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# ENVIRONMENTAL ENGINEERING - INŽENJERSTVO OKOLIŠA



## Scientific and professional journal in the area of environmental engineering

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Mura-Drava confluence near Legrad in the Nort-West of Croatia, representing a so-called "Croatian Amazon", as a part of the Cross-border UNESCO Biosphere Reserve Mura-Drava-Danube. Permission for the cover photo was granted by the Author Goran Šafarek, a biologist, an explorer and a photographer from Koprivnica.



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# **Editor-In-Chief opening remarks**

Dear readers,

It is a great honor to introduce you to the new number of the journal *Environmental Engineering*-*Inženjerstvo okoliša* published by the Faculty of Geotechnical Engineering, University of Zagreb, Croatia.

The final results are 8 papers, including 2 review papers, 4 original scientific papers and 2 professional papers, with co-authors from 12 different institutions from Croatia and abroad, including co-authors from 6 companies.

The papers covered different issues within the field of environmental engineering: a paper dealing with efficient dam management using SQL and GIS; heavy metal monitoring in surface waters of North-West of Croatia; photocatalytic removal of neonicotinoid insecticide imidacloprid in annular photoreactor; removal of pollutants from abattoir wastewater using a pilot-scale bamboo constructed wetland system in Nigeria; a case study on removal methods for invasive species *Amorpha fruticosa* at Odransko polje; emission of fine particles (PM2.5) from residential biomass combustion in Croatia; new development strategy alternatives in strategic environmental assessment; and assessment of water quality status in the impact area of the "Piškornica" landfill in Croatia.

In October 2020 the journal signed a license agreement with EBSCO Publishing, Inc. to enter the EBSCO scientific database. The journal will be promoted by the EBSCO Discovery Service (EDS) and in the Central & Eastern European Academic Source (CEEAS), including current Volume.

I would use this opportunity to express my sincere gratitude to the former dean prof. Ranko Biondić for supporting the journal. I'm confident the support of the new dean prof. Hrvoje Meaški will stay at least the same.

At the end, I would like to give my gratitude to all hard working team members and to our sponsors.

I hope you will enjoy it.

With best regards,



Assoc. Prof. Dr. Nikola Sakač Editor-in-Chief

Unit for Chemical Sensors Department of Environmental Engineering Faculty of Geotechnical Engineering University of Zagreb Croatia

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## **EFFICIENT DAM MANAGEMENT USING SQL AND GIS**

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**Abstract:** This paper discusses use of SQL and GIS tools in nowadays dam management. Dam management requires the use of a highly-sophisticated measuring, monitoring and general management tools, since it is not only economical aspect of importance of these projects, but also about the security risks that require the highest possible caution and a precisely-developed control systems. Therefore, SQL and GIS are tools to be considered and implemented. GIS is widely used in spatial planning and connected management processes - because it allows easy way of storage, processing, analysis, modelling and display of spatial data. It has a wide range of features and is used in many areas. Structured Query Language (SQL) is a programming language for databases, written to be easy to understand and to use. SQL provides integration and presentation of data, optimization, easy reporting and analysis. In hand of trained professional analysts, SQL can make database search efficient and flexible, which is the key feature in demanding management processes as dam management.). Keywords: dams, dam management, SQL, GIS

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> Review paper https://doi.org/10.37023/ee.7.2.1

#### **1. INTRODUCTION**

Dam management is a very demanding task that can be adequately performed only with the help of modern tools for creating and managing databases. The importance of efficient dam management has been recognised and several authors have considered developing their solution. Rodrigues et al. (2002) proposed a system DamAid which is divided into two components, the Emergency Manager component and Geographic Information component. Rodrigues et al. (2002) induce that the main advantage using Geographic Information component are low cost and simple implementation, but the disadvantages are lack of GIS analyses tools and large amount of RAM memory. Jeon et al. (2009) developed KDSMS which is enterprise management system covering the detailed activities, notifications, reports and work flow of all groups from field engineers where all the data is stored in databases. Qi and Altinakar (2012) studied the possibilities of GIS-based dam-break decision support environment systems and they concluded that such system is userfriendly and reliable tool. In this paper examples of mentioned systems will be provided, and different method based on GIS and SQL will be explored. As a database, GIS is widely used nowadays tool. It is difficult to handle the management of spatial planning related processes in general without GIS. GIS allows storage, processing, analysis, modelling and display of spatial data. Because of its wide range of features, this system has great use in many areas. Structured Query Language (SQL) is a programming language intended for working with databases. It is used to create, modify and search specific data that are usually organized in the form of a table. Each table contains its own data and the purpose of SQL is to find and change the information in the way we want it.

#### 2. SQL and GIS

SQL stands for Structured Query Language which is a language for databases querying from language group called RDBMS (Relational Database Management System). In other words, SQL is a database management system like Oracle, IBM DB2, Ingres, Microsoft SQL Server, Microsoft Access and others. It is originally developed in IBM in the 70's and then became the main language for working with databases. SQL is written to be easy to understand and use. Also, it is a declarative type of language, which means it is stated what to get, but without specific instructions on how to get it (as in case often procedural type of language). SQL provides integration and presentation of data, optimization of work, and reporting and analysis. With the knowledge of SQL languages, analysts can compile their SQL queries to search the database making it more efficient and more flexible (Mujadžević 2016).

The spatial database is a database system (DBMS) with additional functionality of spatial data management in a way that spatial data are present in the model and queries (geometry and relationships among them), and that spatial data is integral part of the system in such a way that there are spatial indicators and effective spatial relations algorithms. Spatial database provide the user with dual data benefit: storage mechanism and tools for analysis data, and the goal is not just to enable visualization of spatial data but also to give an answer to complex attribute and geometric queries (Tkalčec & Šimec 2014).

Specifically, databases do this by using geometric data. It is a data type that is equal to all other data types in the database and can be used to store data in tables. In order to manipulate such data type, spatial operators (functions) are defined. So, by using curves that can be converted into lines, SQL can measure the length, distance, and surface. It therefore supports geodetic and planar measurements (planar measurement is simpler in terms of calculation and applies to planar systems) (Tkalčec & Šimec 2014).

Today it is almost impossible to imagine the acquisition of new knowledge and geography research and the successful and efficient management of spatial resources without GIS. GIS (Geographical Information System) is the spatial data management system for integrating, saving, editing, analysing and displaying geographic information. "GIS can be implemented as a comprehensive, multipurpose system (e.g. GRASS, ArcGIS), as a specialized, application-oriented tool (e.g. GeoServer), or as a subsystem of a larger software package supporting handling of geospatial data needed in its applications (e.g. hydrologic modelling system, geostatistical analysis software, or a real estate services Web site). The multipurpose systems are often built from smaller components or modules which can be used independently in application-oriented systems." (Neteler & Mitasova 2013).

GIS enables different users to have access to different information, allowing users to input and modify data while others are allowed to view and analyse them. Through the online user interface, access to the widest circle of users is enabled. GIS can be described as "a smart map" since it enables creating interactive questionnaires (user-generated research), spatial information analyses and data editing. Considering its features, GIS can be used for scientific research, resource management, asset management, development planning, cartography and road mapping.

Since many areas of modern management are based on multidimensionality and interdisciplinarity, especially in analytics and research work, GIS is an inevitable tool, especially in spatial management areas such as spatial planning, nature and environment protection, cultural heritage protection land policy, rural development, tourism development and energy etc. This tool can be used to evaluate landscape, create spatial models and strategic plans, landscape impact assessment including visual analysis and simulation, landscape character assessment, and landscape plans. Therefore, GIS application is needed and it is adequate in various sectoral instruments at all levels of decision-making processes within environmental and spatial planning (Tomić Reljić et al. 2017).

#### 3. DEBATE ON DAM MANAGEMENT EFFICIENCY USING SQL AND GIS

Dam is a building constructed over a river valley or basin to exploit the water mass. Dam enables to create a lake, which is used to regulate the water regime for more efficient flood protection and water use for water supply, soaking, electricity production, navigation and recreation. Dam management is primarily concerned with monitoring and management of river and lake water levels, but there are also all associated management processes, besides, the exploitation of the energy that the dam produces, such as spatial planning or-environmental impact. For example, in order to monitor and take actions to prevent damage or demolition of the dam, all events related to the dam and its environment are constantly monitored (shifts and stresses of the dam and foundation soil, meteorological and hydrological conditions, seismic activity, deformation measurement...) (Martać et al. 2016).

Dams are "of vital importance for society, because they are used to produce electricity and water supply" (Martać et al. 2016), so it is highly important to prevent demolition or damage of the dams. The most important issue in this process "is necessary to establish communication between metering systems and computer models" (Martać et al. 2016).

It is superfluous, but important, to point out that the current dam (safety) management is based, besides the physically, mostly on software-supported technical systems. This established system of dam safety management is used for (Martać et al. 2016):

- tracking and monitoring the behaviour, which consists of continuous monitoring, measurement and determination of compliance measured values and their expected values,
- checking of the dam safety, which may be initial, periodic and extraordinary, and refers to determining the condition of the facilities and determining the degree of the facilities safety.

Workflow of mentioned system is shown on Figure 1.

Monitoring and tracking relies on adequate statistical models. In order to ensure the possible sudden and unpredictable occurrences of the objects, during the demolition of the dams, constant measurement of deformation or scuffle of high structures and hydroelectric power plants and the protection of the environment and downstream area from damage and disaster is carried out. Collecting the necessary data is based on geodetic technical monitoring carried out with the most accurate geodetic measurements, for rational maintenance of facilities during use.

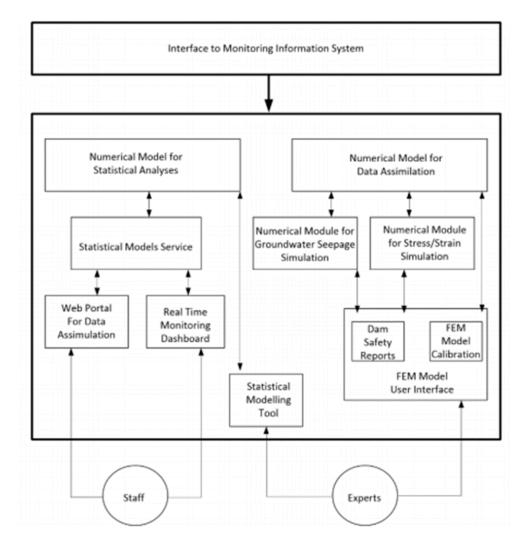


Figure 1. Workflow of dam management software system (Martać et al. 2016)

One of the key processes in dam controlling is geodetic measurements of the displacement. These measurements include all measurements in order to determine the shape or soil shape change under the influence of external or internal forces. The object is idealized with a certain number of points whose position is determined relative to the reference or base geodetic basis outside the range of possible shifts. Geodetic methods determine the position changes of individual points on the object, and deformation can be determined based on the displacement measurement results. The real behaviour of an object can only be determined by well-designed and well-made observations, as well as expert data processing. Example of deformation monitoring is shown on **Figure 2.** 



Figure 2. Deformation monitoring (Jeon et al. 2009)

The most important thing is to timely record all events and conditions that could affect the security of objects, so the database must be multidimensional, multidisciplinary and interactive (Ožanić 2002).

In selection of software system to support dam safety management, it is highly important that the system we choose implements the use of data in real-time, and also "the expandability and interconnection with other information system" (Martać et al. 2016). One of the most used tools to create this sort of systems are spatial databases based on SQL, since it allows users to see "current measurements (measurements in real time) as well as the estimation of the state of the dam at the time" (Martać et al. 2016).

Considering demands of dam management, GIS is the perfect tool, since it enables application of spatial analysis methods that can help explain the fundamental issues of geographic research, understanding of spatial distribution patterns, relationships and processes and modelling their future development (Toskić 2015). "Due to strong spatial component, hydrotechnical systems are ideal for analysing using GIS. All the structures and systems, whether it is a water supply or wastewater drainage system or an irrigation one, are spatially located and have their own numerous characteristics. Their display and a systematic analysis greatly facilitate the application of GIS. Major role in such systems have hydrological data. The spatial distribution of such data, especially rainfall, is extremely important, so monitoring of such data by GIS is very practical." (Dadić et al. 2014).

Using GIS to build a system for the security surveillance, it is possible not only "to manage the data and information of tailings scientifically and effectively, but also give full play to the advantage of computer's storage of massive data" (Martać et al. 2016). GIS offers the interactive operation of spatial query and analysis which provides accurate and convenient search management, alteration and statistics of data.

Figures 3, 4 and 5 presents workflows of dam management systems developed by authors mentioned in Introduction. It is important to see that each solution has GIS component and database component. It is possible to input different types of data in database. Information such as the fluctuation of the water level are possible to obtain with the observation of the height of the seepage line of dam body, the index of dry coast, the water level in the tank, deformation and deviation of the dam body. This is important for forecasting stability of the dam body, achieving safe management of tailing pods and early prediction of danger.

As it is obvious, dams have a wide range of different instruments, such as rain gauges, water level gauges, flow meter, precipitation meter, etc., so in order to improve the observation and supervising, all these instruments should be brought into a single network and it is most important to enable those instruments to communicate with each other. This problem is mainly solved by using SensorML and Wireless Sensor Networks (WSNs).

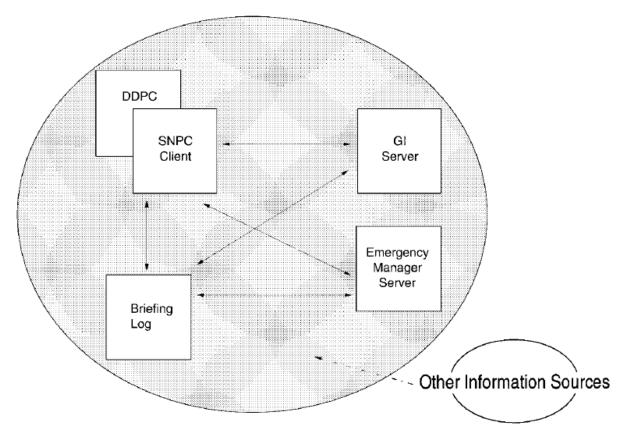


Figure 3. DamAid Architecture (Rodrigues et al. 2002)

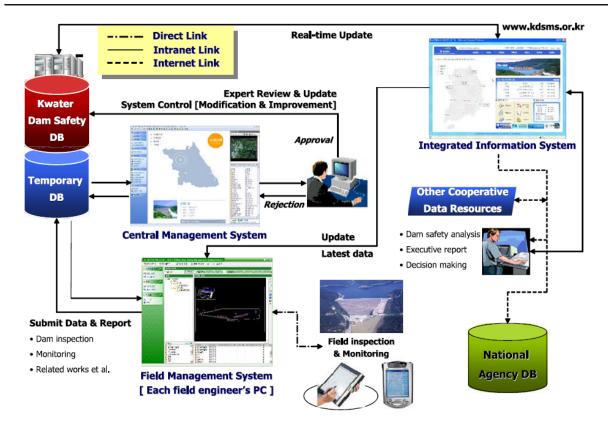


Figure 4. Work process and data management architecture (Jeon et al. 2009)

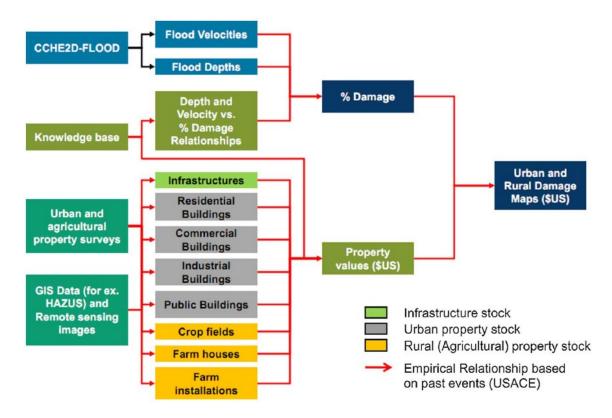


Figure 5. GIS-Based Decision Support System (Qi & Altinakar 2012)

Data collected can easily be implemented in GIS, and based on data, GIS software is able to make map service, develop the web page which can easily communicate with map service and carry on web site management, so that clients can use either vector or raster map and fulfil graphical operation, query, display, statistical and spatial analysis. As seen from **Figures 1, 3, 4** and **5** different authors proposed different solutions

on dam management. For example, The ArcIMS, as one of the WebGIS software, composed of a few independent function units such as Author, Designer, Administrator and Manager etc., "can distribute or share various data on the internet, and it adopts distributed component and three-layer architecture, so the operation efficiency of system is high, and the function of upgrade is strong" (Martać et al. 2016). This kind of software is selected to organize and manage data, and to analyse information as well as to distribute results, etc., and offers next functions: map releasing, basic function, query function, statistic function. The attribute data are managed by SQL Server database, so the attribute database contains many tables, like table with basic information or table with hydrology data, the dam body character table, the sluice building character of dams and the benefit character of dams etc. Each table is connected by only dam code and spatial data is linked with attribute data by dam code, so the system is visual, intuitionistic and vivid, with query function as one of the main functions. Conditional query is also known as SQL. By selecting name, province basin, water system or dam height, users can acquire dam data. Each of mentioned dam management systems have some issues in processing possibilities or data structuring for database input. GIS became irreplaceable tool for managing spatial and other data but authors chose different database tools for managing and querying datasets. Authors of this paper consider SQL as the best solution for querying datasets. It is simple, user-friendly, easy to learn language but it has its limitations on large datasets.

#### **4. CONCLUSION**

GIS enables capturing, storing, checking, and displaying data related to positions on the map and thanks to its multidimensional character, GIS can show many different kinds of data on one map. This feature enables users to define, analyse and understand patterns and relationships in more easy and precisely way, and that is very important in complex and highly demanding management processes such as a dam management. Furthermore, considering the fact that data contained in GIS have their mutual topological and logical connections, GIS can perform various spatial and logical analyses. Results can be interpreted in different ways, depending on user needs. As a platform, GIS enables different kinds of information to be accessed simultaneously by a variety of types of users, ensuring timely data updating and constant, real-time access to the same. Efficient dam management couldn't be considered without support of GIS. However, GIS can have complex structure and it could be difficult to use. In combination with GIS dam management relies on different database solutions. In this paper it is considered the use of SQL which has advantages in ease of use but limitations on large datasets.

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# MONITORING OF SOME DISSOLVED HEAVY METALS IN SURFACE WATERS OF NORTH-WEST CROATIA FROM YEAR 2016 TO 2018

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Abstract: Heavy metals have a negative impact on environment and wildlife. In waters, heavy metals appear in two forms, as dissolved and bioavailable; and as solid and non-soluble. We monitored the concentration of dissolved copper, nickel, manganese and iron in water samples at five river locations of north-west Croatia from 2016 to 2018. Concentrations of dissolved nickel measured at Melačka river, near Vularija in Međimurje county and HE Čakovec dam, near Štefanec in Međimurje county were below 5 µg/l and could be considered as not polluted. Concentrations of dissolved copper measured at Plitvica river, near Zbela in Varaždinska county and Horvatska, near Veliko Trgovišće in Krapinsko-Zagorska county were mostly below 5 µg/l and could be considered as not polluted. At Kosteljina river near Jalšje at the Krapinsko-Zagorska county concentrations of dissolved copper were mostly below 5 µg/l; concentrations of dissolved manganese and iron were higher especially during second part of the year, with some fluctuations. For this reason, Kosteljina river could be considered as medium polluted.

Keywords: heavy metals, pollution, north-west Croatia rivers.

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Original scientific paper https://doi.org/10.37023/ee.7.2.2

## **1. INTRODUCTION**

Heavy metals, in general, have a negative impact on environment and wildlife. The cycle of the heavy metals in aquatic systems is complex and includes physical, chemicals and biological processes at three different parts: water-biota-sediment. (Jordana & Batista Piera 2004) The intensity of their circulation is unequal during the year and mostly depends on the seasonal changes, climate conditions and biological activity. (Fergusson 1991) The translation of heavy metals from one state to another depends on their entering state and concentration, but also on the constitution of water. Since heavy metals are divided on dissolved (hydrated ions, complex with organic and inorganic ligands), colloidal and adsorbed on the particulate matters, their potential bioavailability/toxicity and removing possibility will depend on chemical bonds and physical forms of the metals. (Merian et al. 2004)

Activity mechanisms of dissolved heavy metals with particle matter and biota are regulated with different physical-chemical processes like complexation, adsorption/desorption, dissociation and diffusion (Jordana & Batista Piera 2004). Adsorption of heavy metals on particle matter, which is then precipitated, consequently causes an increased concentration in sediment and aquatic life (fishes and shells). (Wood 1974) When adsorption capacity of the sediment is saturated, the level of heavy metals is increasing in water. It is important to note that the sediment is the most important reservoir in the aquatic systems and it represents a danger of re-activation of accumulated heavy metals, consequently causing their circulation in waters, organisms, soil and air. (Ayandiran et al. 2010)

Concerning the toxicity, metal and metalloid ions in environment are usually divided in nontoxic for environment, toxic and accessible, and toxic with no or low solubility. Solubility is in direct correlation with toxicity. The most dangerous metals and metalloids are Cd, Pb, Sn, As, Hg and Se cations with high toxicity at low concentrations, while Cu, Zn, Co, Mn, Ni and Fe cations are toxic above certain concentrations. (Järup 2003) The threshold limits, surface waters limits and the health impact of selected heavy metals (nickel, copper, iron and manganese) are presented in **Table 1**.

Nickel is a transition element, and in environment its most abundant form are Ni(II) based chemical compounds (sulphates, chlorides, carbonates) with high biological availability. Nickel ions can form complexes with organic and inorganic ligands. Nickel ions with humic and fulvic acids can form medium stable complexes. Environmental nickel pollution originates from the dust formed from the soil and rock erosion, volcanic activity, industrial dust, fossil fuel emission, agricultural fields rinsing, traffic emissions, wastewaters and metallurgy. (Merian et al. 2004)

Copper ions in water originate from the rock erosion, industrial waste waters (heavy metal production facilities, incineration plants, smelters, etc.) and from the agricultural land fields rinsing (pesticides). Copper compounds in

water appear in a solid insoluble form and in a form of a complex compounds. (Martínez & Motto 2000) The most common forms are  $CuCl_2$ ,  $Cu(OH)_2$ ,  $CuSO_4$  and  $CuCO_3$ . Minerals in small fraction sediments have a high affinity to adsorb the copper ions. Copper ions tend to form complex with dissolved humic acids, carbonates and mineral clays, which has a high impact on the nickel behaviour in water. (Merian et al. 2004)

Iron is a transitional element wide spreaded in soil and rocks in a form of silicates, sulphides, oxides and other salts. Iron is usually found in a Fe(II) and Fe(III) form. Fe(II) ions have a moderate mobility, while Fe(III) ions are not mobile. Iron ions mobility is increasing in reducing systems and when pH is decreasing. Solubility, mobility and oxidation state directly depend on the redox system where they appear. In oxidizing environment appears the oxidation of Fe(II) to Fe(III) consequently resulting in the precipitation of it's hydroxides and formation of colloidal suspension. Colloidal Fe(III) can be often found in surface waters. In acidic and reducing conditions Fe(II) is very soluble. With increasing pH and the redox potential, iron concentration is increasing and precipitation is more intense. (Merian et al. 2004)

Manganese a transitional element often found in ground waters originating from the soil and rocks. Higher manganese concentrations in waters are caused by anthropogenic activities. In surface waters, manganese is found in soluble or suspended form. This depends on pH, anions in surrounding, redox potential, etc. (Merian et al. 2004) The mobility is increased by lower pH. Usually manganese appears in oxidized from as MnO<sub>2</sub>. MnO<sub>2</sub> is insoluble and precipitates in the sediment. Manganese often appears with iron ions, but in lower concentration as iron.

