMS). Thus, the Laboratory will keep the leading position in measurements and application of isotopes with the aim to form a regional centre of excellence.

The laboratory is the only one of this kind in Croatia, as well as in the wider region. Besides the regular funding by the Ministry of Science, Laboratory has an excellent track record of participation in international projects funded by European Commission (FP5, FP6, and FP7) and IAEA and has a significant cooperation with numerous cultural institutions, local authorities and industry.



Vacuum line for benzene preparation for ^{14}C activity measurements by LSC



Vacuum line for preparation of graphite for ^{14}C AMS measurement technique



System for electrolytic enrichment of ^3H in water for ^3H activity measurement by LSC



Liquid scintillation counter (LSC) *Quantulus 1220* for ^{14}C and ^3H activity measurements

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Participants of the Case Study I during the field trip below the Great Waterfall



In situ measurements at Lake Prošće



Preparation for sediment sampling at Lake Kozjak