There is a variety of different analytical techniques for quantitative detection of dissolved copper, nickel, iron and manganese ions in water. Some of them are UV-Vis spectroscopy, ion chromatography, Atomic absorption spectroscopy, Atomic emission spectroscopy, inductively coupled plasma emission spectroscopy, etc. (Stencel & Jaffe 1996; Zeiner et al. 2007).

Heavy metal	Threshold limit value	Limit values for surface waters	Target organs	Clinical issues
Nickel	20 µg/l	0.5 mg/l	Lungs, skin	Cancer, dermatitis
Copper	2 mg/l	0.5-1.0 mg/l	Kidneys, nervous system	Wilson's disease
Iron	200 µg/l	200 µg/l	Cardiovascular and immunological system, skin	Alzheimer's disease, anaemia
Manganese	50 µg/l	2 mg/l	Nervous system	Central and peripheral neuropathy

 Table 1. Permitted heavy metal concentrations and their influence on human health (Fergusson 1991)

The Water Framework Directive (WFD) (2000/60/EC) is the fundamental key document for the water management within European Union countries. WFD includes guidelines for water protection, water management and water quality enhancement, including water resources, surface waters, ground waters, etc. WFD is incorporated in the Croatian legislation through the Law on waters (NN 153/09, 130/11, 56/13, 14/14, 46/18) and a Directive for the standard water quality (NN 73/13).

Paragraph 11 in the Directive for the standard water quality (NN 73/13) divides the surface waters based on their ecological quality parameters in:

- 1. very good ecological condition,
- 2. good ecological condition,
- 3. medium ecological condition,
- 4. low ecological condition and
- 5. very low ecological condition.

Monitoring of the surface waters is carried out as a: surveillance monitoring (long-term changes), operational monitoring (changes during treatment of bad water quality areas) and research monitoring (detection of unknown relations).

## 2. MATERIAL AN METHODS

All samplings and analytical measurements were performed by the Public health Institute of Varaždin county as a part of the river waters monitoring plan from 2016 to 2021 within the long term river waters monitoring plan for the north-west Croatia carried out by the Public health Institute of Varaždin county.

#### 2.1. Sampling locations

The sampling locations were placed in the north-west region of Croatia in three counties: Međimurska, Varaždinska and Krapinsko-Zagorska. The rivers on the northern part flow into the Drava river, and rivers on the southern part of the region flow into the Sava river. All the rivers belong to the Danube water area, and Black Sea basin.

River Drava is characterised by the nival hydrological regime (max. flow in June, min. in December), while selected smaller rivers have pluvial hydrological regime (max. flow in March/April) with lower hydrological characteristics compared to Drava. River Sava is characterised as a Peripannonian pluvial-nival type of discharge regime in the upstream river part where the samples were collected, while the downstream discharge regime in the downstream part on the Bosnian border is characterized as a Pannoninan pluvial-nival type. (Orešić et al. 2017)

The sampling locations in **Figure 1** are marked on the Croatian river map obtained from the Hrvatske vode company. The north-west region was magnified for clarity, and it includes all three counties where the sampling was performed.



*Figure 1.* Croatian river map on the left; and a magnified north-west region with the sampling locations and location numbering on the right.

The river sampling locations are:

*1.* **Plitvice, Zbela** - Plitvica river before Zbela bayou (coordinates: 490826 X HTRS, 5125398 Y HTRS) flows into the Drava river.

2. Horvatska, Veliko Trgovišće - Horvatska river, at Veliko trgovišće (coordinates: 450139 X HTRS, 5096157 Y HTRS) flows into the Sava river.

*3.* **Melačka, Vularija** - Melačka river, at Vularija (coordinates: 498809 X HTRS, 5130717 Y HTRS) flows into the Drava river.

4. **HE Čakovec, Štefanec** - Lower circumferential channel of the water storage reservoir at Čakovec/Štefanec dam (coordinates: 497381 X HTRS, 5129590Y HTRS) flows into the Drava river.

5. **Kostejina, Jalšje** - Kosteljina river, at Jalšje (coordinates: 449845 X HTRS, 5099703 Y HTRS) flows into the Sava river.

## 2.2. Sampling

Sampling was performed according to the water sampling regulation ISO 5667-6 "Guidance on sampling of rivers and streams" (5667-6 ISO). Sampling was performed manually, about 15 cm beneath the water surface, and the sample was collected directly into the 1000 ml sampling glass bottles with the bottleneck turned to the water stream (**Figure 2**). At each location one sample was taken. The samples were stored at 4 °C and transferred to the laboratory. Next, the samples were filtrated trough 0.45  $\mu$ m filter paper and the filtrate was transferred to the 50 ml plastic bottles, and ready for measurements. Measuring the dissolved fraction of metals has allowed us to estimate the quantities of the bioavailable heavy metals.



Figure 2. River water samples from the selected locations in north-west Croatia.

#### 2.3. Measuring setup, chemicals and procedure

The samples were analysed by the ion chromatography instrument Dionex DX 500 (Thermo Scientific, USA). The quantification limit of the method was 5  $\mu$ g/l with 15 % uncertainty. The programme for data acquisition was Chromeleon 6.80. The IonPac CS5A was used as a separation column and the CG5A was used as a guard preseparation column. As an eluent, the MetPac PDCA eluent (Thermo Scientific, USA) with 66 mM potassium hydroxide and a 74 mM formic acid was used. 200 ml of the PDCA eluent was diluted with 1000 ml ultrapure water. Dionex 4-(2-Pyridylazo) resorcinol monosodium salt (PAR) (Thermo Scientific, USA) is used for post column derivatization of transition metals separated in the separation column together with the Dionex MetPAC PAR Post Column Diluent (1 M 2dimethylaminoethanol, 0.5 M ammonium hydroxide, 0.3 M sodium bicarbonate) (Thermo Scientific, USA). To prepare the post–column reagent, 0.05 g of 4-(2-Pyridylazo) resorcinol monosodium salt was dissolved in 250 ml MetPa PAR post column diluent.

Other measuring conditions were as follows: flow speed - 1.2 ml/min, injected sample volume - 50  $\mu$ l, speed of the reagent - 0.6 ml/min, wavelength of the detector - 530 nm. As a calibration standard ICP multi-element standard solution IV – Certified reference material (Merck, Germany) with 200  $\mu$ g/l concentration of heavy metals was used as a reference.

## **3. RESULTS AND DISCUSSION**

The content of heavy metals was measured at 5 locations of the river waters in the north-west of Croatia in the period of 2016 to 2018. The samples were taken periodically or every month during this period.

Copper content was measured at two locations: Plitvica river, near Zbela in Varaždinska county and Horvatska, near Veliko Trgovišće in Krapinsko-Zagorska county, in the period from 2016 to 2018 (**Table 2**).

At the Plitvica river, near Zbela the concentrations of the Cu are below 5  $\mu$ g/l, and at the Horvatska, near Veliko Trgovišće the concentrations of the Cu are below 5  $\mu$ g/l, except in August 2018 when the concentration was 7.4  $\mu$ g/l and in October 2018 when the concentration was 7.6  $\mu$ g/l.

In the Regulation on Water Quality Standard NN 80/2018 (Uredba o standardu kakvoće voda, NN 73/13; 151/14; 78/15; 61/16; 80/18) the Average Annual Concentrations (AAC) for the copper compounds in surface waters is from 1.1 to 8.8 µg/l. Copper concentrations at both locations were within the prescribed concentrations.

Nickel content was measured at two locations: Melačka river, near Vularija in Međimurje county and HE Čakovec dam, near Štefanec in Međimurje county, in the period from 2016 to 2018 (**Table 3**).

At the Melačka river, near Vularija the concentrations of the Ni are below 5  $\mu$ g/l, and at the HE Čakovec dam, near Štefanec the concentrations of the Ni are also below 5  $\mu$ g/l, in the measured period

The Regulation on Water Quality Standard NN 80/2018 (Uredba o standardu kakvoće voda, NN 73/13; 151/14; 78/15; 61/16; 80/18) defined 34 µg/l as a Maximum Annual Concentrations (MAC) for nickel and nickel

compounds in surface waters, and 4  $\mu g/l$  as an Average Annual Concentrations (AAC) in a sense of the bioavailability. Nickel concentrations at both locations were within the prescribed concentrations.

		DISSOL	VED COPPER	CONCENTR.	ATION (µg/l)	
			LOC	CATION		
		Plitvica, Zbe	la	Horvatska, Veliko Trgovišće		
	2016	2017	2018	2016	2017	2018
January	/	/	< 5	/	/	<5
February	< 5	/	< 5	<5	/	<5
March	< 5	/	< 5	<5	/	<5
April	< 5	/	< 5	<5	/	<5
May	< 5	< 5	< 5	<5	<5	/
June	< 5	< 5	< 5	<5	<5	<5
July	< 5	< 5	< 5	<5	<5	<5
August	< 5	/	< 5	<5	<5	7,4
September	< 5	< 5	< 5	<5	<5	<5
October	< 5	< 5	< 5	<5	/	7,6
November	< 5	/	< 5	<5	<5	<5
December	< 5	< 5	< 5	<5	<5	<5

Table 2. Dissolved copper concentrations at selected locations in the period from 2016 to 2018.

Table 3. Dissolved nickel concentrations at selected locations in the period from 2016 to 2018.

		DISSOL	VED NICKEL	CONCENTRA	ATION (µg/l)	
			LOC	ATION		
		Melačka, Vula	rija	HE Čakovec, Štefanec		
	2016	2017	2018	2016	2017	2018
January	/	/	< 5	/	/	< 5
February	/	/	/	/	/	< 5
March	/	/	< 5	/	/	< 5
April	/	/	< 5	/	/	< 5
May	/	< 5	/	/	< 5	< 5
June	/	< 5	/	/	< 5	< 5
July	/	/	/	/	< 5	< 5
August	/	/	/	/	< 5	< 5
September	/	< 5	< 5	/	< 5	< 5
October	/	< 5	< 5	/	< 5	< 5
November	/	< 5	< 5	/	< 5	< 5
December	/	< 5	/	/	< 5	< 5

Copper, manganese and iron content was measured Kosteljina river, near Jalšje at the Krapinsko-Zagorska county, in the period from 2016 to 2018 (**Table 4**).

The concentrations of the Cu are below 5  $\mu$ g/l, except of August 2018 (7.4  $\mu$ g/l) and October 2018 (7.6  $\mu$ g/l). Since Kosteljina is a left bayou of the Horvatska river, there is a correlation between the concentrations of copper in both rivers. In fact, measured concentrations are the same. When tracking the pollution source, it can be concluded that the pollution is probably somewhere on the Kosteljina river upper stream.

The concentrations of the Mn in 2016 are below 5  $\mu$ g/l, except in February (9.7  $\mu$ g/l) and June (8.5  $\mu$ g/l). During 2017 the concentrations of Mn were higher than 5  $\mu$ g/l, starting from June (150  $\mu$ g/l) and decreasing up to September (5.2  $\mu$ g/l). Usually, the Mn ions appear together with Fe ions. During 2018 the concentration of Mn was below 5  $\mu$ g/l, except in February (10  $\mu$ g/l), June (92.5  $\mu$ g/l), August (116  $\mu$ g/l) and October (7.7  $\mu$ g/l).

The lowest concentration of the Fe in 2016 was in March (133.5  $\mu$ g/l) and the highest were in August (2415  $\mu$ g/l) and November (2880  $\mu$ g/l). The lowest concentration of the Fe in 2017 was in December (142  $\mu$ g/l) and the highest was in August (1618  $\mu$ g/l) and November (2880  $\mu$ g/l). The lowest concentration of the Fe in 2018 was in January (152  $\mu$ g/l) and the highest was in July (1832  $\mu$ g/l). For this location, higher Mn values are present in the second part of the year for all three observed years.

Higher concentrations of iron and manganese could be explained by the higher agricultural activity in the area, higher industrial activities during summer months and potentially by the low coverage of the sewerage system in this area.

When compared with the Mn concentrations summer months obtained higher ion concentrations than usual. The Regulation on Water Quality Standard NN 80/2018 (Uredba o standardu kakvoće voda (NN 73/13; 151/14; 78/15; 61/16; 80/18) did not defined the Maximum Annual Concentrations (MAC) or Average Annual Concentrations (AAC) for manganese and iron ions. In this way, there is no criteria for water classification. According to available data on selected heavy metal ions concentration in the period from 2016 to 2018 it can be concluded that surface waters at selected locations obtained different pollution levels.

Varaždin county and Međimurje county obtained selected heavy metal ions concentration within the acceptable limits and these waters can be considered not to be polluted. On the other hand, Krapinsko-Zagorska county obtained selected heavy metal ions concentration higher then acceptable limits and could be considered as medium polluted with higher anthropogenic influence. Further monitoring should be carried out to prevent possible higher anthropogenic impact.

	LOCATION: Kosteljina, Jalšje								
	DISSOLVED Cu (µg/l)			DISSC	DISSOLVED Mn (µg/l)		DISSOLVED Fe (µg/l)		
	2016	2017	2018	2016	2017	2018	2016	2017	2018
January	/	/	< 5	/	/	< 5	/	/	152
February	< 5	/	< 5	9.7	/	10.8	803	/	256
March	< 5	/	< 5	< 5	/	< 5	133	/	440
April	< 5	/	< 5	< 5	/	< 5	383	/	210
May	< 5	/	/	< 5	/	< 5	183	257	1072
June	< 5	< 5	< 5	8.5	150	92.5	440	754	591
July	< 5	< 5	< 5	< 5	81.1	< 5	656	556	1832
August	< 5	< 5	7,4	< 5	50	116	2415	1618	583
September	< 5	< 5	< 5	< 5	5.2	< 5	481	722	708
October	< 5	< 5	7,6	< 5	< 5	7.7	896	268	1132
November	< 5	< 5	< 5	< 5	< 5	< 5	2880	581	261
December	< 5	< 5	< 5	< 5	< 5	< 5	345	142	353

 Table 4. Dissolved copper, manganese and iron concentrations at Kosteljina river, Jalšje in the period from 2016 to 2018.

#### 4. CONCLUSION

Concentrations of dissolved nickel measured at Melačka river, near Vularija in Međimurje county and HE Čakovec dam, near Štefanec in Međimurje county, in the period from 2016 to 2018 were below 5  $\mu$ g/l and could be considered as not polluted.

Concentrations of dissolved copper measured at Plitvica river, near Zbela in Varaždin county and Horvatska, near Veliko Trgovišće in Krapinsko-Zagorska county, in the period from 2016 to 2018, were mostly below 5  $\mu$ g/l and could be considered as not polluted.

At Kosteljina river near Jalšje at the Krapinsko-Zagorska county, in the period from 2016 to 2018. concentrations of dissolved copper were mostly below 5  $\mu$ g/l; concentrations of dissolved manganese and iron were higher especially during second part of the year, with some fluctuations. For this reason, Kosteljina river could be considered as medium polluted.

## 5. ACKNOWLEDGEMENT

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# THE REMOVAL OF NEONICOTINOID INSECTICIDE IMIDACLOPRID IN AN ANNULAR PHOTOREACTOR

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Abstract: Heterogeneous photocatalysis has recently attracted an increasing interest of scientists and experts who deal with the waste water and air treatment. An important area of application is removal of persistent organic pollutants, which can not be easily destroyed by conventional methods. Among these pollutants are neonicotinoid insecticides, which are widely used all over the world and currently are included in the watch list of substances of the European Commission within the Water Framework Directive. Therefore, there is a need to study their influence on the environment and to develop appropriate technologies for their removal. In this work, the photolytic and photocatalytic degradation of neonicotinoid insecticide imidacloprid in an annular photoreactor with recirculation under different working conditions (irradiation source, pH, type and concentration of the catalyst) was studied. The photolytic degradation was examined using lamps that emit UVA, UVC and simulated sun light. The photocatalytic experiments in the suspension involved the use of commercial titanium dioxide (TiO<sub>2</sub> P25, Degussa/Evonik), commercial TiO<sub>2</sub> P25 pre-treated with UVC irradiation prior to use in the catalytic system and nitrogen-doped TiO2 (CCR 200 N produced by Cinkarna Celje). The catalysts were characterized using XRD, UV/Vis-DRS and BET analysis. The most efficient photocatalyst was then immobilized on the glass woving fibre, using peroxotitanic acid (produced by Cinkarna Celje) as a binder. The degree of degradation of imidacloprid was determined using high performance liquid chromatography (HPLC). According to the obtained results, UVC-treated TiO2 showed the best efficiency among the examined catalysts in the slurry reactor while using lamp that simulates the sun irradiation. The imidacloprid degradation rate increases with the increase in the catalyst concentration. The immobilized UVC-treated catalyst gave satisfying results in terms of stability, activity and reuse.

Keywords: heterogeneous photocatalysis, neonicotinoid insecticides, imidacloprid, annular reactor

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#### **1. INTRODUCTION**

Neonicotinoid insecticides are relatively new group of insecticides, widely applied for the seed treatment. Because of their high solubility in water and low adsorption to the soil, they can reach underground and surface water during rainfall rinsing. In the last ten years several investigations connected some neonicotinoids with bees poisoning all over the world (Žabar et al. 2012). At present, their use is restricted, but still not completely banned. Some insecticides from the group of neonicotinoids, e.g. imidacloprid, are included in the watch list of substances for Union-wide monitoring in the field of water policy, established by the European Commission Implementing Decision 2018/840 pursuant to Directive 2008/105/EC (Commission implementing decision (EU) 2018/840).

The existing water treatment processes cannot remove persistent organic compounds sufficiently, which is why the advanced oxidation processes (AOPs) are increasingly explored as an alternative to conventional methods. Among the most investigated AOPs is heterogeneous semiconductor photocatalysis based on the excitation of semiconductor particles in the aqueous media using corresponding source of irradiation (UV or visible irradiation) (Ibhadon & Fitzpatrick 2013). First photocatalytic studies began with titanium dioxide (TiO<sub>2</sub>), which has been the most studied photocatalyst till now. TiO<sub>2</sub> has many advantages, for instance high chemical stability, non-toxicity, availability, environmental acceptability and low prices compared to other semiconductor oxides. The most commonly studied TiO<sub>2</sub> catalyst is commercial P25 (80% anatase structure, 20% rutile structure) from Evonik/Degussa. The bandgap energy of the TiO<sub>2</sub> P25 is about 3.2 eV, corresponding to the wavelength of activation  $\leq$  390 nm. High bandgap energy and the ability to absorb only UV radiation, which consists only 5 % of the solar spectrum, limits the use of TiO<sub>2</sub> for commercial purposes (Yang et al. 2018). Therefore, there is a large number of photocatalytic investigations directed to the modification of TiO<sub>2</sub> in order to achieve photocatalytic activity in the visible area of the solar spectrum ( $\lambda$ > 390 nm). These procedures include the modification of surface TiO<sub>2</sub> by sensitization to organic dyes, polymers or surface-bound organic complexes and creating composites with other semiconductor materials (Rehman et al. 2009). In addition to surface modification, the activity of  $TiO_2$  in the visible part can be achieved by narrowing the bandgap by doping/codoping  $TiO_2$  with nonmetals and transition metals (Zaleska-Medynska 2008). Also, some studies have shown that reduction of  $Ti^{4+}$  to  $Ti^{3+}$  ions results in creating oxygen vacancies due to the release of oxygen ions from the band structure. These vacancies are formed between the valence and conduction bands in the  $TiO_2$  band structure and they act as an electron captures from the valence band, which consequently enhances photocatalytic activity of  $TiO_2$  in the visible region (Zuo et al. 2010). Reduction of  $TiO_2$  in this way was carried out in several studies using different strategies, for instance plasma, vacuum  $TiO_2$  heating, steam chemical vapor deposition or bombarding  $TiO_2$  with high energy particles.

In this paper we studied pretreating of  $TiO_2$  with UVC light in order to obtain reduced  $TiO_2$  with enhanced photoactivity in the visible part of the sun spectrum. The obtained catalyst, the so called UVC-TiO<sub>2</sub> was compared to two commercial catalysts in the suspended form. Also, some experiments were performed using UVC-TiO<sub>2</sub> in the immobilized form.

#### 2. MATERIALS AND METHODS

#### 2.1. Chemicals

An analytical standard imidacloprid, used for HPLC analysis was purchased from Sigma Aldrich Company Ltd. The experiments were performed using commercial plant protection product Boxer 200 SL supplied by Sharda Ltd. Peroxotitanic acid (PTA) and nitrogen-doped TiO<sub>2</sub> (N-TiO<sub>2</sub>, CCR 200 N) were donated by Cinkarna Celje. TiO<sub>2</sub> P25 was purchased from Evonik. Formic acid 98 % p.a. and acetonitrile HPLC grade were purchased from VWR. All aqueous solutions were prepared with ultra-pure water.

#### 2.2. Characterization of the catalysts

The specific surface area, total pore volume and average pore diameter of the powder samples were determined with nitrogen adsorption-desorption isotherms, using the Brunauer–Emmet–Teller (BET) method on the Micrometrics ASAP 2000. The crystalline phase composition of the prepared samples was determined by X-ray diffraction measurements (Shimadzu 6000) with CuK $\alpha$  radiation. The UV–vis spectra of the prepared powder samples were obtained using DRS (Perkin-Elmer Lambda 35) equipped with an integrating sphere. The spectra were recorded at room temperature in the wavelength range of 200–800 nm. BaSO<sub>4</sub> was used as a reference.

#### 2.3. Apparatus

The photocatalytic experiments were performed in an annular batch reactor (including recirculation in a closed system) with the source of irradiation placed in the central part of the reactor. The same reactor was used for 2-hour pretreatment of commercial  $TiO_2$  using UVC lamp before photocatalytic reaction. The reaction mixture was recirculated using recirculating pump and the temperature was kept constant using a thermostat (Julabo–Model ED, Heating Immersion Circulator). The reaction conditions were given in the **Table 1**.

INITIAL CONCENTRATION OF IMIDACLOPRID, ppm		10	
TEMPERATURE, °C		30	
REACTOR VOLUME, mL		450	
INITIAL pH OF THE SOLUTION		6.5-7.0	
<b>RECIRCULATION FLOW RATE, (L/min)</b>		1.4	
FORM OF THE CATALYST	suspended	immobilized	without catalyst- photolysis
TYPE OF THE CATALYST	TiO <sub>2</sub> P25, N- TiO <sub>2</sub> (CCR 200 N), UVC-TiO <sub>2</sub>	UVC-TiO <sub>2</sub>	-
CATALYST CONCENTRATION, (g/L)	0.05-0.5	0.036-0.110	-
IRRADIATION SOURCE	Arcadia Natural Sunlight 8 W	Arcadia Natural Sunlight 8 W	UVC 8 W, UVA 8 W, Arcadia Natural Sunlight 8 W

 Table 1. Reaction conditions

The immobilized type of the catalyst was prepared using peroxotitanic acid (PTA) as a binder. The suspension of catalyst and binder was prepared by mixing 1 g of catalyst in 100 ml of PTA. The prepared mixed solution was applied in thin layers on the glass woving fibre. Different amount of catalyst on the support was achieved by applying several layers and drying between each layer. The immobilized  $TiO_2$  layer was placed close to the reactor walls using specially designed inert photocatalyst holder. After "dark" period (establishing of the adsorption equilibrium), the reaction mixture was illuminated with the corresponding lamp. The concentration of model compound imidacloprid was analyzed at different reaction times on a 5  $\mu$ m, 250 x 4.6 mm Zorbax SB-C18 column by high performance liquid chromatography (Shimadzu LC 20AT Prominence) equipped with an autosampler and diode array detector (DAD).

#### **3. RESULTS AND DISCUSSION**

#### 3.1. Characterization of the powder catalysts

**Figure 1** presents UV-Vis spectra of the commercial nitrogen doped TiO<sub>2</sub>, N-TiO<sub>2</sub> (produced by Cinkarna Celje) and UVC-treated TiO<sub>2</sub> P25 (UVC-TiO<sub>2</sub>). The band gap energy,  $E_g$ , was estimated by plotting modified Kubelka-Munk function for indirect electron transition,  $(F(R)hv)^{1/2}$  vs. photon energy (hv), the so–called Tauc's plot, followed by extrapolation of the linear region onto the energy axis (Valencia et al. 2010). The estimated band gap energies, together with wavelength of activation, are shown in **Table 2**. Pretreatment of TiO<sub>2</sub> P25 with UVC radiation during 2 hours led to decreasing of  $E_g$  to 2.6 eV compared to 3.2 and 3 eV as characteristic values for the anatase and rutile phase of TiO<sub>2</sub> P25, respectively. The decrease in value of  $E_g$  resulted in a change of wavelength activation from 390 nm for TiO<sub>2</sub> P25 to 476 nm for UVC-TiO<sub>2</sub> and, consequently, enabled photocatalytic experiments in the visible part of solar spectrum ( $\lambda > 390$  nm).

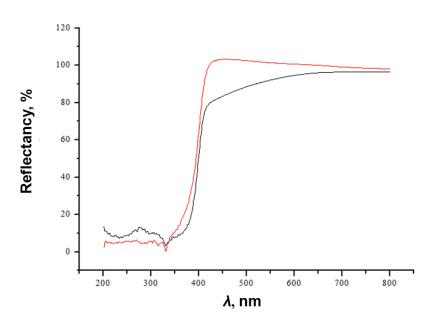


Figure 1. Diffuse reflectance spectra of N-TiO<sub>2</sub> (black line) and UVC-TiO<sub>2</sub> (red line)

The XRD patterns of the N-TiO<sub>2</sub> and UVC-TiO<sub>2</sub> are shown in **Figure 2.** The XRD spectra of the UVC-TiO<sub>2</sub> correspond to the spectra of TiO<sub>2</sub> P25 before UVC irradiation that was found in literature (Wang et al. 2011). It can be concluded that irradiation of TiO<sub>2</sub> P25 with UVC light did not affect the crystalline structure of the photocatalyst, but probably led to formation of oxygen vacancy states between the valence and conduction bands in the TiO<sub>2</sub> band structure, that take part in the photoexcitation process. That is, the electron may be excited to the oxygen vacancy states from the valence band even with the energy of visible light (Nakamura et al. 2000). DRS spectroscopy of N-TiO<sub>2</sub> (Fig. 1) showed that this photocatalyst is also active in the visible part of spectrum, but from the XRD spectra it is visible that this photocatalyst consists only of rutile crystal phase, which is less active than anatase (**Figure 2**). The lower activity of N-TiO<sub>2</sub> was confirmed while performing photocatalytic experiments, as mentioned later in the text. The results of the N<sub>2</sub> adsorption/desorption analysis showed that treating TiO<sub>2</sub> P25 with UVC light did not affect the textural properties of the catalyst (**Table 3**) As expected, addition of PTA as a binder for immobilization of TiO<sub>2</sub> on a glass woving fibre lead to decreasing of specific surface area of prepared UVC-TiO<sub>2</sub>/PTA sample in comparison to the pure UVC-TiO<sub>2</sub> was higher than for TiO<sub>2</sub> P25.

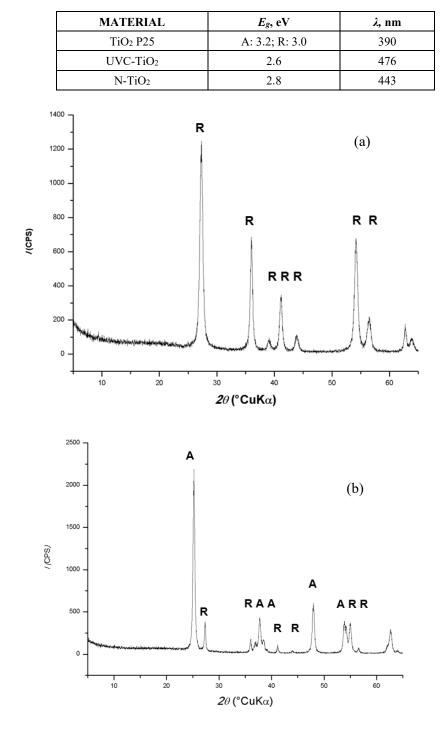


Table 2. Values of indirect band gap energy for the examined TiO<sub>2</sub> photocatalysts

*Figure 2. XRD* spectra of N-TiO<sub>2</sub> (a) and UVC-TiO<sub>2</sub> (b)

 Table 3. Textural properties of powder catalysts determined using the nitrogen adsorption/desorption analysis

MATERIAL	<i>S<sub>BET</sub></i> , (m <sup>2</sup> /g)	<i>V</i> <sub><i>P</i></sub> , (cm <sup>3</sup> /g)	<i>d</i> <sub><i>P</i></sub> , nm
TiO <sub>2</sub> P25	56	0.25	17.50
UVC-TiO <sub>2</sub>	54.28	0.27	20.22
UVC-TiO <sub>2</sub> /PTA (50 g/L TiO <sub>2</sub> )	17.93	0.05	11.44
N-TiO <sub>2</sub>	87.92	0.47	21.40

#### 3.2. Testing of the photocatalytic properties

The photolytic and photocatalytic activity of the suspended and immobilized  $TiO_2$  photocatalysts is evaluated by photodegradation of imidacloprid in the simulated sunlight conditions. In order to study the contribution of photolysis on the degradation of imidacloprid, three different irradiation sources were examined. The results showed that the lamp of interest (Arcadia natural sunlight), that closely simulates sun spectrum, did not degrade imidacloprid even after 3.5 hours of irradiation in an annular photoreactor. On the other side, the strong UVC light completely degraded imidacloprid after 1 hour of irradiation (**Figure 4**).

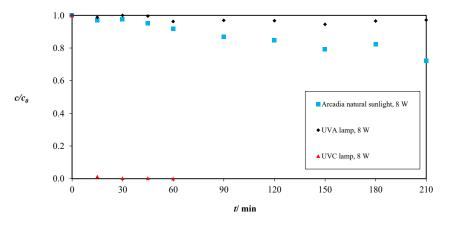


Figure 4. Photolytic degradation of imidacloprid using different irradiation source

Further experiments were performed using simulated sunlight under the presence of photocatalysts. Three  $TiO_2$  catalysts in the suspended form were compared in the same reaction conditions and it was shown, according to our expectations, that the best efficiency was obtained using UVC-TiO<sub>2</sub> (Figure 5). N-TiO<sub>2</sub> was not efficient in our reaction system, although the same photocatalyst exhibited excellent photocatalytic activity in the presence of natural or artificial UV and visible light for the decomposition of nitrogen monoxide (NO).

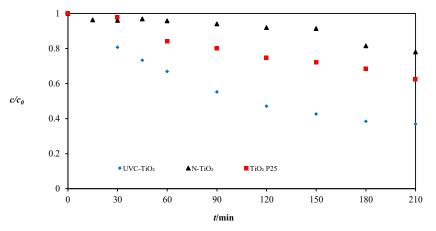


Figure 5. Comparison of three  $TiO_2$  catalysts in the suspended form at the same reaction conditions

Furthermore, the influence of different concentration of UVC-TiO<sub>2</sub> photocatalyst on the degradation efficiency was examined. The higher catalyst concentration led to greater decrease in the imidacloprid concentration (**Figure 6**). This is obvious since the higher catalyst concentration leads to more photocatalytically active sites available for the photoexcitation process. Some authors have reported on the optimal catalyst concentration than optimal led to decrease in the degradation rate of model pollutant (Kitsiou et al. 2009). This was explained with possible agglomeration of TiO<sub>2</sub> particles and decreased system opacity, which consequently blocked reaching of light to the surface of catalyst particles (Affam & Chaudhuri 2013). This phenomenon was not noticed in the concentration range of TiO<sub>2</sub>, studied in this paper (0.05 - 0.5 g/L).

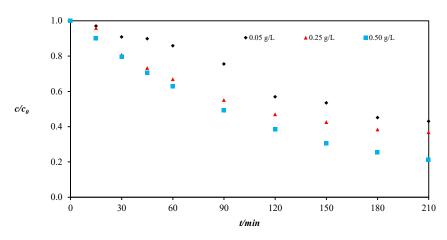


Figure 6. Influence of the concentration of UVC-TiO<sub>2</sub> on the degradation of imidacloprid

Afterwards, the immobilized UVC-TiO<sub>2</sub> was evaluated in the photocatalytic degradation of imidacloprid in the same reaction conditions as in the suspended form (concentration of imidacloprid, irradiation source, recirculation flow rate and reaction temperature). "Dark" experiment during 1 hour showed that the adsorption process did not contribute to decrease of imidacloprid concentration (Figure 7).

The influence of different number of layers of immobilized UVC-TiO<sub>2</sub> that consequently led to different amount of catalyst on the support, was examined (**Table 1**). It was shown that there was no significant change in the degradation rate with catalyst concentration in the prepared layer (**Figure 8**). The degradation rate obtained with the immobilized TiO<sub>2</sub> was much lower than with suspended TiO<sub>2</sub> as expected. Regardless of the lower efficiency, the prepared immobilized layer of TiO<sub>2</sub> showed good stability and no Ti leaching. Peroxotitanic acid as a binder ensured good adherence strength of the immobilized photocatalyst layer to the substrate surface.

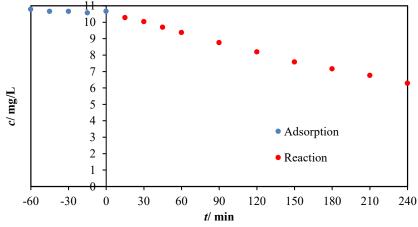
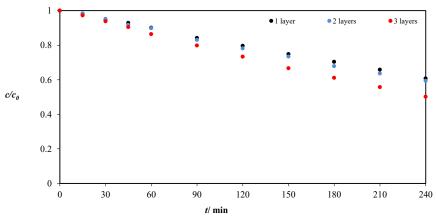


Figure 7. Contribution of adsorption process to the elimination of imidacloprid



*Figure 8.* Influence of the number of layers of UVC-TiO<sub>2</sub> impregnated on glass vowing fibre on the degradation of imidacloprid

## 4. CONCLUSION

The UVC-treated TiO<sub>2</sub> photocatalyst showed the higher visible light activity for imidacloprid removal among the examined TiO<sub>2</sub> catalysts under simulated sunlight conditions. Neither the crystal structure nor the specific surface area was observed to change between the commercial TiO<sub>2</sub> P25 and UVC-treated TiO<sub>2</sub> P25 photocatalyst. The appearance of the visible light photocatalytic activity in UVC-treated TiO<sub>2</sub> is due to a new photoexcitation process by the formation of the oxygen vacancy state located between the valence and the conduction bands. This phenomenon will be confirmed performing ESR measurements in the future work. The imidacloprid degradation rate increased with the increase in the catalyst concentration in the studied concentration range. The immobilized UVC-treated TiO<sub>2</sub> gave satisfying results in terms of stability, activity and reuse.

## 5. ACKNOWLEDGEMENT

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# REMOVAL OF POLLUTANTS FROM ABATTOIR WASTEWATER USING A PILOT-SCALE BAMBOO CONSTRUCTED WETLAND SYSTEM

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**Abstract:** Wastewater from abattoir sources in urban areas can adversely affect the environment and cause health problems. This research investigated the ability of a bamboo constructed wetland system (BCWS) using Bambusa vulgaris, to treat wastewater from abattoir by removing nutrients and organics. This study adopted pilot scale reactors with bed dimension of 1 m length x 1 m width x 1 m depth to simulate a horizontal sub-surface flow constructed wetland and planted with six strands of bamboo plants. Parameters analyzed include the nutrients (in the form of phosphate and nitrate) and the organics (in the form of Chemical oxygen demand, COD and Biochemical oxygen demand, BOD). The effluent analysis that were carried out within a 28-day retention period showed that there was a very good decrease in the nutrient pollutant parameters; phosphate (99.6 %), nitrate (98.5 %). The organics showed a lesser performance with a 39.3 % removal efficiency for COD and 49.9 % removal efficiency for BOD. Bamboo can be used in a BCWS for low cost green technology in urban areas and can be improved upon by increasing the number of bamboo shoot in order to have a larger root system. **Keywords:** abattoir, phytoremediation, constructed wetland, bamboo.

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## **1. INTRODUCTION**

Water is one of the most abundant natural resources needed for anthropogenic activities, however, its occurrence does not translate to ready availability for man's use. This is because more than 90 % of the world's water can be found in oceans and seas and therefore saline in nature thus leaving only about 1 % to be available for domestic, industrial, and other uses. The UN estimates that by 2050 AD, more than two billion would be added to the world population (UN News Centre 2012). Developing countries are perpetually faced with the problem of release of wastewater into receiving water bodies in urban areas thereby altering the biodiversity and introducing algal populations which hampers water supply for domestic uses (Smith et al. 1999). The reuse of wastewater constitutes a very vital aspect of the sustainability of water resources because it can be recycled after treatment to ensure the removal of pathogens and pollutants and protect humans from health defects (Grant 2011). The treatment process can be carried out naturally or in artificial treatment systems. Some of the systems that can be used to remove pollutants from wastewater include microbial fuel cells, anaerobic sludge blanket, electrocoagulation, and constructed wetland.

Constructed wetlands (CW) are artificial green technology that are designed and constructed to remove pollutants by simulating a natural process that occur in wetlands under natural conditions. The treatment processes that occur in CW are physical, chemical and biological in nature and include suspended particles settlement, oxidation of organic matter, photolysis, and microbial communities, mineralization and uptake of plants (phytoremediation), etc.(Badejo et al. 2018; Home & Muthigo 2013).

Phytoremediation involves the use of plants to extract or remove pollutants. It is environmentally friendly and ensure Plants remove harmful chemicals when their roots take in water and nutrients from polluted streams, and groundwater (Baah 2011). It can remove pollutants using five different mechanisms; phytostabilization, rhizosphere bioremediation, phytoextraction, and rhizofiltration (Mudgal et al. 2010; Aisien et al. 2010; Badejo et al. 2018).

Bambusa vulgaris, a common bamboo plant in Nigeria is an open-clump type bamboo species. It is also native to China and Madagascar. Among bamboo species, it is one of the largest of its species. It has certain attractive features such as a good growing rate, high biomass production ability to deal with different environmental conditions and also adaptation to survive in some polluted areas such as mines (Chen et al. 2015). Just like other species of bamboo, it has a high accumulation rate in roots and is more than in shoots, stems, and leaves (Liu et al. 2015). Rajkumar et al. (2012) reported that this specie has high biomass production and fast-growing rates are the dominant characteristics that facilitate phytoremediation.

Abattoir are structures that are used to slaughter animals for food for humans. The carcass and other wastes generated from the animal slaughter are often disposed of in flowing streams located around neighbourhoods where there are residential buildings in urban areas. Domestic utilization of these wastewater sources as well as the flow of the effluent into water bodies can adversely affect the environment and cause public health problems. In Abeokuta, there are many abattoirs within the city one of which is located at Alade-sanmi area along the Abeokuta-Ibadan expressway which was where the wastewater samples were collected. Abattoirs are generally known all over the world to pollute the environment either directly or indirectly from their various processes (Adelegan 2002).

The study investigates the development of a constructed wetland system (CWS) to remove pollutants from an abattoir with a bamboo specie, *Bambusa vulgaris* and also to evaluate the performance of the system.

## 2. MATERIALS AND METHODS

The wastewater sample was collected in a stream located in close proximity to the abattoir located in the Aladesanmi area of Abiola way off the Abeokuta-Ibadan express way in Abeokuta south local government area of Ogun state, Nigeria with a latitude of N709'51.696" and longitude of E3022'33.12048". The samples were collected using a grab sample method of wastewater collection into ten 25 litres containers.

Young plants of *Bambusa vulgaris* were nurtured at the nursery in Funaab-Leventis farm, regularly irrigated and monitored for maturity to facilitate proper growth for ten (10) weeks after which six of it were transplanted into one of the pilot scale tanks located behind the Civil Engineering building, Federal University of Agriculture, Abeokuta, Nigeria so as to enable it become acclimatized with the new environment for two weeks. The plants were irrigated regularly with water from a nearby borehole source to enhance its growth.

Two pilot scale tanks with dimensions 1m \* 1m \* 1m were used for the study to simulate a horizontal subsurface flow constructed wetland in which one was used as the bamboo reactor while the other was used as the control. Each tank was filled with 125 litres of abattoir wastewater. Each tank has a valve connected to an outlet at the bottom designed to collect the water samples for analysis. The path of flow was by gravity.

Water samples were collected in triplicates using sample bottles that were earlier washed in detergent, rinsed in distilled water, and subsequently rinsed with the sample before being taken to the laboratory for analyses. The collection of samples was done on a 7, 14, 21, and 28-day hydraulic retention periods (Badejo et al. 2012). The effectiveness of treatment in this research were observed from the nutrient removal (in terms of phosphate and nitrate) and organics removal (in terms of chemical oxygen demand, COD and biochemical oxygen demand, BOD) which were determined in the laboratory using standard analytical procedures as described by APHA (1998).

#### **3. RESULTS AND DISCUSSION**

The characterization of the initial water samples collected were adopted as values on the 0th day. The charts shown below in the figures indicate the performance of both pilot scale reactors for the 0, 7, 14, 21, and 28-day retention periods. From the results obtained, the young bamboo plants showed ability for phytoremediation of the abattoir wastewater.

#### 3.1. Nutrient removal

Two nutrients were observed in this research which include Phosphorus in terms of phosphate and Nitrogen in terms of nitrates. The phosphate content before treatment in the reactor was about 6.04 mg/l as shown in **Figure 1** but after a 28-day retention period, the concentration decreased to 0.02 mg/l thus indicating a 99.6 % removal efficiency. The reactor also showed the ability to remove over 65 % of phosphate in the first two weeks of operation. The successful ability of the reactor to achieve the removal efficiency may partly be due to the substrate that was used as the sorption property of sand used to fill the reactor could have had a big influence on the removal of phosphate which is further buttressed from the performance of the control. However, when compared to both reactors of control and the reactor, it showed the very good bamboo constructed wetland system's ability for phosphate removal (Michal et al. 2018; Vymazal 2004; Saeed & Sun 2013)

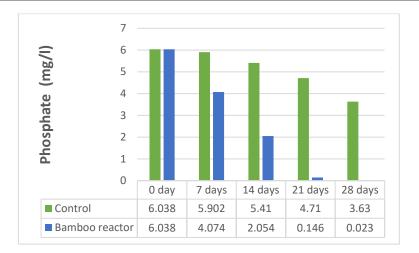


Figure 1. Retention period for phosphate removal

There was a reduction in the nitrate concentration at the end of the experiment from 21.12 mg/l to about 0.31 mg/l as shown in **Figure 2** thus accounting for about 98.5 % reduction with over 60 % of it removed by the end of the second week. This is higher when compared to the nitrate removal efficiency of *Canna sp.* as previously reported (Winanti et al. 2017). The high percentage removal could be attributed to the degradation of the abattoir wastewater and an adequate nitrification process within the bamboo construction wetland system. The bamboo constructed wetland system probably activated the conversion of ammonium in the wastewater to nitrates by *Nitrosomonas* bacteria (Fan et al. 2013; Yuan et al. 2016) and was subsequently absorbed by the bamboo to further undergo the process of conversion to nitrogenous oxides by chemo autotrophic bacteria (Vymazal 2007; Saeed & Sun 2013).

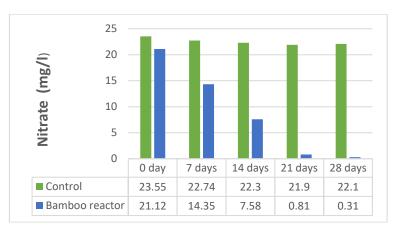


Figure 2. Retention period for nitrate removal

## 3.2. Organics removal

The chemical oxygen demand (COD) content decreased from a concentration of 4971.1 mg/l to 3018 mg/l within the 28-day retention time as can be seen from **Figure 3** thus, accounting for almost 39.3 % of the removal efficiency. The relatively low number of shoots and corresponding root system may have played a role thereby leading to a non-optimal organic biodegradation. Bacteria plays an influential role in COD and may have shown a less prominent influence more than the vegetation considering that the bamboo plants are relatively young (Akratos & Tsihrintzis 2007; Camacho et al. 2007). The bacterial role was to ensure microbial decomposition when the matrix layer was adsorbed to the plant roots. This mechanism may have resulted from the production of oxygen by photosynthesis in the leaves and routed to the root system to enable bacteria to flourish and degrade the organic content (Yang et al. 2007; Sawaittayothin & Polprasert, 2007).

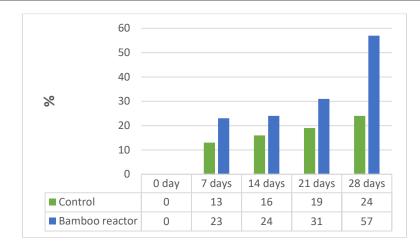


Figure 3. Retention period for COD removal

From **Figure 4**, BOD decreased from 2144.35 mg/l to 1075 mg/l signifying 49.9 % removal efficiency. The high organic load may have been too much for the bamboo plants to bear and therefore may have resulted in non-optimal biological processes of organics and subsequent unfinished adapting process of the plants in the new media of constructed wetland system. However, the bamboo reactor performed well when compared to the control and it is possible that for such young plants, further retention time may further increase the removal efficiency. When compared to the results of some researchers it could be seen that 22 % removal efficiency was achieved when *Typha angustifolia* was used (Katsenovich et al. 2009), a 52 % BOD was achieved during the treatment of secondary wastewater, in Mexico, with *Typha latifolia* and *Phragmites australis* (Rivas et al. 2011). This is not to overrule the fact that other systems have been able to achieve very high BOD removal efficiencies of more than 85 % (Chang et al. 2012; Saeed et al. 2012; Abou-Elela et al. 2014).



Figure 4. Retention period for BOD removal

## **4. CONCLUSION**

This paper investigates the ability of a pilot scale bamboo constructed wetland system to treat wastewater from abattoir. Results show that under 28-day retention time, the bamboo constructed wetland system achieved up to 99.6 % phosphate removal, 98.5 % nitrate removal but performed poorly in the COD removal efficiency of about 39.3 % but fairly in the BOD removal efficiency of 49.9 %. This CWS could be used for field applications in urban areas if the number of bamboo shoots are increased in order to create a more effective root system.

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# **REMOVAL METHODS FOR INVASIVE SPECIES AMORPHA FRUTICOSA – EXAMPLE OF ODRANSKO POLJE**

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Abstract: Amorpha fruticosa is an invasive plant species that occurs in wide range of habitat types, including lowland floodplains. It grows very dense and changes the composition of communities by suppressing indigenous species, resulting in significantly reduced variety of flora in the area. In Odransko polje Amorpha fruticosa is widely spread. One of the tasks of Appropriate assessment of project "Flood protection system of Sisak area" was to determine the locations where material for embankment construction should be taken. The locations should be acceptable both from the aspect of nature protection and from the economic point of view (proximity to embankment due to lowering material transport costs, locations which are not private property, etc.). The locations where A. fruticosa is dominant plant were suggested for excavation. This paper will give overview of removal and disposal methods for this invasive species, which reduce the possibility of its spreading and reappearing. Also, positive impacts of using proposed locations for material excavation will be shown – decrease in A. fruticosa abundance, increase of habitat diversity, increase in the presence of target habitats and target species habitats etc. Additionally, good practices for selection of excavation sites will be given, including guidelines for their sanation and landscape design.

Keywords: Amorpha fruticosa, invasive species, Odransko polje, floodplains

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## **1. INTRODUCTION**

*A. fruticosa* L. (desert false indigo, false indigo-bush, bastard indigobush) is a deciduous shrub from the legume family (*Fabaceae*), usually 1-2 m high, but can grow up to 6 m. The leaves are pinnately compound, with 5-12 (sometimes up to 17) pairs of elliptical leaflets. The flowers build characteristic upright, thick, 10-15 cm long, dark petal wraps. *A. fruticosa* blossoms from April to June and attracts numerous pollinating insects with numerous noticeable flowers and nectar. After successful pollination and fertilization, a 6-9 mm long, glandular pod develops. In addition to seeds, the *A. fruticosa* spreads rapidly vegetative through stem shoots and root suckers (Nikolić et al. 2014).

*A. fruticosa* prefers medium-moist to moist soils, with a moderate amount of humus, moderately rich to rich in nitrogen. It is indicator of moderately acidic soils. It prefers areas directly exposed to sunlight and can only tolerate partial shading. It is prone to highly thermophilic habitats of almost sub-Mediterranean features. It occurs in semi-natural and natural habitats (Nikolić et al. 2014).

*A. fruticosa*, native to North America, was introduced into Europe in the 18th century as an ornamental plant and as a plant for soil stabilization (Nagy et al. 2018). It is also used as a hedge, whether for land delimitation or as a windshield. *A. fruticosa* is a highly appreciated honey plant, which honey is dark red color, translucent and of a pleasant taste, crystallizes slowly and contains 53 % sugar. Bees also collect large quantities of pollen, which is also highly appreciated (Kozuharova et al. 2017). As a honey plant, it has been reported in the literature by honey producers as '*A. fruticosa* pasture' (Nikolić et al. 2014). Shredded seeds are used as a spice while the stem is used for litter (Krpan et al. 2011). The stem parts have an insecticidal effect, so the plant is also used as a repellent (Kozuharova et al. 2017). From the above it can be seen that it is a plant with a wide range of possible uses (Jakovljević et al. 2015).

In Europe, it is considered an invasive species because it forms dense groups of plants in the area where it grows and adversely affects the development of native plant species and reduces biodiversity due to the easy germination of seeds, their easy spread (wind, water) and rapid growth (Novak & Novak 2018). A. fruticosa grows in very dense assemblages and reaches extremely high density on occupied surfaces and is almost the only species. It alters the composition of communities by aggressive penetration that slows development of

other plants (Horvat & Franjic 2016). In areas where it grows flora diversity declines dramatically, resulting in negative changes in overall biodiversity and other unwanted habitat changes (food chains, matter circulation etc.) (Horvat & Franjić 2016). It grows much faster than autochthone forest species, and overgrowth and congestion can lead to decay of young forest (Nikolić et al. 2014). Because of its rapid growth and high resilience, *A. fruticosa* has potential as a renewable energy source (Agroklub 2019, Krpan et al. 2011, Krpan et al. 2014).

In Croatia, it is most widely spread in the valleys of the Sava, Drava and Danube rivers, where it aggressively conquers forest areas, causing major problems with the natural regeneration of pedunculate oak and narrow-leafed ash forests (Jakovljević et al. 2015, Krpan et al. 2011). Problems occur where natural restoration has not been properly carried out and weed species emerge (Agroklub 2019). In addition to young forest plantations, it is common in floodplains, along riverbanks and roads.

Considering all the above, A. fruticosa is an example of a plant that causes multiple damage on the one hand and is successfully used on the other.

This paper will give overview of removal and disposal methods for this invasive species, which reduce the possibility of its spreading and re-appearing. Also, positive impacts of using proposed locations for material excavation will be shown – decrease in *A. fruticosa* abundance, increase of habitat diversity, increase in the presence of target habitats and target species habitats etc. Additionally, good practices for selection of excavation sites will be given, including guidelines for their sanation and landscape design.

#### 2. ODRANSKO POLJE

Odransko Polje is located on the right bank of the Sava River, between the towns of Velika Gorica and Sisak, about 30 km long and about 8 km wide. The river Odra forms the backbone of the hydrological-hydraulic regime of this area, on which the alluvial forests of pedunculate oaks and wet grasslands depend. The preserved wetland areas are located in the middle and lower reaches of the river and are characterized by great biodiversity. The left bank of Odra, Gornja Posavina, is covered by lowland wet grasslands and pastures - the natural habitat of horse Hrvatski posavac and Posavska goose, as well as endangered species that depend on the mowing of the grasslands and extensive livestock farming. On the right bank, Turopolje, in the forests of pedunculate oak there is a natural habitat for other autochthonous Croatian breed - Turopolje pig, as well as for white-tailed and lesser spotted eagles, and one of the richest areas in Croatia with amphibian and reptile fauna (Glasnović Horvat & Vizner 2011).

The flooding of the Odransko Polje occurs in the cold part of the year (November-April), when the high waters of Kupa enter the Odransko polje through the mouth of Odra near Sisak. As the height difference between the source and the mouth of the river Odra is less than 3 m and the riverbed is relatively shallow, water from the river flood the Odransko Polje (Vita projekt 2019).

There are several protected areas in this area - protected landscapes Turopoljski lug and Odransko Polje and ecological network areas HR2000415 Odransko Polje (Habitats directive site) and HR1000003 Turopolje (Birds directive site) (**Figure 1**). Native animal breeds are a significant value of the natural and cultural heritage of an area and have been maintained in the Odransko Polje thanks to traditional livestock farming, as an important branch of local economy. Traditional animal husbandry enables the maintenance of pastures and wet grasslands, which are habitats for numerous plant and animal species, and represents a special landscape feature of this region. All these are the reasons for declaring Odransko Polje a protected landscape (Općina Lekenik 2019).

As mentioned earlier, *A. fruticosa* is widespread in the valleys of large rivers in continental Croatia, and one of the areas with high representation is the Odransko Polje. According to the map of terrestrial non-forest habitats of the Republic of Croatia (2016), in the ecological network site HR1000003 Turopolje, *A. fruticosa* is spread on between 930.97 ha and 1.578,10 ha, which is between 4.65 % and 7.89 % surface of this area, while in the HR2000415 Odransko polje, *A. fruticosa* is spread on between 813.25 ha and 1.357,46, which is between 5.92 % and 9.88 % surface of the area (**Figure 2**).

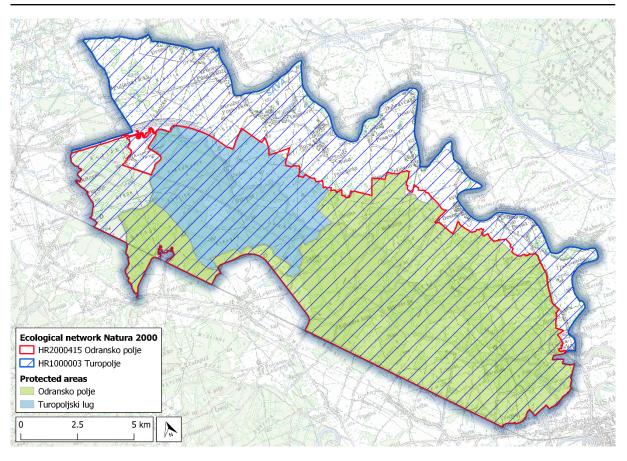


Figure 1. Protected areas and ecological network areas in Odransko polje

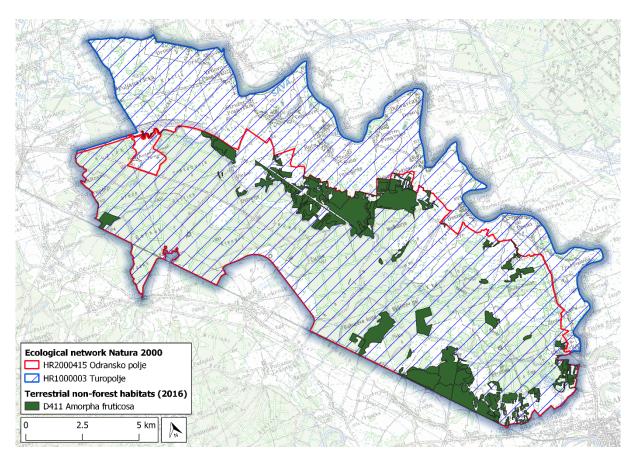


Figure 2. Areas with Amorpha A. fruticosa in Odransko polje

## **3. SISAK AREA FLOOD PROTECTION SYSTEM**

The construction of the Sisak area flood protection system is part of a larger flood protection project in the Kupa River basin - Karlovac-Sisak area flood protection. The flood protection system of the Sisak area is based on the construction and reconstruction of embankments, revetments and walls along the Kupa River and the embankment in Odransko Polje. This project will protect settlements along the Kupa River from flood waters of Kupa and settlements along the edge of the Odransko Polje area from flood waters of the Odra. **Figure 3** shows the planned embankments in Odransko Polje. The concept of flood protection of areas along the edge of Odransko Polje is based on "enclosing" the Odransko polje with embankments, while the natural regime of flooding will not change and existing hydrological conditions will be maintained, which will enable the survival of the oak forests and wet grasslands.

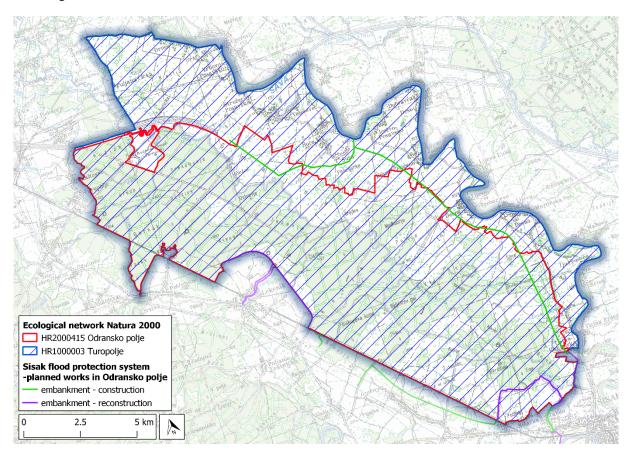


Figure 3. Planned works in Odransko polje

## 4. BORROW PITS

Planned works in Odransko Polje includes construction of about 29 km of embankment and the reconstruction of another 18 km, which requires large quantities of construction material. During the Appropriate assessment of project "Sisak area flood protection system" (2019), the locations of borrow pits that are acceptable from the aspect of nature protection were determined. When proposing and selecting locations, the conditions were set that needed to be met to the maximum extent possible: a) borrow pit should be near construction / reconstruction of the embankment site in order to reduce the cost of transporting the material; b) site locations are owned by the Republic of Croatia in order to reduce land acquisition costs and c) *A. fruticosa* is dominant plant on borrow pits locations.

The use of locations where *A. fruticosa* is present reduces the total area in the Odransko polje where this species is represented. In addition to the positive impact of reduction of *A. fruticosa* spread area, adequate borrow pit design after exploitation of the soil material creates new areas of subnatural habitat types, thus increasing the habitat area suitable for many animal species (invertebrates, amphibians, reptiles, birds). Exploitation of material will result in small depression, which will be filled with precipitation and ground water and small water bodies will be formed. Since the Odransko polje is a natural floodplain where species typical for wet habitats occur, the new water bodies will ideally blend in there. Adequate design of these depressions, as well as forbidding their use for fishing purposes, creates new aquatic and wetland habitats that will allow greater biodiversity of the area.

## 5. A. FRUTICOSA REMOVAL AND DISPOSAL

In order to create the desired habitat conditions at the borrow pits locations, and to prevent the spread of A. *fruticosa* to locations of embankment construction / reconstruction, special attention should be paid to the following:

a) *A. fruticosa* and surface soil layer removal and disposal - Blagojević et al. (2015) state that the quantity of *A. fruticosa* seeds in the soil decreases with the depth and that at a depth of more than 30 cm the quantity of seeds is negligible (Blagojević et al. 2015). Since *A. fruticosa* is very successfully vegetative propagated, in order to prevent its spread and regrowth, residues of plant material (trunks, branches, roots) should be adequately disposed in a safe place after removal (Nikolić et al. 2014). The material can be burned, chopped small, and it can also be deposited in borrow pits and then covered with soil material 1.5 m thick that does not contain parts of the plant. After removal of the overground part of plant and its root, it is also necessary to remove a surface soil layer of at least 0.5 m thickness, in order to reach soil material that will be used for construction / reconstruction of the embankment, which does not contain the seed of the plant. This removed soil layer can also be deposited in the borrow pits and, like the previously removed parts of the plant, covered with uncontaminated soil material. *A. fruticosa* is plant with negative allelopathic potential (Novak et al. 2018). It contains allelochemicals which may be decomposed or transformed in the soil and may have influence on germination and growth of different species. This is also reason why it is necessary to remove at least 0.5 m of surface soil layer, as this will also remove allelochemicals that may have negative impact on plants that are planned to be planted at the edges of borrow pit.

b) Excavating and transporting soil material for embankments - before loading and transporting materials, vehicles and equipment must be thoroughly cleaned and washed to prevent transposal of plant material remains. Also, before excavating material, it is necessary to thoroughly inspect the surface of the site and remove any plant remains. This will reduce the risk of the plant material being transposal to new locations.

c) Borrow pits design - in order to create new subnatural habitats that will increase the biodiversity of the area and provide habitat for many native plant and animal species, the site needs to be design for this purpose. Borrow pits should have irregular shape and irregular surface of the bottom, with as much indentation as possible, slight slopes (1: 3 to 1:20) of terraced form with gradual transitions to deeper parts and, if possible, small islands. Autochthones alluvial forest and marsh vegetation should be planted along the site, which will stabilize the edge of borrow pit and prevent erosion (e.g. *Salix* sp., *Populus nigra, Alnus glutinosa, Alnus incana, Ulmus minor, Ulmus laevis, Fraxinus angustifolia, Carex* sp., *Phragmites* sp.) This will also contribute significantly to the quality of the habitat, as riparian vegetation is extremely important for species depended on aquatic habitats (shelters, feeding sites and hatcheries of many species are found here). At the highest edges of borrow pit and in area adjacent to the site, it is recommended to form a forest belt with alluvial species. This will allow the development of multiple layers of riparian vegetation, each representing an important micro-habitat for many animal species (Institut IGH d.d. 2016).

## 6. EXAMPLES OF BORROW PITS DESIGNS

Below are 2 examples of borrow pits design that have a positive impact on the biodiversity of the area.

## 6.1. Borrow pit in Odransko polje near Desna Martinska Ves settlement

At the site about 2.5 km south of the settlement Desna Martinska Ves, the soil material was excavated about 15 years ago. Depression of irregular shape with different slopes was formed, in which water is present all year (the site dried up only in years with below average rainfall). In addition to the design of the borrow pit shape, no further work was taken, but with this little effort, an area of significant biodiversity was created. The presence of dragonflies, numerous other invertebrates and several species of amphibians was recorded here during location visit in July 2019. This area is regularly flooded in spring, when several fish species migrate from Sava, Kupa and Odra river in flooded areas where depressions like this are used as spawning site (e.g. *Leuciscus aspius, Abramis brama, Leuciscus idus, Chondrostorma nasus* and *Vimba vimba*) (Vita projekt d.o.o., 2019). Figure 4 shows the current look of the site. Unfortunately, the problem of *A. fruticosa* spread is also present in this area and it is significantly represented north of borrow pit.



Figure 4. Borrow pit near Desna Martinska Ves settlement

## 6.2. A14 Cambridge to Huntingdon

The construction of the A14 highway between the cities of Cambridge and Huntingdon is a major road project in England. The project includes construction of a new highway and widening and upgrading of an existing road in length of 34 km. About 5,000,000 m<sup>3</sup> of soil material was needed for construction and the proposed borrow pits locations were located near the new highway route. Six sites of borrow pits have been selected and their design with main objective of increasing the biodiversity of area after exploitation is planned. The entire area along the planned highway route is characterized by a mosaic of agricultural land, with a small area of forest and aquatic habitats. In borrow pits design projects, the following conditions were set that needed to be met to the maximum extent possible: create several habitat types that will increase number of species in area and increase the biodiversity of the area; create connected corridors of habitats such as shrubs that will allow the movement of animal species across a wider area; integrate borrow pits into a wider landscape; enable use of the sites for recreational purposes (emphasis on non-intensive use, with only paths and benches); integrate borrow pits in function of flood retention where possible, etc.

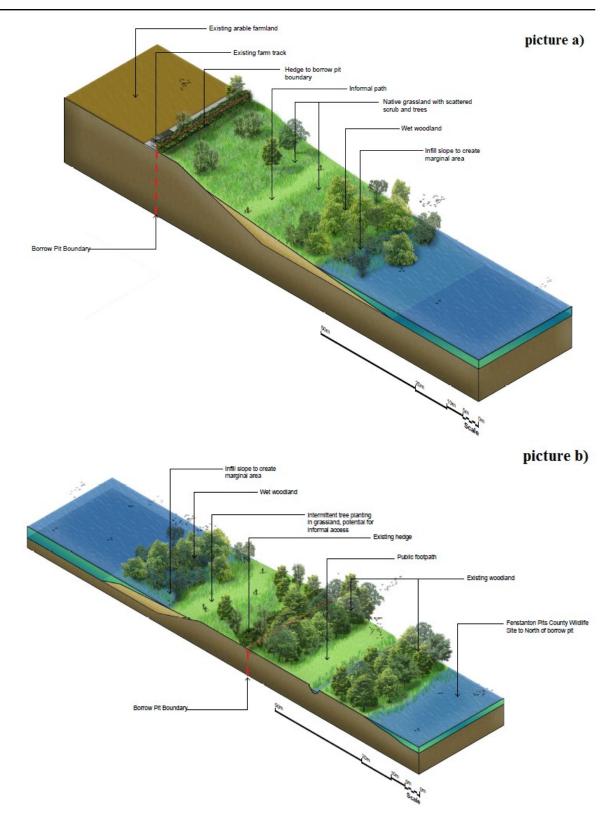
In borrow pits designs, care was taken to minimize slopes (slope up to 1:20), which will allow the development of wetland vegetation and the gradual transition from aquatic habitat to terrestrial, and thus greater diversity of micro-habitats. Also, care was taken to ensure that the locations were as protected as possible from noise and disturbing from highway (trees zone), as well as to prevent animals from getting on the road.

**Figure 5** shows borrow pit no. 1 before exploitation and visualization of the site after its design, while **Figure 6** shows cross-sections of the coastal area on newly formed water bodies. From the figures can be seen that the formation of several irregular-shaped water bodies with partially developed riparian vegetation is planned. Compared to the current state, where agricultural land and very small areas of forest vegetation is present, habitat diversity will be increased and increase in animal species number and biodiversity can be expected (Highways England 2015).





*Figure 5.* Borrow pit no. 1 (a – before exploitation, b – borrow pit design) (Highways England 2015)



*Figure 6.* Cross-sections of the coastal area on newly formed water bodies (a – one costal area, b – two costal area) (Highways England 2015)

### 7. CONCLUSION

Borrow pits are necessary for the construction of infrastructural projects such as roads or embankments for flood protection. Borrow pits locations should preferably be located near construction sites to minimize the cost of transporting materials. In addition to meeting the economic requirements of reducing the cost of construction, site locations can also be designed to increase the biodiversity of area. This applies in particular to cases of embankment construction in alluvial plains, where often borrow pits are converted to new water bodies after the material has been exploited.

In this paper, using the example of the Odransko Polje, where the construction and reconstruction of the embankment is planned, and where the invasive plant species A. fruticosa is a major problem, it is shown that by carefully selecting the locations of borrow pits, as well as planning their design after exploitation, it is possible to achieve multiple benefits for biodiversity of the area - reduce A. fruticosa spread area and increase the area of quality habitats for a large number of animal species. Two examples from Croatia and England are also presented where borrow pits have been designed to increase the biodiversity of the area. Water bodies are important habitats for large numbers of invertebrates, amphibians, reptiles, mammals such as beavers and otters, birds who use them as resting, nesting and wintering areas, and also for a variety of plants. As the wider area of the Odransko Polje is protected in the category of protected landscape, and two ecological network areas are present here, the anticipated positive impacts on biodiversity are even more significant.

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# EMISSION OF FINE PARTICLES (PM<sub>2.5</sub>) FROM RESIDENTIAL BIOMASS COMBUSTION IN CROATIA AND HOW TO REDUCE IT

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**Abstract:** Wood burning in residential appliances is very represented in the Republic of Croatia. It is a main or an additional form of heating for many households in rural and urban areas and is therefore an important source of air pollution. The choice of energy and the combustion appliance used in home have a significant impact on PM<sub>2.5</sub> emissions. The paper informs the reader about PM<sub>2.5</sub> emissions, their main sources and impacts on human health, environment, climate, air quality, and the reason why PM<sub>2.5</sub> emissions from residential wood burning are harmful. Paper also gives an overview of spatial PM<sub>2.5</sub> emission distribution in Croatia, their five air quality zones and four agglomerations. The paper analyses the sources and their contribution to PM<sub>2.5</sub> emissions with the relevance of PM<sub>2.5</sub> emissions from residential plants, the use of fuels in residential plants and their contribution to PM<sub>2.5</sub> emissions and PM<sub>2.5</sub> emissions and PM<sub>2.5</sub> emissions by fuel combustion technologies in residential sector. Appropriate strategies, policies, and actions to reduce the impact of residential biomass (wood) burning on the environment, air quality and human health are considered.

Keywords: air pollution, spatial emission distribution, combustion impact, environmental protection strategy, air quality zones

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#### **1. INTRODUCTION**

In the Republic of Croatia, the wood consumption in residential sector is a main source of energy use for space heating, cooking, and water heating. Therefore, the residential biomass combustion is estimated as a key source of fine particles (PM<sub>2.5</sub>) emissions in Croatia (Ministry of Environment and Energy 2019). This paper considers primary particulate matter emissions data from the anthropogenic sources. For performed analysis, the main source of data is Croatian national emission inventory. The biomass (fuelwood) is a renewable source of energy that has advantage regarding climate (European Biomass Industry Association 2019). In theory, the combustion of biomass considers a sustainable CO<sub>2</sub> neutral source of energy (European Commission 2003; IPPC 2006). In reality, the carbon dioxide is emitted when burning wood but it the fact is that this carbon was taken up by the tree from the air during its growing and this part of the emissions is considering as carbon-neutral (Leturcq 2014; World Bioenergy Association 2012).

Burning wood at home appliances is in generally under non-optimal operating conditions (e.g. with low efficiency fireplaces and stoves, poor fuel quality, bad burn practises, lacking proper maintenance of fireplaces and stoves) which results with significant emissions of air pollutants and particularly PM<sub>2.5</sub>. The combustion of the fuel wood in small appliances is incomplete which result with many times greater emissions that in bigger plants (European Environment Agency 2016).

Rising energy prices of natural gas and electricity, and in some extend, poor financial situation of many Croatian citizens leads to the bigger use of biomass as a residential fuel. This result in negative impacts on air quality, human health, environment, climate, and visibility. To minimize the negative impact of fuelwood combustion in residential sector and to reduce the PM<sub>2.5</sub> emissions joint actions on global, national, regional, local, and home level are required.

#### 2. PM<sub>2.5</sub> EMISSIONS, SOURCES, AND IMPACTS

Particulate matter (PM) is a widespread air pollutant, consisting of a mixture of solid and liquid particles suspended in the air. The mass concentration of particles with a diameter of less than 10  $\mu$ m (PM<sub>10</sub>) and particles with diameter less than 2.5  $\mu$ m (PM<sub>2.5</sub>) is commonly used indicator for describing PM that are relevant to health (World Health organization 2013).

Emissions of PM<sub>2.5</sub> originate from a variety of anthropogenic i.e. made by human and natural activities and may be directly emitted ("primary PM") or formed in the atmosphere ("secondary PM"). Primary emissions of PM can exist as solid or liquid matter (the "filterable" portion) or as gases (the "condensable" portion). The sources

of primary anthropogenic PM<sub>2.5</sub> emissions (see figure 1) may be point, area, line, and fugitive ones. Activities from which are primary anthropogenic PM<sub>2.5</sub> emissions originate include wood (biomass) and fossil fuel combustion, building construction and demolition, quarrying and mining, vehicle tyre and break wear, road abrasion, and agricultural activities. Natural sources such as forest fires and volcanos may have local and global impact on environment, climate, air quality and human health in respect of PM pollution. Secondary PM formed by physical and chemical reactions from other pollutants (SOx, NOx, VOCs, NH<sub>3</sub>) called precursors. Secondary PM can be formed at locations distant from the sources that release the precursor gases.

Impacts of PM<sub>2.5</sub> emissions are various. The particle pollution can causes adverse health effects like: coughing or difficulty breathing, increase the risk of asthma attack, heart attack, decreased lung function, causes premature death and decreasing the air quality (outdoor and indoor) (American Lung Association 2019, Doctors and Scientists Against Wood Smoke Pollution 2019, World Health Organisation 2018).

It has negative impact on the climate in many ways: wood smoke (PM) absorbs sunlight, impacts on cloud formation and precipitation as well as deposition on ice surfaces. As particles from wood burning are transported over large distances, they also harm sensitive ecosystems, such as the arctic that are far away from the initial sources of pollution (Deutsche Umwelthilfe 2016).

Fine particles (PM<sub>2.5</sub>) are the main cause a deterioration of visibility, environmental damage, and damage of materials (United States Environmental Protection Agency 2018). Environmental damage with PM manifests as ecosystem degradation, depleting the nutrients in soil, damaging sensitive forests, damaging farm crops, affecting diversity of ecosystems, contributing to acid rain effects, and affecting animal health and productivity. Deposition of PM causes damage of materials like stain and damage of stone and other materials, like culturally and historically important objects such as statues, monuments, and buildings.

Figure 1 shows various sources of PM<sub>2.5</sub> emissions and their multiple impacts i.e. adverse effects.

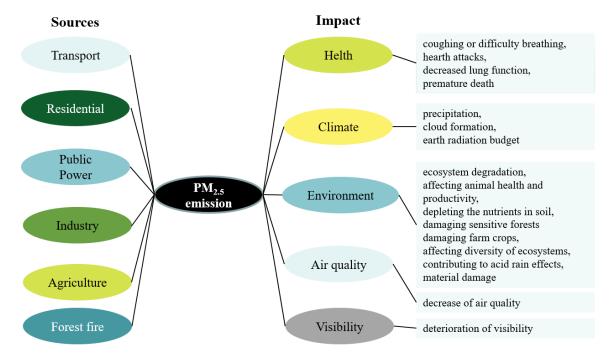


Figure 1. Sources and impacts of PM<sub>2.5</sub> emissions

Biomass (wood) burn is considered to have neutral impact on  $CO_2$  emissions (carbon neutral) and on the other hand is a cause of air pollution in urban and rural areas (**Figure 2**). Carbon neutral theory for wood burning (World Bioenergy Association 2012) stems from theory that trees assimilate the same amount of  $CO_2$  throughout their lifetime as the amount released when burning the wood at home. However, even if the wood burning is considered as the carbon neutral, the truth is that it is not climate neutral if biomass is used not sustainably and that there are reasons for be concern about the fact that wood is widely used energy in residential sector.

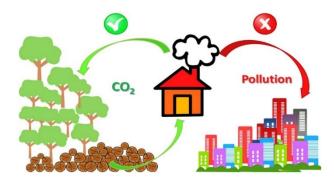


Figure 2. Impact of biomass (wood) burn on  $CO_2$  and air pollutants emissions (Cincinelli et al. 2019)

Reasons for being concern about residential wood combustion are the impact on ambient air pollution and health, the climate policy, and economic hardship that usually leading to fuel switching. Its negative impact on ambient air pollution and health can be found in many studies (e.g. Caseiro et al. 2009; Chen et al. 2012; Crilley et al. 2015; Hellen et al. 2008; Herich et al. 2014; Naeher et al. 2007; Pascal et al. 2013; Saarikoski et al. 2008; Saarnio et al. 2012).

Exceedances of the EU's air quality limit values are still one of the major environmental problem in EU. For 2015 up to 8 % of the urban population was exposed to concentrations above the EU limit value of 25  $\mu$ g/m<sup>3</sup> for fine particulate matter (PM<sub>2.5</sub>), and more than 82% to levels above the much stricter WHO guideline value of 10  $\mu$ g/m<sup>3</sup> (European Commission 2019).

According to Chafe (2015) combustion of wood in residential areas and often under cold, calm meteorological conditions can lead to high exposure compared to other pollution sources, owing to the principle of intake fraction (the proportion of a released material that is inhaled by humans) (Figure 3).

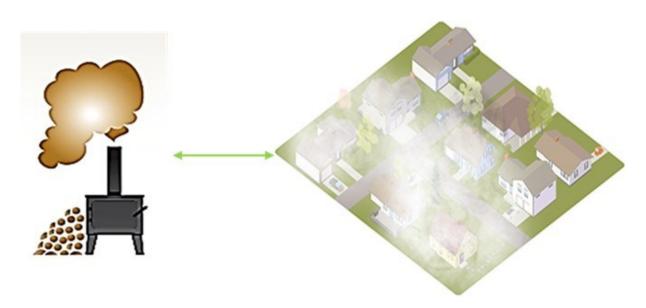


Figure 3. Residential biomass (wood) combustion as source of fine particle pollution (Doctors and Scientists Against Wood Smoke Pollution 2019)

Burning wood in homes produces more neighbourhood-level particulate matter pollution than using electricity, natural gas, or liquid fuels for heating, and effecting on ambient air quality (Chafe 2015). WHO also reported that, in 2012, 3.7 million premature deaths occurred due to exposure to outdoor (ambient) particulate air pollution, including 482,000 in Europe and 94,000 in Canada and the United States, and that residential wood combustion is a contributor to mentioned outdoor air pollution (World Health Organisation 2014).

The reason why PM pollution from burning wood in homes is harmful for humans lay down at the fact that fine particles (PM<sub>2.5</sub>) have a small diameter and are able to inhale by humans and income deeply into the respiratory tract, reaching the lungs, blood and can get embedded in organs (**Figure 4**).

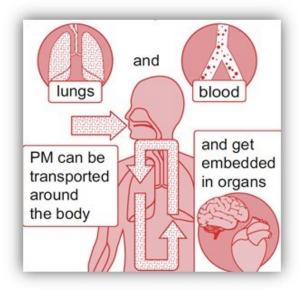


Figure 4. Impact of fine particles PM<sub>2.5</sub> when inhaled by humans (Department for Environment, Food & Rural Affairs 2019)

Another reason for concern comes from the climate and energy policies. Biomass fuels were included in the European Commission's strategy for reaching the "20-20-20" targets (20 % reduction in greenhouse gas emissions, 20% of final energy consumption from renewable energy and 20 % increase in energy efficiency by 2020) (European Commission 2010). However, it has been evidenced that climate-oriented policies may not always work in line with air quality-oriented policies, and vice-versa. Residential heating with wood is encouraging in many European countries and touted as a renewable fuel that can assist with climate change mitigation, contribute to energy security, and contribute to the alleviation of energy poverty (e.g. International Energy Agency 2013, Kyprianou et al. 2019, Levander & Bodin 2014, Ofgem 2014). Due to government incentives and subsidies, the increasing costs of other energy sources and the public perception that it is a "green" option, the presence of residential wood combustion is still high and rising in some countries (Chafe 2015).

Poor economic situation, energy poverty and affordability that consequently leads to fuel switching in homes from e.g. natural gas to fuel wood, wood waste or from electricity to fossil fuels or fuel wood is also reason for concern (Saffari et al. 2013).

Burning conditions of residential wood combustion are often inefficient due to incomplete combustion and there are often no household-level emissions controls for PM or regulations as is the case with emissions from transport, industry and power plants that are already controlled or legislation is in place to their reduction. Therefore, wood stoves even that with eco designed emit more fine particulates (PM<sub>2.5</sub>) than most diesel vehicles. **Figure 5** shows comparison of estimated PM emission rates from a 5kW stove (g/h) compared to typical exhaust PM emissions (g/h) from different Euro standards diesel road vehicles based on emissions limits (Air Quality Expert Group (UK) 2017). According to comparison made by (Air Quality Expert Group (UK) 2017), it can be concluded that one conventional wood fired stove emits PM like 40 diesel passenger cars (EURO 5/6) and approximately 13 new heavy duty vehicles (Euro IV) (**Figure 5**). They also find out that one eco-designed wood fired stove emits PM like 18 diesel passenger cars (EURO 5/6).

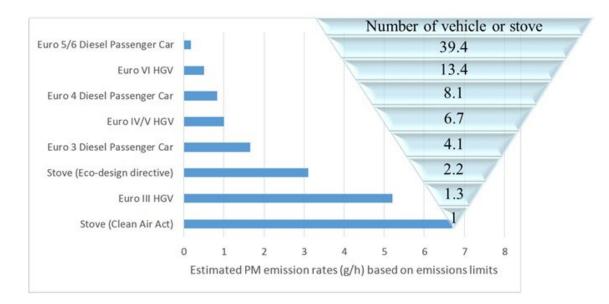


Figure 5. PM emissions from 5 kW wood stove (g/h) compared to exhaust PM emissions (g/h) from diesel vehicles (Air Quality Expert Group (UK) 2017)

# 3. USE OF BIOMASS (WOOD) IN RESIDENTIAL COMBUSTION AS A SOURCE OF AIR POLLUTION WITH $\rm PM_{2.5}$ IN CROATIA

The source that is contributing most to PM<sub>2.5</sub> emissions in Croatia, is a Small combustion (**Figure 6**). Within the Small combustion installations activities that are considered to have a thermal capacity  $\leq 50$  MW<sub>th</sub>, a Residential sector has a domination regarding PM<sub>2.5</sub> emissions in Croatia during the history and nowadays (**Figure** 7). In 1990, the Small combustion was responsible for 75 % of PM<sub>2.5</sub> emissions in Croatia. The Industry represented only 10 %, and all other sources 15 % of PM<sub>2.5</sub> emissions in Croatia in 1990. The Off-road transport and Road transport were responsible for 5 % and 3 % of total PM<sub>2.5</sub> emissions in Croatia in 1990. There has been little change over 27 years, so in 2017, the Small combustion was responsible for 68 % of total PM<sub>2.5</sub> emissions, while the Road transport accounted for 9 % (that is an increasement of approx. 13 %) and Industry 8 % (that is a decrease of approx. 64 %) in Croatia.

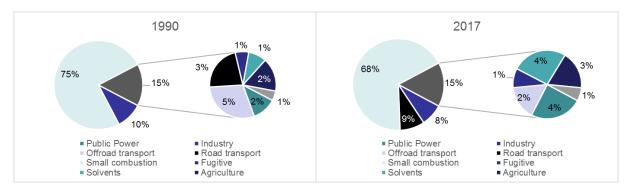


Figure 6. Emissions of PM<sub>2.5</sub> in Croatia, 1990 and 2017 (CEIP - EMEP Inventory files NFR for Croatia 2019)

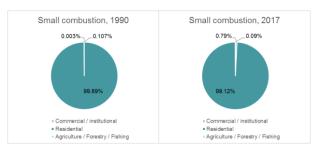


Figure 7. Relevance of residential plants on PM<sub>2.5</sub> emissions in Croatia, 1990 and 2017 (CEIP - EMEP Inventory files NFR for Croatia 2019)

In the Republic of Croatia, there is a biomass (wood) domination in residential stationary fuel consumption both now and in the 90's. Since 1990 a total energy consumption in residential sector in 2017 has increased by 2 %. The use of solid fuels (coal) and liquid fuels have decreased by 97 % and 63 % respectively in the observed period, while the use of natural gas and biomass have increased by 144 % (approx. by 2.44 times) and 8 % respectively (**Figure 8**).

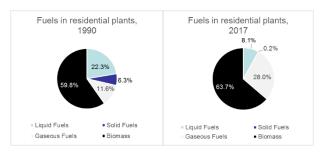


Figure 8. Fuel consumption (PJ) in residential plants in Croatia, 1990 and 2017 (CEIP - EMEP Inventory files NFR for Croatia 2019)

In residential sector a variety of fuel combustion technologies are applied. Emissions of PM<sub>2.5</sub> from residential combustion appliances are function of fuel combustion technology type and fuel type (**Figure 9**) but as well of fuel quality, operational practices, and maintenance. Figure 9 shows that the most polluting appliance is open fire fireplaces burning wood, following by wood fired conventional stoves. The less polluting residential combustion appliances in respect of PM<sub>2.5</sub> emissions are gas fired boilers, following by liquid fired boilers, fireplaces on natural gas and pellet stoves. By comparison of PM<sub>2.5</sub> emissions characteristic for each residential heating appliance type provided by EMEP/EEA Guidebook 2016 (European Environment Agency 2016), it can be stated that that the PM<sub>2.5</sub> emissions from one open fire fireplace are equivalent to the emissions of approximately 4100 natural gas fired boilers, 28 pellet stoves or 9 modern advanced/ecolabelled stoves/boilers burning wood. From the above it follows that significant air quality benefits can be expected by changing fuel from wood to natural gas or by replacement of an old conventional stove with new efficient appliance or modern pallet system.

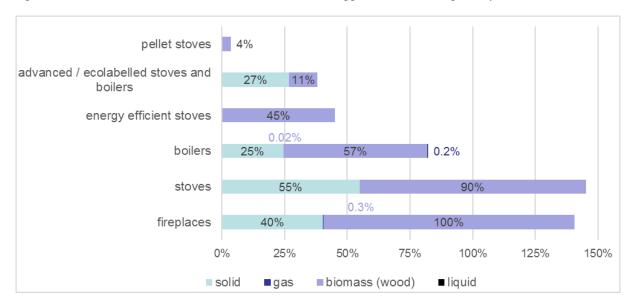


Figure 9. Relative  $PM_{2.5}$  emissions by type of residential plants (100% = 820 g/GJ) (European Environment Agency 2016)

### 4. SPATIAL DISTRIBUTION OF PM2.5 EMISSIONS IN CROATIA

EKONERG Ltd. has developed a model to distribute emissions from the national emission inventories on an EMEP grid, resolution  $0.1^{\circ} \times 0.1^{\circ}$  (longitude, latitude) in a geographic coordinate system (WGS84)  $\approx 7 \text{ km} \times 7 \text{ km}$ . The model is covering the Croatian land and sea territory along with Croatian 5 Air quality zones and on an EMEP grid, resolution 0.5 km x 0.5 km (longitude, latitude) covering the Croatian 4 agglomerations. Zones and agglomerations were set according to the Regulation determining zones and agglomerations according to levels of air pollution on Croatian territory (Official Gazette 1/2014-24). The new spatial high-resolution distribution model for emissions to air (EKOREGIS) has been developed according to the requirements for reporting of gridded

emissions to the EMEP/EEA guidance. The results of this model are spatial emissions data that are an input for the air quality modelling, which is an input for assessment of atmospheric concentrations and deposition. The results of model assessments inform national and international policies used to improve the environment and human health (Official Gazette 1/2014-24). EKOREGIS is developed to generate improved quality of spatial emission data for use in air quality modelling in assessing the existing air quality situation, air quality forecasting, air quality planning, source apportionment and air pollution exposure studies. EKOREGIS includes emission distributions for each of NFR and SNAP source category in the Croatian inventory system: stationary combustion, mobile sources, fugitive emissions, industrial processes and product use, agriculture, waste, forest fires. The results of the model EKOREGIS are available at: https://emep.haop.hr/.

In Croatia there are three main climatic regions continental, central (mountain) and costal (maritime). These three climatic regions are conditioned with an extremely varied relief with three main types: lowland Pannonian, mountainous Dinaric and coastal Adriatic. The central part of Croatia is the coolest one with the mountain climate and the continental part is with the continental climate that is slightly milder than in the central part. The coastal part of Croatia has mild Mediterranean climate. The last digital Köppen-Geiger climate classification at an unprecedented 1-km resolution for the present-day (1980–2016) (Beck et al. 2018) for Croatia is available at https://commons.wikimedia.org/wiki/File:Koppen-Geiger\_Map\_HRV\_present.sv. This climatic classification was used as one of variables for spatial distribution of PM<sub>2.5</sub> emissions at the Croatia (Figure 10). Areas where the most of national PM<sub>2.5</sub> emissions are allocated, are at the continental and central part of Croatia, and at the most populated urban areas - big cities. The coastal part of Croatia is the area where the less of PM<sub>2.5</sub> emissions are allocated, with exception of the big cities.

Figure 11 shows  $PM_{2.5}$  gridded emissions by 5 Croatian air quality zones. These maps cover the total national  $PM_{2.5}$  emissions without  $PM_{2.5}$  emissions for four agglomerations.

Figure 12 shows  $PM_{2.5}$  gridded emissions by four Croatian agglomerations in resolution 0.5 km x 0.5 km (longitude, latitude) created at the base of EMEP grid.

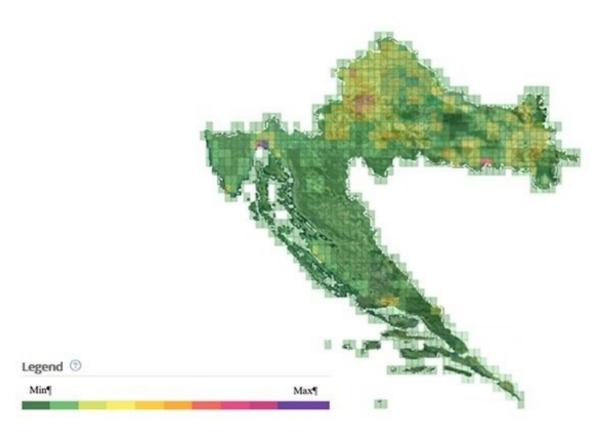
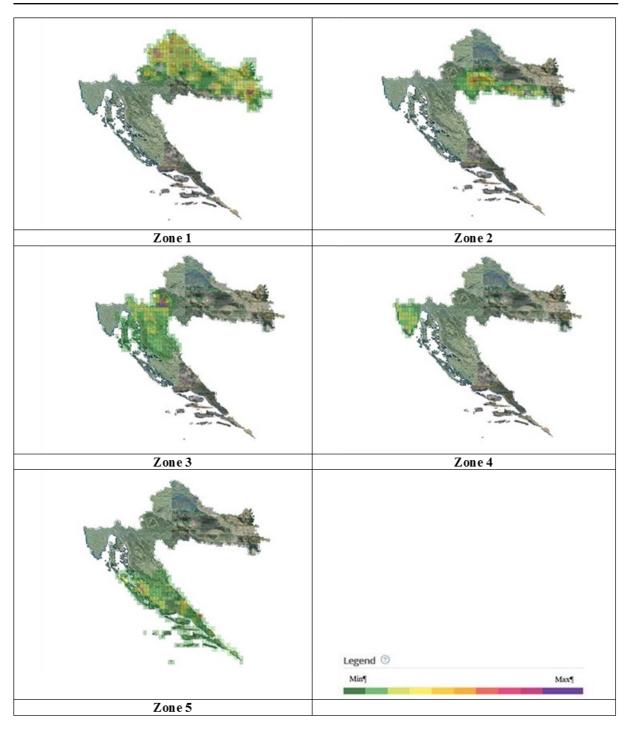


Figure 10. Spatial distribution of PM<sub>2.5</sub> emissions in Croatia, 2015 (Ministry of Environment and Energy 2018)



*Figure 11.* Spatial distribution of PM<sub>2.5</sub> emissions in Croatia by air quality zones, 2015 (*Ministry of Environment and Energy 2018*)

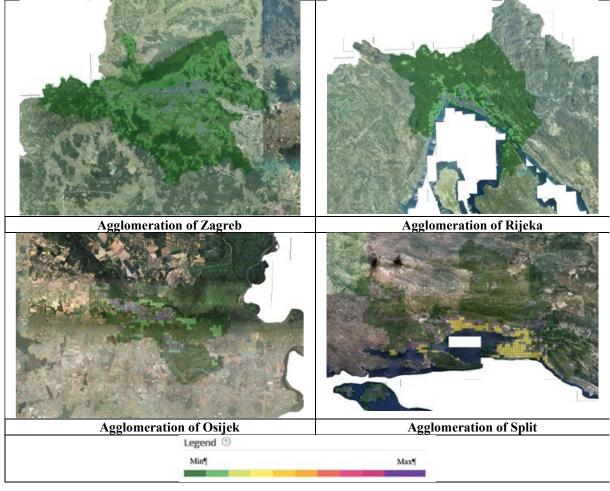


Figure 12. Spatial distribution of PM<sub>2.5</sub> emissions in Croatia by agglomerations, 2015 (Ministry of Environment and Energy 2018)

### 5. HOW CAN PM<sub>2.5</sub> EMISSIONS FROM RESIDENTIAL WOOD STOVES BE REDUCED

For  $PM_{2.5}$  emissions reduction from residential wood stoves requires joint actions on global, national, regional, local and home level.

Global actions are taking on EU level trough the National Emission Ceilings Directive (NEC Directive) (Directive (EU) 2016/2284) and Ecodesign Directive (Directive 2009/125/EC). NEC Directive establishes the emission reduction commitments for the Member States' certain anthropogenic atmospheric emissions including fine particulate matter ( $PM_{2.5}$ ). Ecodesign Directive establishing a framework for the setting of ecodesign requirements for energy-related products is implemented with two Regulations that define ecodesign requirements on solid fuel stoves (Commission Regulation 2015/1185) and boilers (Commission Regulation 2015/1189). Ecodesign requirements will enter into force in 2020 for boilers and in 2022 for solid fuel local space heaters that will also assist in tackling emissions of PM. Ecodesign requirements are defined for seasonal space heating energy efficiency and for emissions of particulate matter (PM), organic gaseous compounds (OGCs), carbon monoxide (CO) and nitrogen oxides (NOx).

National/regional/local policy and actions that can reduce the impact of  $PM_{2.5}$  emissions from domestic wood burning are addressed to fuel switching, technology exchange and educational efforts addressing burning practice. National/regional/local authority can support fuel switching from wood to cleaner fuels (e.g. natural gas or electricity), support replacement of old stoves with new ones with eco-labels or high efficiency, support pellet systems, introducing of district heating and public education programs. Objectives of educational campaigns and programmes can be addressed to promote responsible wood burning appliances but without encouraging of more wood burning, educate wood burning users on what and how they burn and on haw is that connect with the impact on their health and environment, promote energy efficiency and savings.

Home individual actions are harmonized with national, regional, and/or local policy and actions. Using cleaner energy (e.g. gas, electricity), replacing of old wood stove with ecodesigned and efficient new one or replacing it with pallets system, regularly maintaining the heating appliance and chimney by a competent person and personal education on wise burning wood, will all contribute to PM<sub>2.5</sub> emission reductions, improve local air quality regarding PM<sub>2.5</sub> concentrations and minimize its negative impact on health.

### 6. CONCLUSION

Residential combustion of biomass (wood) is major source of fine particulate matter  $PM_{2.5}$  emissions in Croatia. For  $PM_{2.5}$  emission reduction from residential biomass (wood) stoves requires joint action by decision makers and residents. To protect health and environment, there is a need for policymakers in areas that have relatively high levels of outdoor air pollution from household heating-related combustion to provide incentives to switch from biomass to gas- or electricity-based for heating or to provide incentives for replacement of old stoves on wood with new ones with lower  $PM_{2.5}$  emissions (EC).

When assessing the environmental impact of the operation (e.g. road construction, construction of transport facilities, construction of buildings, etc.) in areas with poor air quality with respect to  $PM_{2.5}$ , measures should be consider to prevent additional ambient air pollution with  $PM_{2.5}$ .

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# DEVELOPMENT AND ASSESSMENT OF DEVELOPMENT STRATEGY ALTERNATIVES IN STRATEGIC ENVIRONMENTAL ASSESSMENT

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**Abstract:** Development and evaluation of alternatives is a key process in the strategic environmental assessment (SEA), which enables improvement of the environment, informed decision-making, greater transparency and better opportunities for public participation. It is also the most challenging part of the assessment, because the alternatives are often avoided or considered to the extent to meet the legal requirements. The absence of alternatives in the assessment process significantly diminishes the contribution of SEA to the environmental protection system. The paper will outline the generally applicable methodology for the development and assessment of alternatives in the SEA process, on the example of the Development Strategy of the City of Solin, which is based on the development of the environmental alternative, which significantly contributes to the development of sustainable strategic solutions.

Keywords: strategic assessment alternatives, environmental alternative, environmental assessment, environmental report

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### **1. INTRODUCTION**

The Strategic Environmental Assessment (hereinafter referred to as SEA) is an analytical instrument, which through the integration of environmental protection requirements into the strategies, plans and programmes of a particular area, forms the basis for promoting sustainable development (Environmental Protection Act, Official Gazette 2013., 2015., 2018.a and 2018.b). Since the concept of sustainability is a critique of current policy-making practices and trends (strategies, plans and programmes), in its essence it entails the obligation to create alternatives that in the long term will be more sustainable and attractive to preserve ecological stability, and ultimately the well-being of people (González et al. 2018). The obligation to identify, describe and evaluate the likely significant impacts of reasonable alternatives of a strategy, plan and program on the environment is also legally regulated through the Regulation on strategic environmental impact assessment of the strategy, plan and programme (OG of the Republic of Croatia 3/17) as well as the Strategic Environmental Assessment Directive (Directive 2001/42 / EC).

The Guidelines on the Developing and Assessing Alternatives in Strategic Environmental Assessment (González et al. 2018) establish it as the key process in the environmental impact assessment, which is iterative and starts already in the scoping phase (Figure 1).

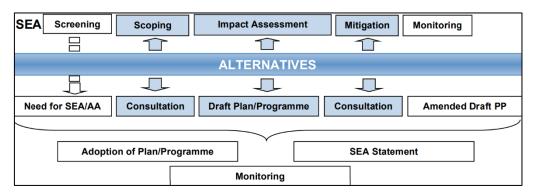


Figure 1. Consideration of alternatives during particular stages of the SEA procedure (González et al. 2018)

The purpose of development and evaluation of alternatives is to find the most sustainable approach to meeting the objectives of the strategy, plan or program proposal, which is done in two ways: by maximizing the benefits for the environment, and by reducing or avoiding a potentially significant negative impact generated by the implementation of the documents under assessment (DEAT 2004).

Only by the development and comparison of alternatives can the information about the likely impacts be obtained that will enable decision-makers to determine which would be the most acceptable (optimal) way of achieving strategic goals by making trade-offs between biophysical, social, economic, historical, cultural and political factors, thereby achieving sound decision-making based on the principles of sustainable development (DEAT 2004).

Moreover, documenting the impacts of all variants and decision-making processes leads to the acknowledgement that policy decisions are shaped, channelled, learned, reasoned, and structured before they are "officially made" (Stinchcombe & Gibson 2001).

Alternatives should be developed using a structured and transparent approach, and can be framed around one or several themes (González & Therivel 2014):

- strategic (high-level options that achieve a given objective)
- values-oriented (addressing policy priorities, cultural values or safety issues)
- effects-oriented (addressing the sources of any potential impacts identified during scoping)
- sectoral (formulated to address sectoral feasibility and needs or to promote one sector versus another)
- spatial (location options for the implementation of planning policies and/or objectives)
- modal (technologies/methods for achieving the same objective)
- temporal (timing of implementation of plan measures)

SEA Effectiveness Reviews in many EU countries (e.g. Ireland (EPA 2012), Germany (Geißler et al. 2019) have shown that the development of reasonable alternatives is one of the greatest challenges of the process. The following problems mentioned in the Reviews, are without exception also encountered in Croatian practice:

- higher-level plans can constrain the alternatives available for consideration in lower-level plans,
- alternatives for higher-level plans may be theoretical and academic because of the level of detail available,
- some alternatives being considered are purposely unrealistic and are put forward only to satisfy the requirements of the SEA Directive,
- alternatives are often developed retrospectively,
- political requests and instructions can limit the scope for developing alternatives,
- environmental reports justify why variants have not been considered at all.

The absence of alternatives and the documentation of their development process significantly diminishes the importance of strategic assessment in the environmental protection system, since in the Republic of Croatia, the measures to reduce the negative impacts arising from the SEA are basically optional for the proponent, i.e. decision makers.

Many countries have issued methodological guidelines for conducting strategic environmental assessment, which include the development and impact assessment of alternatives. While administrative implementation is clearly described through legislation and guidelines in Croatia, the methodology in the strategic process is left at the discretion of SEA practitioners. This paper therefore constitutes a contribution to the methodology in the part of development and evaluation of alternatives.

The main objective of the paper is to present the process of reasonable variants development, in situations where the alternatives have not been specified either by the draft document under assessment or by the scoping report, and finally, to determine the degree to which the process contributed to the way in which environment is treated by the document for which SEA is being conducted.

### 2. MATERIALS AND METHODS

The procedure of preparation and assessment of alternatives is demonstrated on the example of the strategic environmental assessment conducted for the Development Strategy of the City of Solin by 2025 (Official Gazette of the City of Solin 8/20) (hereinafter: The Development Strategy). The Development Strategy originally did not comprise alternatives, making their development the task of SEA practitioner in the procedure of preparation of the SEA report.

Since the reasonable alternatives represent diverse ways of addressing significant environmental protection issues, i.e. ways to achieve the objectives set by the document under assessment, in order to be able to ensure the comparability of the assessment, the alternatives also have to correspond to the scope and level of detail of the document under consideration. It was therefore essential to analyse in detail the structure and contents of the Development Strategy.

The analysis of the structure in the greater context regards establishing the position of the document in the vertical and horizontal hierarchy of documents in reference to its purpose, that is, its relevance in approval process

for the implementation of other documents or projects. In such a way, the appropriate level of detail of information comprised in the reasonable alternatives is established, which will further be reflected on the level of detail of the assessment in the following steps of the procedure.

By the analysis of the structure, that is the organization of the document, it was determined which elements of the environment may be affected and in what way. The way the individual elements were formulated and how they interacted as a part of a functional unit was identified. Generally, the analysis of the structure should answer the following questions:

- What is the smallest unit of the document concerned that can affect the environment?
- How does it relate to the other elements of the document (e.g. whether it depends on the hierarchy or not)? and
- Which is the smallest piece of information that may be used to determine the intensity of the environmental impact, when determining the magnitude of the impact?

The Development Strategy initially comprised the development vision supported through three general objectives with appertaining priorities as per individual sectors. In addition, measures were formed for each individual priority. Quantitative or qualitative outcome indicators with initial and target values were attributed to every objective, priority and measure, intended to serve as the criteria for regular monitoring and control of the Development Strategy implementation. The outcome indicators of measures, formulated as specific development activities, were identified as the smallest unit of the document that can affect the environment. It was therefore established that the alternatives have to rely on the hierarchy of indicators for the achievement of the vision established as: the measure  $\rightarrow$  priority  $\rightarrow$  goal  $\rightarrow$  vision. The initial and target values of such indicators reflect the intensity of change, and represent the key factor in determining the significance of impact. Upon the analysis of the structure of the document, the next important steps in development of reasonable alternatives were to analyse the content of the Development Strategy and its likely environmental impacts.

The analysis of the content of the Development Strategy resulted in insights into how the document was taking into account environmental issues with a focus on existing environmental problems, and in relation to the environmental protection objectives established by international treaties and agreements, as well as other strategies, plans and programmes.

Furthermore, the proposed development solutions were screened for their genuine need or demand, or justification for their implementation, and subsequently whether environmental issues were properly prioritized, given the severity of their consequences and the requirements of the hierarchy of documents, as well whether the proposed solutions respected the latest insights into existing environmental measures and procedures, and whether the proposed sites were suitable for development with respect to environmental sensitivity (where applicable).

In parallel with the content analysis, the impacts of the solutions of the Development Strategy were assessed in reference to the existing environmental conditions ("null variant", i.e. the "do-nothing" alternative), and whether it was possible and in what manner, to amplify the effects of positive impacts, or to diminish the negative ones.

The main objective of document content analysis and its impacts was to identify the "missed opportunities" for improving the environmental conditions, then, to identify the parts of the document that, individually or cumulatively, were likely to cause significant negative or positive impacts on any element of the environment, as well as those the impacts which were conditional, that is, which may be negative, neutral or positive, depending on the circumstances of their implementation.

By structuring the results of the content analysis and its environmental impacts, a window was opened to significantly improve the Development Strategy by modifying the development solutions, which included:

- eliminating the solutions, the negative impacts of which could not have been mitigated by measures,
- change of approach in meeting the needs or demands (e.g. traffic congestion construction of a new road vs. stimulation of the use of public transport),
- changing the priorities in response to the demand of the situation (e.g. tourism growth construction of drainage and wastewater treatment systems vs. investment in tourist attractions),
- change of capacity, target values, locations, implementation time, etc. to minimize negative and / or amplify positive impacts,
- incorporating solutions that would maintain stable the present state of the environment or improve it,
- conditioning the implementation of specific activities, by conducting previous research, development of analyses, studies, protocols, etc. (for which no EIA is prescribed by law).

The process resulted in the creation of an "environmental alternative", which was based on the integration of all the proposed development solutions aiming at improvement of the existing the state of the environment. In this way, the environmental objectives of the environmental report have become fully integrated into the objectives of the Development Strategy.

The environmental alternative and the documented process of its development (impact assessment), was established as the option with maximum possibilities for preserving and improving the environment, which at the same time revealed the likelihood of negative implications of the implementation of the initial draft of the Development Strategy. Upon its presentation to the stakeholders, the environmental alternative was used as the foundation for the discussion on aligning the stakeholders' interests, i.e. balancing their desires and needs when faced with limited environmental capacity. Through the process of interest coordination, during which the strategic framework was repeatedly changed, in cooperation with the developers of the Development Strategy, a new, in this case, the final, "alternative of an equable development" was formed, which incorporated most of the proposals from the environmental alternative.

The final step of the strategic assessment was to test the alternative of equable development against the environmental objectives of the environmental report, which resulted in environmental protection measures to mitigate its negative impacts, conceived to serve as a guidance at the project level. By including these measures in the final alternative, the final version of the document for public consultation was prepared.

#### **3. RESULTS AND DISCUSSION**

The strategic assessment process, with the development of alternatives and documentation of the whole process, was made possible by the positive cooperation of the SEA practitioners, the Development Strategy developers, the competent authority and the decision-makers from the very beginning of the preparation of the document. All the stakeholders mentioned agreed that the final document, which was created on the basis of the alternative of an equable development, was significantly improved compared to the initial draft of the Development Strategy, as shown on **Figure 2**.

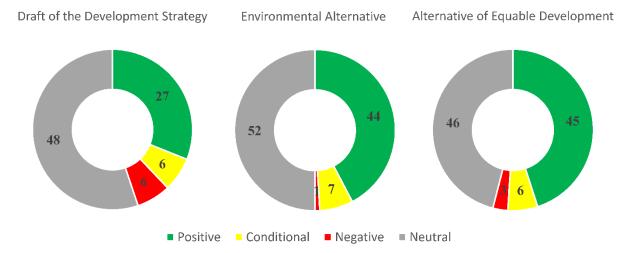


Figure 2. Comparison of alternatives with respect to the number of identified environmental impacts according to their course of action

Although the presentation of quantified impacts of alternatives is only informative, since it does not show their full intensity, scope and duration, it may nevertheless give us an impression on the improvement the equable development alternative made as regards the initial draft of the Development Strategy. The improvement is not only measured by the reduced number of development solutions with negative impacts and mitigated negative impacts (by 50 %), but also by the introduction of a new environmental protection priority, and the integration of a series of measures and development activities targeted at environmental and nature protection into all other priorities, which consequently significantly increased the number of positive impacts (by 40 %).

It is certain that the contribution of customary impact assessment that results only with mitigation measures, without the process of developing and comparing alternatives, to the environmental protection system would be considerably smaller.

In the process of strategic assessment, the decision maker was unwilling to give up or find a compromise for some of the indicators, for which the likely significance of negative impacts had been identified, and for which mitigation measures were proposed by the environmental alternative. Such political decisions are legitimate, and made transparent through the environmental report where decision-making process is recorded as the evidence that the decision maker was well aware of the implications at the time of the decision. Also, that way the public participating in the process is given all the information available at the time, which adds to the extraordinary value of this procedure.

Based on the conclusion of all the stakeholders that the SEA procedure conducted for the Development Strategy presented in this paper significantly contributed to the improvement of the environmental protection system in the City of Solin, the methodology for the development and assessment of the environmental impact of the development strategy alternatives in the strategic assessment has been established in the text below (**Figure 3**).

The methodology involves a two-stage analysis and consists of several steps:

- 1. Initial analysis of the structure, content and impact assessment of the proposed document on the environment, i.e. with respect to the null variant of the plan or the do-nothing alternative (V0),
- 2. Forming the most environmentally sound alternative within the structure and objectives of the document being evaluated, and integrating in the draft document modifications that reflect the maximum conservation and improvement opportunities for the environment,
- 3. Development of one or more new variants in the process of aligning stakeholder interests with biophysical factors, based on the documented development process of the alternative most favourable for the environment,
- 4. Deciding on the selection of the final alternative,
- 5. Conclusive assessment of the environmental impact of the final alternative, which results exclusively in measures to be used as guidelines for reducing negative impacts at a lower level,
- 6. Preparation of the final document by including mitigation measures into the selected alternative.

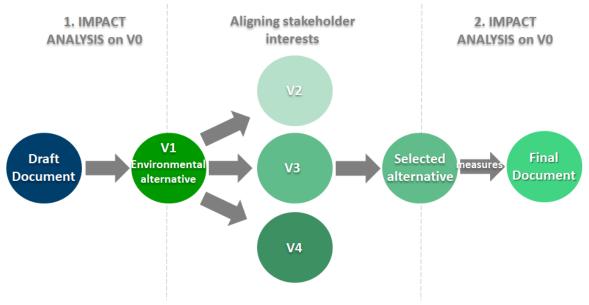


Figure 3. Development and assessment of impacts of the Development strategy alternatives in strategic assessment

Since it is intended that the decision makers used the environmental alternative as the background document in reviewing the interests of various stakeholders, documenting the process and development of an environmental alternative proves to be crucial in the process. Thereby, the quality of the final document will also depend on the quality of data used in the assessment, interpretation of impacts and creating the environmental alternative development solutions. In the past work, the problematic part of the impact assessment has been identifying the information that is used to determine the intensity of environmental impact, without which it is difficult to make a valid impact assessment, and consequently, the creation of alternatives.

In the case of the Solin City Development Strategy, this was simple because all the outcome indicators had an assigned initial and target value, however often documents of the same type do not contain this information. In such situations, the level of uncertainty of the estimate is very high, quality of the final results may be compromised, and the alternatives are mostly not considered.

Documenting the process of assessment and developing the environmental alternative builds the framework for environmental protection aimed actions, through which environmental improvement options, that would otherwise go unnoticed, may be put forward, and the alternatives for individual solutions with greater environmental benefits, opportunities for economic use of neglected natural resources in conditions of their maximum conservation, etc. may be identified. On the other hand, harmful consequences of implementation of certain proposed solutions or sets of solutions are described, and environmentally friendly alternatives are proposed, if possible. In view of the above mentioned, it is important to emphasize that other reasonable alternatives, potentially developed on the basis of the environmental one, need not to be further evaluated before selecting the final one, since through the process described all the implications are already known. The final impact assessment results in measures to mitigate the negative environmental impacts of the selected alternative which, in relation to the procedure described earlier, have no strategic significance.

Regardless of the alternative selected, all the information remains permanently recorded in the Environmental Report, which by presenting detailed information on likely positive and negative implications of implementation

of policies, directly ensures transparency of the process which may, consequently, stimulate a more significant involvement of the public in environmental issues.

Also, the procedure is sufficiently general and simple that it can be applied in a broader context, at other levels and for other types of documents, using other assessment tools. Thus, in the process of drafting a spatial plan, the environmental alternative for the layout of e.g. tourist zones may be easily created by using spatial multicriteria analysis tools. The environmental alternative, in the form of a high suitability environmental map for the arrangement of tourist zones, will further serve as the basis for balancing the interests of other stakeholders, i.e. the development of other reasonable alternatives.

### 4. CONCLUSION

In case the development of alternatives is the task of the SEA practitioner, creating an "environmental alternative" has proved to be an effective approach to presenting all the positive and negative environmental implications of a document under assessment, and consequently an excellent background for further discussion on adopting sustainable development solutions.

Given the fact that the inclusion of strategic assessment findings in a draft document is not compulsory in the Republic of Croatia, and that most projects comprised in the strategic level documents are subject to environmental impact assessment, it is evident that mitigation measures resulting from the customary impact assessment of project-level interventions on the strategic level contribute only to a smaller degree to the environmental protection system, while the true value lies precisely in the process of development and acknowledgement of alternatives.

The approach to strategic assessment in which the assessed document is addressed as an integral issue, rather than a collection of individual projects for which the environmental protection measures are prescribed on the project level, shows that the concept of strategic environmental assessment can be moved away from the concept of environmental impact assessment at the project level, and that in this way it may significantly contribute to the state of the environment at the strategic level.

The limiting factor in performing a high-quality environmental assessment and the possibility of development of alternatives is also the quality of the structure of the document for which SEA is being conducted. Therefore, it is highly recommended that during the preparation of strategies, programmes and plans, indicators based on the initial and target status be considered for all planned activities within the given planning period.

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# ASSESSMENT OF WATER QUALITY STATUS IN THE IMPACT AREA OF THE "PIŠKORNICA" LANDFILL

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Abstract: Disposal of household and industrial waste at the Piškornica site began in 1982 on what was then an unmanaged landfill cell, which allowed contamination to pass into underground layers. Landfill rehabilitation was conducted between 2005 and 2013 and conformed to the environmental protection conditions and measures that were prescribed by an EIA procedure, but rehabilitation still has not been fully completed. An environmental permit was issued for rehabilitation of the landfill. The decision and environmental permit prescribed groundwater quality monitoring. Prior to these documents, five piezometers were placed into operation in 1991. The objective of this paper is to determine the potential differences in ground and surface water quality that may have resulted from landfill operations, effectiveness of the rehabilitation efforts, and the potential risk of contamination of the Ivanščak water well. The results of the research were subjected to statistical analyses (e.g., T-test and ANOVA). Based on the regional flow model, a numerical groundwater flow model and contamination transport model were created, which provided scenarios for the potential spread of pollution from the Piškornica landfill while considering different water well operation regimes. It was concluded that a) even though rehabilitation has not been completed, the groundwater quality status improved and b) none of the analysed real flow scenarios generated redirection of streamline patterns towards the Ivanščak water well. Considering future development and likely increase of the Ivanščak well capacity, the expansion of monitoring was proposed for additional measuring locations.

Keywords: monitoring, landfill impact, landfill rehabilitation, contamination transport, contamination risk

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### **1. INTRODUCTION**

The Piškornica landfill is located in the area of Koprivnički Ivanec municipality, which is north of the city of Koprivnica and is approximately 1 km from the nearest settlement of Pustakovec, approximately 2 km from the Koprivnički Ivanec settlement and approximately 8 km from the centre of the City of Koprivnica. The landfill location was included in the spatial plan of Koprivnica-Križevci County. At the current location, the disposal of industrial and municipal waste has occurred since 1982, while prior to rehabilitation, disposal had been carried out in an unsanitary manner in which an impermeable bottom, as a solution for drainage of seeping water from the treatment plant, had not been constructed. In 1991, the first preliminary design for landfill rehabilitation was developed and was planned to be included for continuation of operations as a sanitary landfill. Approximately ten years later (2001), a new "Preliminary Design of a Category I Landfill at the Piškornica - Koprivnica Site" was developed and in March 2001, an Environmental Impact Study was adopted (IPZ Uniprojekt MCF 2001). The location and building permits for the rehabilitation and final landscaping of the Piškornica landfill were issued in 2004. Landfill rehabilitation began in 2005 and has been implemented in several phases over several years. As of today, rehabilitation of cells 1, 2 and 3 at the Piškornica landfill has been carried out and since 2018, waste has been disposed of in cell 4 in a sanitary manner. The current status is that approximately 100,000 m<sup>3</sup> of waste has been left unrehabilitated outside the landfill boundary and is located outside the present fence and is south of the landfill body (Figure 1).

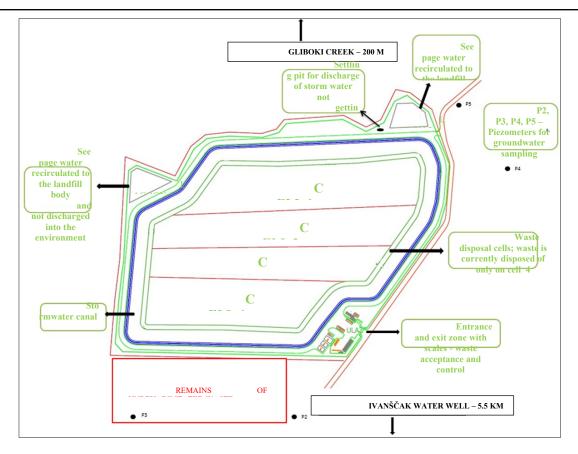


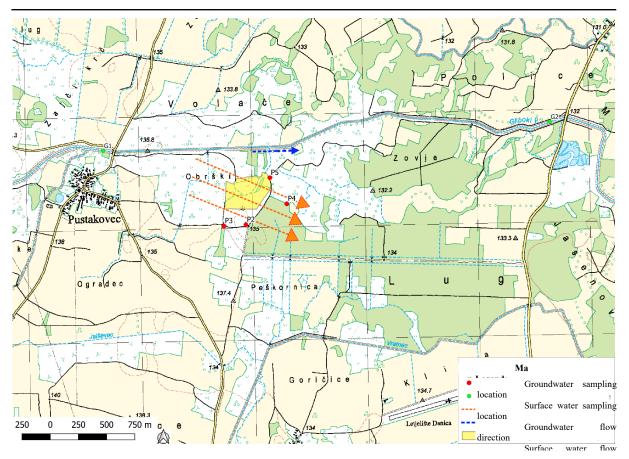
Figure 1. Layout of the Piškornica landfill with the unrehabilitated cell

To monitor groundwater quality in the immediate vicinity of the landfill, five piezometers (e.g., P1-P5) were installed in 1991. Today, based on the environmental permit (Okolišna dozvola 2016), the Piškornica landfill is obligated to conduct measurements of basic water quality indicators in groundwater at piezometers P2, P3, P4 and P5 and in the surface water of the Gliboki water body at locations G1 (Pustakovec Bridge) and G2 (Delekovec Bridge) with a minimum sampling frequency of four times per year during landfill operations by applying analytical measuring methods (**Figure 2**).

Testing of groundwater and surface water quality status in recent years, including 2018, has been conducted by the accredited laboratory at the Public Health Institute of Koprivnica-Križevci County in cooperation with the Public Health Institute of Primorje-Gorski Kotar County and the Andrija Stampar Teaching Institute of Public Health in Zagreb.

It is presumed that all measurements were performed in the referenced laboratory and that all parameters were investigated with the same methodology.

The Gliboki watercourse is a torrential watercourse where flow amounts are significantly affected by precipitation. As we had no information regarding the water flows at the points where samples were taken, it was also presumed that sampling was performed at approximately equal flow rates.



*Figure 2.* Piezometer locations and sampling points of the Gliboki water body (measuring profile G1 upstream) and measuring profile G2 downstream from the landfill which are marked with the flow directions of groundwater and surface water in the area of the Piškornica landfill (Source: Ruk, D. et al. (2018))

### 2. GROUNDWATER AND SURFACE WATER ANALYSIS

Testing was conducted in the periods before and during rehabilitation until 2012 and after rehabilitation was carried out until year 2018. The rehabilitation period itself, which ran from 2005 to 2013, was considered as the pre-rehabilitation period (Mikulic, N. et al 2019).

The testing results of water samples from the piezometers (P2, P3, P4 and P5) were analysed and included determinations of electrical conductivity, COD, BOD and iron plus the testing results of surface water samples from the nearest water body, Gliboki, which is situated north of the Piškornica landfill. The Gliboki water body was sampled at two locations, namely, upstream of the landfill site at the Pustakovac Bridge (G1), which was used as a control sample, and downstream of the landfill itself, at the Delekovac Bridge (G2), which is potentially affected by the landfill. For the Gliboki water body, the electrical conductivity, COD, BOD, copper and zinc values were analysed.

Heavy metals may be present in landfill leachates and their concentrations depend not only on waste compositions but also on the decomposition stage

Organic compounds in leachates create anaerobic conditions which release dissolved iron and manganese. We note that the alluvial aquifers of the River Drava are rich in iron and manganese salts. Because iron is present with naturally high concentrations in the underground waters of the observation area, it is difficult to assess iron impacts only by using its related concentrations (Elinder CG. 1986).

The analyses of heavy metal pollution origins in watercourses show that copper and zinc concentrations depend only partially on landfill emissions but are also influenced by untreated waste water emissions and agriculture along the watercourse

The parameters with the longest testing periods and those covering prior periods (during) and post rehabilitation, which were obtained both at the piezometers and at Gliboki Creek, were obtained for processing. Heavy metals that had the longest measurement times were selected for analysis of groundwater and surface water.

In addition, to identify possible differences in the quality of groundwater and surface water in the area of the Piškornica landfill as well as in the vicinity of the landfill site itself, at different stages of landfill operations (i.e., the pre- and post-rehabilitation periods until 2018), statistical analyses of selected datasets were carried out.

The starting point for analysis was the assumption that all testing was carried out in the same reference laboratory by using the same methodology for all analysed parameters. Groundwater flows were taken according to the flows used in the model and are presented later in this paper.

Similar to surface water quality monitoring, for monitoring the water quality of the nearest surface water body, Gliboki, parameters with the longest testing history were selected which were electrical conductivity, COD, BOD5 and the heavy metals, copper and zinc.

The testing results of the following samples were statistically processed:

- Groundwater samples from piezometers at locations around the landfill (e.g., P2, P3, P4 and P5) were tested for the following water quality characteristics: COD, BOD, electrical conductivity and Fe.
- The surface waters of the Gliboki watercourse that were sampled upstream (G1 location) and downstream (G2 location) from the landfill were tested for the following water quality characteristics: COD, BOD, electrical conductivity, Cu and Zn.

By applying appropriate statistical methods (e.g., T-test and variance analysis), the mean values of the testing results that were obtained before the completion of rehabilitation, i.e., until the end of 2012 (V1) were compared with the results obtained after completion of rehabilitation, i.e., from 2013 to 2018 (V2) for all observed quality characteristics and for all locations (e.g., P2, P3, P4, P5, G1 and G2).

Furthermore, the trends from sample testing were statistically processed and analysed for:

- Groundwater samples from the piezometers at locations around the landfill (e.g., P2, P3, P4 and P5) were tested for the following water quality characteristics: COD, BOD, electrical conductivity and Fe
- Surface waters of the Gliboki watercourse that were sampled upstream (G1 location) and downstream (G2 location) from the landfill were tested for the following water quality characteristics: COD, BOD, electrical conductivity, and Cu and Zn

### 3. DETAILS OF THE PROCESSING RESULTS OF DATA OBTAINED THROUGH MEASUREMENTS

#### a. Groundwater

The COD groundwater trend is shown in Figure 3.

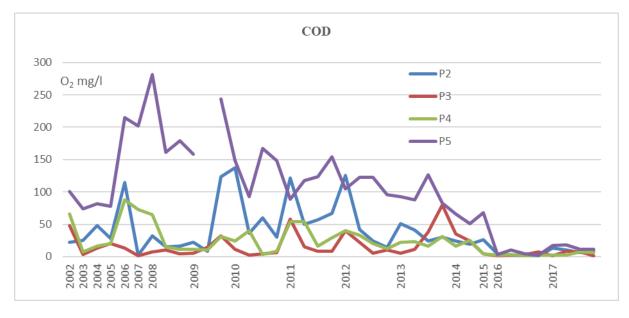
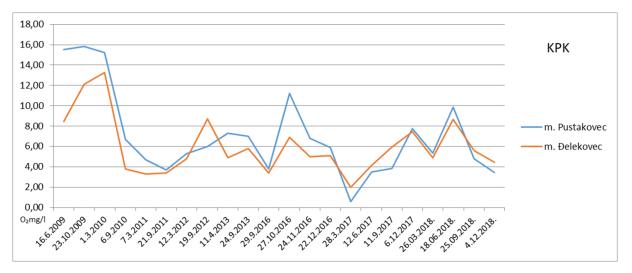


Figure 3. COD trends at the P2, P3, P4 i P5 piezometers in the period 2002-2018

The results show that a trend of decreasing COD was observed for all piezometers, especially after 2012, when landfill remediation was mostly completed.

#### b. Surface water

COD trends in surface water are shown in Figure 4.



*Figure 4. COD* (*KPK*) *in the surface water sampled upstream for profile G1 (m. Pustakovac) and downstream for profile G2 (m. Đelekovac) from the landfill during the period from 2008 to 2018.* 

COD distribution trends do not lead to the conclusion that the Piškornica landfill has had a significant impact on the Gliboki watercourse.

### 4. STATISTICAL ANALYSIS

The aim of the statistical analysis and trend analysis was to assess, with reasonable certainty, the effectiveness of the Piškornica landfill rehabilitation, which was carried out from 2005 to 2012 in accordance with the terms of the referenced contract.

#### a. Groundwater

The results of t-tests related of the quality indicators (e.g., COD, BOD, conductivity and Fe) are shown in **Table 1**. By testing the differences in mean values of the results obtained from the P2 through P5 piezometers before (V1) and after (V2) landfill remediation, we can evaluate the impact of specific parameters on groundwater quality (Mendenhall W. 1986).

**Table 1.** Significance differences between variances before remediation (V1) and after remediation (V2) forthe P2 to P5 piezometers (t-test, alpha level 95 %) and O= total number of individual observations)

Attribute	Piezometer	V1 (before remed.)	V2 (after remed.)	t-exspon.	Note
	P2	50,89 (O=24)	17.47 (N=15)	3.56	V1>V2
COD	Р3	15.15 (O=24)	15.4 (N=15)	0.04	V1=V2
COD	P4	31.13 (O=24)	11.05 (N=15)	3.65	V1>V2
	Р5	141.69 (O=23)	43.48 (N=15)	5.93	V1>V2
	P2	13.16 (O=24)	5.64 (N=15)	2.44	V1>V2
DOD	Р3	3.88 (O=24)	6.76 (N=15)	1.15	V1=V2
BOD	P4	4.91 (O=24)	2.96 (N=15)	1.47	V1=V2
	Р5	28.67 (O=23)	5.22 (N=15)	7.55	V1>V2
Conductivity	P2	949 (O=27)	923 (N=12)	0.15	V1=V2
	Р3	515 (O=25)	472 (N=12)	1.13	V1=V2
	P4	649 (O=26)	682 (N=12)	0.24	V1=V2
	Р5	2330 (O=27)	1454 (N=12)	2.45	V1>V2

Fe	Р2	25191.2 (O=27)	3548.5 (N=12)	1.96	V1=V2
	Р3	2993.3 (O=26)	1579.2 (N=12)	1.995	V1=V2
	P4	11676.6 (O=27)	2682.8 (N=12)	2.02	V1=V2
	P5	15292.7 (O=27)	4354.3 (N=12)	1.77	V1=V2

Regarding the iron content values, no significant differences were found at any of the piezometer locations (P2 to P5) between the results of testing that was performed before completion of rehabilitation (V1) and the results of testing for Fe contents that were obtained after rehabilitation was carried out (V2). In addition, there were no significant differences between the mean values of the testing results obtained from piezometer locations P2 through P4 when compared to the values at piezometer location P5. The high variance values suggest that there is a large scatter in individual Fe testing results from which the mean values were calculated.

The t-test results show a significant decrease in COD values from P2, P4 and P5 after rehabilitation. The findings from ANOVA further reveal the results of rehabilitation (**Table 2**).

Group	Observation	Sum	Mean	Variance		
P2	24	1221,38	50.89	1751.0426		
P3	24	363.55	15.15	222.45279		
P4	24	747.15	31.13	560.82877		
P5	23	3258.77	141.69	3004.9011		
ANOVA						
Source of var.	SS	df	MS	F	P-value	F critic
Between groups	223617.3	3	74539.1099	54.52739	2.9024E-20	2.7047034
Within groups	124397.3	91	1367.003088			
Total	348014.6	94				

Table 2. COD variance analysis for piezometers P2 through P5 before remediation.

F>Fcrit- differences are significant

Group	Observation	Sum	Mean	Variance		
P2	15	262.12	17.47	228.69796		
P3	15	231.02	15.4	461.80418		
P4	15	165.76	11.05	102.61599		
P5	15	652.18	43.47	1670.9321		
ANOVA						
Source of var.	SS	df	MS	F	P-value	F crit.
Between groups	9677.305	3	3225.768293	5.2365301	0.00294979	2.7694309
Within groups	34496.7	56	616.0125538			
Total	44174.01	59				

Table 3. COD	variance analysis	for piezometers P2	2 through P5 after rehabilita	ation

F>Fcrit- differences are significant

Our conclusion, which is based on the statistical analysis performed, is that the Piškornica landfill resulted in significant reductions in COD, BOD and electrical conductivity values at the location of piezometer P5 and to lesser extents at locations P2 (for COD and BOD values) and P4 (for COD values). We conclude from the results that the COD and electrical conductivity values at the P5 location were significantly higher than those at other locations (e.g., P2 to P4) and note that the differences between measured values after landfill rehabilitation were smaller than the differences measured before rehabilitation. These results indicate the significant relationship between flow routes and piezometer locations.

#### Surface water b.

The results of t-tests that were related to the quality indicators (e.g., COD, BOD, Cu and ZN) were obtained by testing samples from Gliboki Creek before (V1) and after (V2) landfill remediation are shown in Table 4.

Table 4. Significances of differences between variances before remediation (V1) and after remediation (V2) for the G1 profile (upstream) and for the G2 profile (downstream) (t-test, alpha level 95%)

Attribute	Sampled	G1	G2	t-exp.	Note
COD	V1 (before rem.) (O=9)	10.1	8.76	0.48	G1=G2
COD	V2 (after rem.) (O=13)	5.97	5.37	0.65	G1=G2
BOD	V1 (before rem.) (O=9)	3	3.33	0.68	G1=G2
BOD	V2 (after rem.) (O=13)	2.58	1.53	2.12	G1>G2
conductivity	V1 (before rem.) (O=9)	420	466	1.37	G1=G2
	V2 (after rem.) (O=13)	445	481	1.77	G1=G2
Cu	V1 (before rem.) (O=9)	2.25	1.43	0.74	G1=G2
	V2 (after rem.) (O=13)	7.74	7.63	0.03	G1=G2
Zn	V1 (before rem.) (O=9)	15.26	14.65	0.08	G1=G2
	V2 (after rem.) (O=13)	42.64	73.61	0.6	G1=G2

From the statistical analysis, we conclude that, for the selected attributes, no significant differences were found between the results obtained before rehabilitation and those obtained after rehabilitation of the Piškornica landfill. There are two exceptions:

- For profile G2 (downstream) there was a significant BOD reduction after rehabilitation which should be investigated,
- After rehabilitation, Cu concentrations increased for both sampling profiles, i.e., both upstream and downstream from the landfill location.

Based on the results of statistical analysis of the measured values of the observed quality characteristics (e.g., COD, BOD, electrical conductivity), and Cu and Zn, we conclude that the impact of the Piškornica landfill on the surface water quality of the Gliboki watercourse is not significant but note that the possible cause of increased Cu contents after rehabilitation in the studied area is from the impacts of agricultural activities on the testing results.

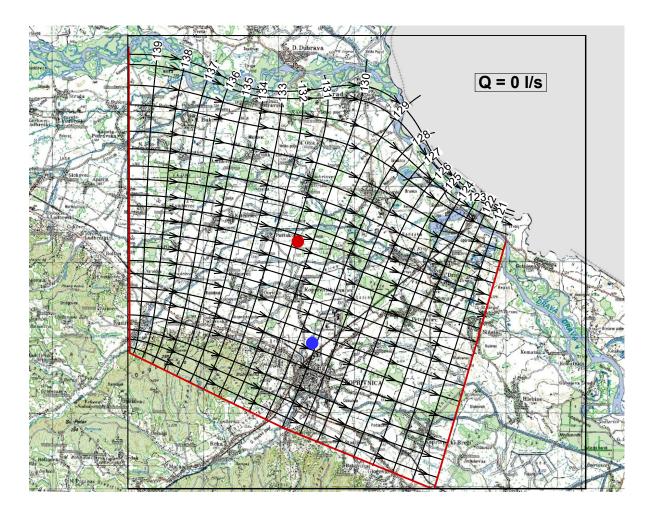
### 5. REGIONAL FLOW MODEL IN THE PIŠKORNICA AREA

Regional flow and transport modelling are standard tools for analysing water quality in landfill areas. Flow analysis is usually conducted by using finite element methods (e.g., Ackerer et al. 1999; Voss 1984; Holzbecher, 1998) while transport analysis is determined by a random walk Lagrangian approach (e.g., Rubin 2003; La Bolle et al. 1998; Park et al. 2008). To numerically model groundwaters flow and pollution transfer over a broad area around the Piškornica landfill (Duić & Urumović 2007), the Fi programme was used (Gotovac 2002; Jović, 1993; Urumović 2003). This programme was written in the Fortran language and is used for numerical analysis of stationary seepage through a two-dimensional porous medium by using the finite element method.

Eight-node finite elements were used to discretize the geometry of the area. Hydraulic conductivity is represented as a full conductivity-tensor that is constant in the elements but is variable by area. This allows for observations of stationary flow through a heterogeneous aquifer (each element may have a different conductivity tensor). Essential or Dirichlet boundary conditions were defined as specified piezometric heights (potential). Pumping and recharge points are included as concentrated inflows into the network nodes, distributed load or production of the required field by area (constant within elements) as well as the fluxes at the edges of the elements, which were defined as one-dimensional elements and were separately set. Such fluxes represent natural or Neumann boundary conditions. The equation system was solved by a frontal procedure.

### 5.1. Description of Boundary Conditions

Figure 5 shows the boundaries of the regional flow model. To obtain a realistic flow state in the area around the Piškornica landfill, it was necessary to correctly set the boundary conditions. On the north side, Drava was the boundary that was used to determine the global regional flow in the model. Drava was defined as an impermeable boundary (streamline) so that the regional flow would run parallel to Drava, as was indicated by field measurements. For the eastern portion, a boundary with a Dirichlet boundary condition of 140 m was defined. On the western side, a boundary with a Dirichlet boundary condition of 120 m was defined. The south boundary was a defined as an impermeable boundary (respectively, streamline) that was roughly parallel to the Drava flow and the other side was at a sufficient distance from Piškornica and the water well to not affect the model results. Such definitions of boundary conditions agree with those of (Urumović et al. 1996).



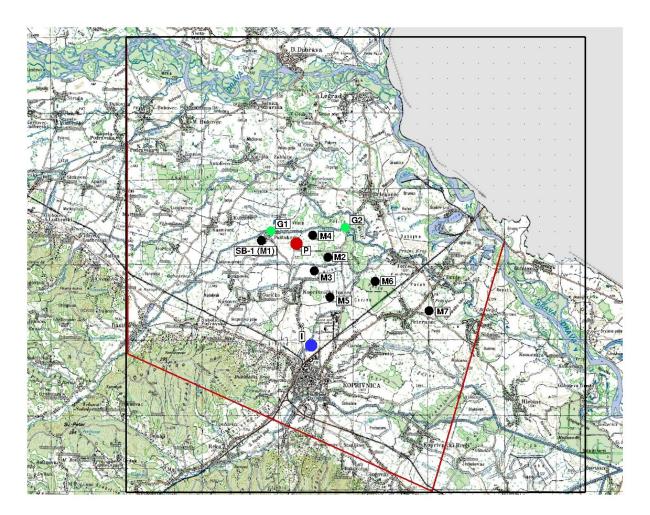
*Figure 5.* View of the regional flow model domain in the area of Piškornica (red circle – landfill, blue circle – Ivanščak water well, red lines – domain boundary)

### 5.2. Ivanščak Water Well

The Ivanščak water well (**Figure 6**) is located approximately 5.5 km from the landfill. Hydrogeological analysis of the water well was conducted in a study by Urumović et al. (1996). The water well had a significant impact on the hydrodynamic flow configuration in the observed domain. Significant over-pumping could cause a direct connection between the Piškornica landfill and the water well that supplies the city of Koprivnica. It should be noted that the landfill area does not fall into the I, II or IIIa water well protection zones. The water exploitation so far does not confirm any impacts by the landfill on the water quality in the water well. Considering that the water well is the most important water source in the observed domain and its impact on the results of the regional flow model, five basic flow scenarios, S1-S5, were defined and the velocity field was the main input variable for analysing conservative transport at the landfill that defines the advective transport component:

- S1 Q = 0 (l/s); No pumping.
- S2 Q = 100 (l/s); Corresponds to the current average pumping.
- S3 Q = 200 (l/s); Corresponds to the current maximum pumping.

S4 - Q = 420 (l/s); Corresponds to the maximum pumping with respect to the current water well capacity. S5 - Q = 600 (l/s); Corresponds to the pumping level that would cause a direct hydrodynamic connection between the water well and the Piškornica landfill.



**Figure 6.** View of the observation points used in the transport analysis for the area of the Piškornica landfill (landfill – P, Ivanščak water well – I, Gliboki Creek – G1 and G2, and piezometers M1 to M7 that represent future monitoring).

Each flow scenario was defined by a different streaming image which implies different cloud expansion properties in the sense of their spatial and temporal movements as well as concentration magnitudes.

Figure 6 shows the observed area with ten observation points at which the pollution cloud movement was monitored and the possible effects on water bodies were analysed. The three primary observation points are the Piškornica landfill - P, Ivanščak water well - I and Gliboki Creek - G. The other observation points represent piezometers M1 to M7 which can be used for future monitoring. M1 is the piezometer located approximately 2 km from the landfill and is at the site where the deep well SB-1 is located. It was proposed that this well be used as M1 and would determine the flow conditions and water quality upstream from the landfill. The M2 piezometer is located approximately 1.75 km from the landfill and is on a stream that comes from the landfill and was used for pumping simulation S2 which corresponds to present day pumping conditions. The M3 piezometer is located approximately 1.75 km from the landfill and is located on a stream coming from the landfill and was used for pumping simulation S5, which is the case when a direct hydrodynamic connection between the landfill and the water well is established. M4 is located approximately 1.25 km from the landfill near Gliboki Creek. M4 can be compensated for by the measurements in Gliboki Creek and monitors the pollution cloud toward this water body. The M6 and M7 piezometers determine the movement of the pollution cloud from the main possible propagation direction along with M2. M6 is 4.87 km from the landfill and M7 is approximately 8.12 km from the landfill. M5, at a distance of 3.3 km, was used determining the movement of the cloud from the landfill toward the Ivanščak water well along with M3. In this way, all three possible downstream directions of cloud propagation in space and time were monitored.

The basic input data were defined in the regional flow model, namely, the domain, edges, finite element network and velocity field for flow scenarios S1-S5. An effluent, which is a pollution cloud defined as a series of particles in the transport analysis, forms at the landfill. In this analysis, we observe the momentary injection of waste at the moment the landfill is opened when 2,000 particles are injected into the model (**Figure 6** - shown in red circle - P). This is a simpler version while the other approach is to define a continuous pollution source (which in reality occurs at the landfill and requires introducing new particles at each temporal step. However, this simpler

version shows all of the essential properties of conservative transport in terms of the spatial and temporal distributions of the pollution cloud. A realistic scenario would be much more important if reactive chemical transport were also considered.

### 5.3. Explanation of Results Obtained Through Models

Based on five flow scenarios, S1-S5, for different pumping amounts of the Ivanščak water well, the pollution cloud transport behaviours downstream from the Piškornica landfill were analysed. The pollution cloud propagation in space and time was analysed and the cloud was monitored at ten observation points. Thus, pollution was monitored at the upstream piezometer M1 and at the landfill body (point P) and also in three basic directions: 1) the direction of the main regional flow extending from the northwest to the southeast between Gliboki Creek and the Ivanščak water well (piezometers M2, M6 and M7); 2) the direction from the landfill to the Ivanščak water well (piezometers M3, M5 and I); and 3) the direction from the landfill to Gliboki Creek (piezometer M4 and existing measuring stations G1 and G2).

The results of the analysis show that, for the S1-S3 flow scenarios, there are no significant differences among the pollution transport results. The regional flow runs from the northwest to southeast. Advection causes the cloud to travel between Gliboki Creek and the water well but, however, is closer to the creek. There is no direct hydrodynamic connection between the landfill and water well or between the landfill and Gliboki Creek. Therefore, the field of streams from the landfill that defines the advection forces the pollution cloud to travel with its centre along the P-M2-M6-M7 route.

Due to pumping at 600 l/s at the Ivanščak water well, the streams rotate toward the water well so that a direct hydrodynamic connection is established between the landfill and water well. Therefore, the field of streams from the landfill that defines the advection forces the pollution cloud to travel directly towards the water well. **Figure** 7 shows that the maximum concentrations at the M2 piezometer (40 % of the initial concentration) decrease compared to scenarios S1-S3 and significantly decrease at M6 (0.7 %) while the pollution cloud does not reach M7 (0 %). The concentration curves in the piezometers have shapes that are very similar to normal distributions where they reach a maximum at M2 in six years and at M6 in 12 years. All c-t curves have zero values until the first pollution particles reach their environment. Therefore, the first travel times of the pollution cloud are to M2 at approximately five years, to M6 at approximately 12 years, and to M7 at approximately 25 years. The c-t curves have non-zero values during the time period when the pollution cloud travels across their respective areas. After the cloud passes, the concentrations in the c-t transient curves are once again zero. This non-zero-time segment defines the variance of the c-t transient curve (the variance equals its sixth), which is approximately one year for piezometers M2 and M6.

The dimensions of the pollution cloud at the landfill were estimated as 0.5 \* 0.5 km. The pollution cloud is carried downstream by advection and dispersion increases and dilutes the cloud and after 15 years, divides the cloud into two parts such that one part moves towards the water well and the other part moves towards the Drava River.

**Figure 8** shows the characteristics of pollution transport towards the Ivanščak water well. In this flow scenario, S5, the cloud directly reaches the water well. It takes 20 years for the cloud to reach the water well and, after 60 years, approximately 43% of the initial pollution mass has been incorporated into the affected drinking water. After 26 years, the maximum pollutant concentration at the landfill is 5.1 %. The two piezometers placed between the landfill and water well show that at M3, the maximum concentration is 7.5% and at M5, it is 5.7 %.

The remaining question is whether the pollution cloud threatens Gliboki Creek in scenario S5. Considering the direct connection between the landfill and water well, the regional flow is altered to a completely different direction, so at M4 and Gliboki Creek - G, the concentrations are zero which mean that there is no pollution and that Gliboki Creek is not in direct contact with the pollution cloud from the landfill.

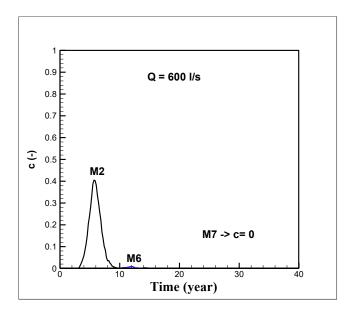
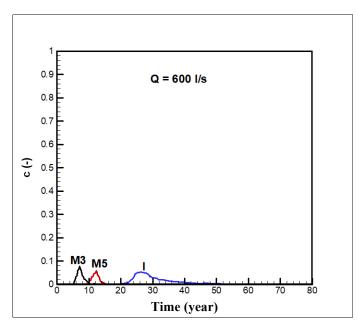


Figure 7. Representation of the dependence of non-dimensional concentrations and times for flow scenario S5 at observation points M2, M6 and M7



*Figure 8.* Representation of the dependence of non-dimensional concentrations and times for flow scenario S5 at observation point I – Ivanščak and piezometers M3 and M5

The results show that in all realistic scenarios of S1-S4 flows, there is no propagation of the pollution cloud into the water bodies of Gliboki creek and the Ivanščak water well. In the direction of regional flow (**Figure 5**) for flow scenario S3, it is evident that the maximum concentrations are at the M2 piezometer (59 % of the initial concentration) and decrease gradually at M6 (25 %) and M7 (16 %). The concentration curves for the piezometers exhibit shapes that are very similar to normal distributions for which they reach a peak at M2 in 7.5 years, at M6 in 19 years, and at M7 in 35 years. The first travel times of the pollution cloud are: to M2 at approximately three years, to M6 at approximately 13 years, and to M7 at approximately 26 years. The pollution cloud passes the farthest piezometer M7 after 35 years when it has dimensions of approximately 4\*3 km. Likewise, scenario S4 shows that even at the maximum water well capacity of 420 l/s, pollution of the Ivanščak water well does not occur. Any increase in the pumping capacity in the future to approximately 600 l/s in flow scenario S5 would cause a direct hydrodynamic connection between the landfill and water well and drinking water pollution would occur after approximately twenty years from the cloud formation at the landfill if the landfill had not been fully rehabilitated. Finally, the ten observation points used in the pollution transport analysis will serve as a template for future monitoring.

#### 6. CONCLUSION

Based on the analysis of laboratory test results, we conclude that landfill rehabilitation resulted in a significant positive change in groundwater quality status in the landfill environment by examining the COD, BOD and electrical conductivity values while the testing results of Fe contents did not change significantly after landfill rehabilitation was carried out.

The greatest changes in the values of the observed water quality characteristics after rehabilitation were observed at location P5, which is situated near the northeastern part of the landfill while at the location of the P3 piezometer, which is situated near the southwestern part of the landfill, no significant changes in the values of water quality characteristics were observed after landfill rehabilitation.

Furthermore, the analysis showed that the impact of the Piškornica landfill on the surface water quality of the Gliboki watercourse is not significant.

The results of the analysis based on the model show that in all realistic flow scenarios S1-S4, there is no propagation of the pollution cloud into the water bodies of the Gliboki creek and the Ivanščak water well. Moreover scenario S4 shows that even at the maximum water well capacity of 420 l/s, pollution of the Ivanščak water well does not occur. Any increase in the pumping capacity in the future to approximately 600 l/s in flow scenario S5 would cause a direct hydrodynamic connection between the landfill and water well and drinking water pollution would occur after approximately twenty years from initial cloud formation at the landfill if the landfill had not been fully rehabilitated. Finally, the ten observation points used in the pollution transport analysis will serve as a template for future monitoring.

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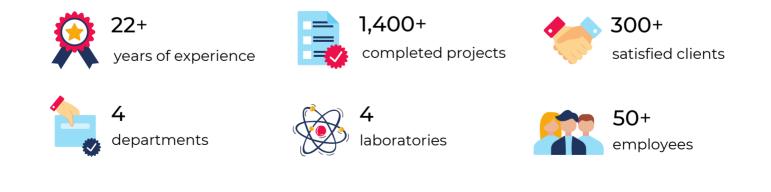
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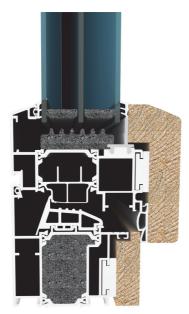
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- Izrada geotehničke dokumentacije (izvješća, elaborati, projekti)
- Geotehnički nadzor i savjetovanje

# UNIVERSITY OF ZAGREB FACULTY OF GEOTECHNICAL ENGINEERING DEPARTMENT OF HYDROTECHNICS

# Main research areas:

Water management

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- Groundwater protection
- Hydrology
- Hydrogeochemistry
- Advanced technologies for water treatment

# Experience and knowledge transfer applications:

- Preparation of methodology for karstic groundwater bodies quality status and risk assessment
- Preparation of national methodology for status assessment of coastal karstic groundwater bodies
- Delineation of drinking water protection zones and protection measures
- Preparation of mathematical models of intergranular aquifers























GRADUATE STUDY OF ENVIRONMENTAL ENGINEERING WATER MANAGMENT





SVEUČILIŠTE U ZAGREBU GEOTEHNIČKI FAKULTET Hallerova aleja 7, 42 000 VARAŽDIN tel.: 042 / 408 – 900 fax: 042 / 313 – 587 M.B. 03042316



GEOTEHNIČKI FAKULTET Zavod za hidrotehniku Laboratorij za geokemiju okoliša tel.: 042 / 408 - 937 fax: 042 / 313 - 587



LABORATORIJ ZA GEOKEMIJU OKOLIŠA

- osnovan je 2006. godine sa znanstvenom, stručnom i obrazovnom svrhom
- opremljen instrumentima i pratećom opremom za prikupljanje uzoraka tala, sedimenata, prirodnih i otpadnih voda
- vrši terenske i laboratorijske analize prikupljenih uzoraka
- obavlja usluge agrokemijskih analiza tla za poljoprivrednike na temelju kojih se daje preporuka za gnojidbu



Zavod za hidrotehniku



# LABORATORIJ ZA GEOKEMIJU OKOLIŠA

Tel.: 042 / 408 - 937 Fax: 042 / 313 - 587 E-mail: Igo@gfv.unizg.hr

### LABORATORIJ ZA GEOKEMIJU OKOLIŠA

Laboratorij za geokemiju okoliša osnovan je u sklopu Zavoda za hidrotehniku Geotehničkog fakulteta u Varaždinu. Laboratorij sudjeluje u izvođenju praktične nastave iz kolegija preddiplomskog i diplomskog studija te Združenog međunarodnog doktorskog studija kao i u znanstvenim te stručnim projektima. Na taj naci i ispunjava svoju obrazovnu, znanstvenu i stručnu svrhu. Smješten je na 100 m prostora i opremljen modernom opremom za provedbu geokemijskih terenskih aboratoriju se obavljaju i usluge agrokemijskih analiza tla.

#### Pokazatelji koje mjerimo u uzorcima voda, eluata tala i sedimenata:

- atomskom apsorpcijskom spektrometrijom: A, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Si, Sr, Ti, V, Zn
- ~ amonijak, nitriti, nitrati, ukupni dušik
- ~ bromidi, fenoli, fluoridi, fosfati, jodidi, kloridi
- ~ silikati, sulfidi, sulfati, sulfiti
- ~ suspendirana tvar, mutnoća, KPK
- ~alkalitet, ukupna tvrdoća, karbonatna tvrdoća, nekarbonatna tvrdoc kalcijeva tvrdoća, magnezijeva tvrdoća
- ~ slobodni CO<sub>2</sub>, koncentracija otopljenog kisika i zasićenost kisikom
- ~ pH, električna vodljivost, ukupna otopljena tvar TDS
- ~ trasiranje podzemnih tokova (koncentracija natrijevog fluoresce
- ~ ukupni organski ugljik i ukupni dušik TOC/DOC/TN
- ~ razaranje tla zlatotopkom
- ekstrakcija izmjenjivih kationa iz tla amonijevim acetatom i kalijevim kloridom

Ispitivanje fizikalnih i kemijskih svojstava prirodnih i otpadnih voda.

spitivanje sastava

eluata otpada.



Provođenje agrokemijskih analiza tla u svrhu modernizacije poljoprivredne proizvodnje, racionalizacije gnojidbe, povećanja prinosa i zaštite prirodnih resursa.



Određivanje pH, pKCl, ukupnog CaCO3, NO3<sup>-</sup>, NO2<sup>-</sup>, NH4<sup>+</sup>, fosfora i kalija, humusa, teških metala i drugih kemijskih svojstava tla.

<u>Kontakti</u>: izv.prof.dr.sc. Anita Ptiček Siročić voditeljica laboratorija *tel: 042 / 408 - 957* e-mail: anita,pticek.sirocic@gfv.unizg.hr dr.sc. Dragana Dogančić stručna suradnica *tel: 042 / 408 – 956 ili 042 / 408–937* e-mail: ddogan@gfv.unizg.hr Saša Zavrtnik, dr.med.vet. laborant *tel: 042 / 408—937* e-mail: Igo@gfv.unizg.hr

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# DEPARTMENT OF ENVIRONMENTAL ENGINEERING



# **MAIN RESEARCH AREAS:**

- Waste management
- •Solar photocatalysis
- Waste treatment technologies
  - Chemical sensors
  - •Environmental monitoring
    - Waste mechanics

# Laboratory of Environmental Engineering

Special interest in wastewater management, air quality, waste management and disposal, energy efficiency and renewable energy sources, R&D of chemical sensors for environmental and industrial applications, microfluidics.





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**Fitness park** ⁄ Fitness Park

**Solarni park** / Solar Park

Ulaz u podemnu garažu / Underground Garage Enterence



f scvarazdin

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# **Student Council Faculty of Geotechnical Engineering**



- $\checkmark$  As the student representatives we promote student interests and take care of the student standard at the Faculty council.
- $\checkmark$  We take care on student rights, encourage students to be involved in international mobility, advise students in their needs, etc.
- $\checkmark$  We are participating in many form projects; student promotions, study promotions, to scientific and professional project with our professors.
- ✓ We working are the on networking of current students with former students and potential employers.
- ✓ Through various activities our goal is to be the leader of the student standard promotion in Varaždin.

CONTACT: Email: studentski.zbor@gfv.unizg.hr



Studentski zbor Geotehničkog fakulteta





 $\checkmark$  Every student is important to us.



# **KRITERIJI ZA UPIS**

Lista poretka prijavljenih kandidata za upis sastavlja se prema sljedećem sustavu bodovanja:

- a) Na temeliu uspieha u srednioi školi = do 500 bodova
- b) Na temelju položenih ispita na državnoj maturi - matematika (osnovna razina) = do 500 bodova
- c) Na temelju provjere posebnih sposobnosti = nema bodova
- d) Temeljem dodatnih postignuća učenika = IZRAVAN UPIS (1000 bodova)
  - osvojeno jedno od prva tri mjesta na državnim natiecaniima u RH iz matematike, fizike, kemije, biologije, informatike, astronomije, statistike ili tehničkih znanosti za vrijeme srednjoškolskog obrazovanja

# AKADEMSKI NAZIVI

Završetkom preddiplomskog studija Inženierstvo okoliša stieče se 180 ECTS bodova te akademski naziv sveučilišni prvostupnik/prvostupnica\_inženier/inženierka Inženjerstva okoliša (univ.bacc.ing.amb.).

Završetkom diplomskog studija Inženjerstvo okoliša stječe se 120 ECTS bodova te akademski naziv magistar/magistra inženjer/inženjerka Inženjerstva okoliša (mag.ing.amb.).

Završetkom doktorskog studija Inženjerstvo okoliša stječe se 180 ECTS bodova te akademski naziv doktora znanosti (dr.sc.).

# Opis zvanja - kompetencije i osposobljenost

Završetkom sveučilišnoga preddiplomskog studija na Geotehničkom fakultetu steći ćeš osnovne kompetencije u identificiranju, definiranju i rješavanju inženjerskih zadaća u Inženjerstvu okoliša.

Od praktičnih znanja kao prvostupnik Inženierstva okoliša posjedovat ćeš sposobnost korištenja laboratorijske i terenske opreme, promatranja, bilježenja i analize podataka dobivenih laboratorijskim i terenskim ispitivanjima. Znat ćeš izraditi tehničke nacrte ručno i pomoću računala, te pripremiti prezentaciju tehničkih izvješća.

Znanja i kompetencije koja stekneš završetkom sveučilišnoga preddiplomskog studija odgovarajuća su za praćenje diplomskoga sveučilišnog programa na Geotehničkom fakultetu, a omogućavaju ti i praćenje diplomskih studija iz srodnih područja na drugim tehničkim studijima te praćenje različitih programa cjeloživotnog obrazovanja.

Diplomski studij Inženjerstvo okoliša traje dvije godine, a uključuje smjerove Geoinženjerstvo okoliša, Upravljanje vodama i Upravljanje okolišem. Ovaj studij mogu upisati studenti koji su završili sveučilišni preddiplomski studij ili strani studij ekvivalentnog programa.

Završetkom diplomskoga studija bit ćeš osposobljen upravljati okolišem na održiv način i preuzeti osobnu i timsku odgovornost za strateško odlučivanje i uspješnu provedbu zadataka pri izradi elaborata, studija i projekata iz inženjerstva okoliša, kao i primijeniti legislativu iz područja zaštite okoliša te preuzeti društvenu i etičku odgovornost za posljedice

Doktorski studij Inženjerstvo okoliša traje tri godine, a njegovim završetkom stječu se kompetencije za provođenje



# DODATNE INFORMACIJE



tel: 042/408-901 ured.tajnika@gfv.unizg.hr

REFERADA: pon-pet: 09:00 - 12:00 tel: 042/408-904 studentska.referada@gfv.unizg.hr

Točne datume upisa i ostale relevantne informacije možete potražiti na web stranicama fakulteta: www.gfv.unizg.hr

ADRESA: Geotehnički fakultet Sveučilišta u Zagrebu, Hallerova aleja 7, 42000 Varaždin

Studij inženjerstva okoliša – Geotehnički fakultet



inzenjerstvo\_okolisa

STUDIJ INŽENJERSTVA OKOLIŠA

# Mogućnost zaposlenja

Znanstvenu karijeru možeš nastaviti razvijati upisom na poslijedoktorski studij Inženjerstvo okoliša na našem Fakultetu. A ako si bio vrlo uspiešan student, možda započneš svoju akademsku karijeru kao asistent na našem Fakultetu.

Izvan akademske ili znanstvene sredine, popis mogućih poslodavaca kod kojih se možeš zaposliti doista je raznolik. To su sve institucije državne i lokalne uprave, kao i svi gospodarski subjekti koji zapošljavaju osobe za obavljanje stručnih poslova zaštite okoliša, kao što su na primjer komunalna poduzeća, centri za gospodarenje otpadom, pročišćivači otpadnih voda, eksploatacijska polja. Nadalje, to su i svi oni gospodarski subjekti koji se bave obnovljivim izvorima energije te oni koji svojim proizvodnim procesom mogu naštetiti okolišu.

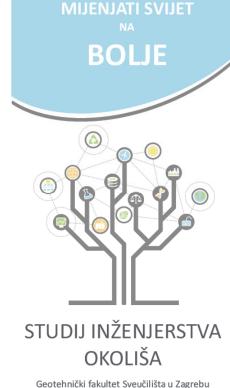
Ako želiš možeš postati i inspektor za zaštitu okoliša, a s ovim stručnim nazivom ti ni vrata Europske unije neće biti zatvorena.

### Pogodnosti studiranja

Tijekom studiranja na našem Fakultetu kao student Sveučilišta u Zagrebu na raspolganju imaš razne pogodnosti. Detaljnije o pogodnostima možeš saznati u našem vodiču za brucoše:

http://www.gfv.hr/modules/m\_gfv/datoteke/vodic\_za\_b rucose\_a5\_final\_v1.pdf





FAKULTET



# Znanost i suradnja s gospodarstvom

Na Geotehničkom fakultetu provode se i znanstvena istraživanja. Fakultet raspolaže akreditiranim geotehničkim laboratorijem, kao i laboratorijem za inženjerstvo okoliša, laboratorijem za geokemiju okoliša, informatičkim centrom za GIS. Primjereno smo opremljeni i za terenske istraživačke radove. Budući da istraživači koji ih provode sudjeluju i u izvođenju nastave, studentima se prenose najnovije spoznaje i rezultati istraživania.

Velik doprinos nastavi i znanstvenom radu daje znanstvena i stručna suradnja Geotehničkog fakulteta sa srodnim visokoškolskim institucijama u Republici Hrvatskoj i svijetu. Usporedno s nastavom i znanstveno-istraživačkim radom, Fakultet održava i razvija i suradnju s gospodarstvom kroz izradu mnogobrojnih studija i projekata iz područja Inženierstva ol





Sveučilište u Zagrebu GEOTEHNIČKI FAKULTET

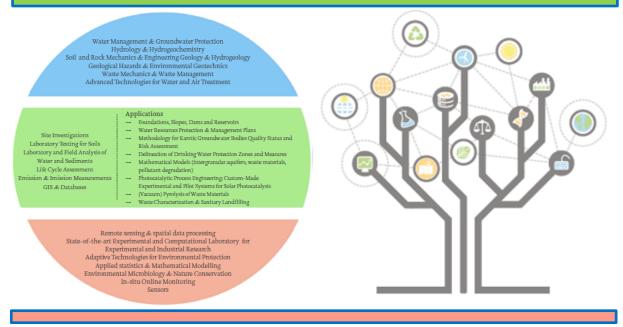


# Sveučilišni doktorski studij Inženjerstva okoliša

odgovor je na zahtjeve naše svakodnevice gdje se susrećemo s problemima onečišćenja okoliša, klimatskim promjenama, potrošnjom resursa kao što su mineralne sirovine, tlo, vode, neadekvatnog upravljanja otpadom i niz drugih okolišnih problema. https://www.gfv.unizg.hr/static/doktorski-studij

Nastavna struktura doktorskog studija koncipirana je u formi pet izbornih modula:

Održivo gospodarenje otpadom
 Okoliš i priroda
 Geoinženjerstvo okoliša
 Upravljanje vodama
 Energetika



# Postgraduate doctoral study of Environmental Engineering

Problems concerning the field of environmental engineering demand both professional and scientific research approach, which is the only way of finding specific solutions to them. The programme emphasizes current socitetal needs concerning circular economy, which should enable sustainable waste management, natural resources management and protection, introduction of renewable energy sources and contributes to the mitigation of climate changes.

https://www.gfv.unizg.hr/static/doktorski-studij

The curriculum of the doctoral study consists of five modules:

Sustainable waste management
 Environment and nature
 Environmental Geoengineering
 Water management
 Energetics

# Prvih pola stoljeća Geotehničkoga fakulteta (1969.-2019.)

Tijekom rujna 2020. godine iz tiska je izašla monografija Geotehničkoga fakulteta "Prvih pola stoljeća Geotehničkoga fakulteta (1969.-2019.)". S velikom tradicijom u geotehnici i hidrotehnici Fakultet se zadnjih petnaestak godina sve više okreće prema okolišu s interdisciplinarnog gledišta i pozicionira kao jedan od stožernih fakulteta Sveučilišta u Zagrebu koji se bave istraživanjem okoliša s inženjerskog aspekta.

U monografiji je prikazan povijesni pregled od osnutka do današnjih dana te istaknuta naša vizija razvoja u narednom razdoblju, prikazane su aktivnosti zavoda i laboratorija, studijski programi, znanstvenoistraživački projekti, izdavačka djelatnost te popis djelatnika i svih završenih studenata od osnutka institucije do današnjih dana.

Vjerujemo da će ova monografija brojnim bivšim studentima i prijateljima Fakulteta pobuditi draga sjećanja, a široj zainteresiranoj javnosti pružiti bolju informaciju o dugogodišnjoj tradiciji i razvojnom putu našega Fakulteta.

Glavni urednik: Prof.dr.sc. Ranko Biondić



# **PREVIOUS ISSUES**

### https://www.gfv.unizg.hr/static/online-library-open-access



# **INSTRUCTIONS FOR AUTHORS**

The journal "*ENVIRONMENTAL ENGINEERING-INŽENJERSTVO OKOLIŠA*" publishes scientific and technical papers and other articles in the interdisciplinary area of environmental engineering. The scientific topics covered by the Journal include geo-engineering, water resources management, technical aspects of environmental protection and similar areas. The journal publishes papers in English. Papers are accepted for publication after they have received a positive review and are categorized as an original scientific paper, preliminary comunications, review paper or technical paper.

The journal is published biannually. There are no charges for printing the paper. As a rule, the length of the paper is not limited. However, it is recommended that it should not be longer than 15 single-spaced A4 pages, all figures included.

Figures are printed in greyscale, and authors should take it into account when preparing their manuscript. However, authors may, in agreement with the editorial board, prepare figures in colour when they deem it necessary for the understanding of what the figure shows. The figures in colour approved by the editorial board will not be additionally charged.

When a paper is submitted for review, this implies that the paper has not been previously published or that it is not being reviewed by another journal. The author is responsible for the content of the paper and for obtaining consent, where applicable, to publish particular data.

The first page should contain the title of the paper, the authors' names, the institution of employment, the authors' email addresses, the abstract and keywords. It is recommended that the title of the paper should be illustrative and clearly reflect the content of the paper. If the title contains local names, then a generally recognizable name in a wider region should be included. The abstract should not exceed 300 words, and there should be 4 to 6 keywords. If none of the authors has been specified as lead author, the editors will exclusively contact the first mentioned author.

Authors should submit their paper by e-mail to: **casopis@gfv.unizg.hr**. The paper should be prepared in Microsoft Word in A4 page format, with 25 mm margins and 1.5 line spacing, in one column aligned to both sides. The text should be written in 10 pt Times New Roman, and the pages should have automatic numbering in the bottom right corner. Depending on the content, the text should be divided into several sections whose headings are in 11 pt bold and aligned to the left. The paper should be written in the third person singular and has to be terminologically harmonized with legal regulations in force and the international system of units (SI). All equations have to be numbered; tables and figures should also be numbered with a heading and inserted in the appropriate place in the article. For citation of equations, figures and table in text use bold font. All figures (images, diagrams, photographs) have to be prepared for graphic reproduction at a minimum resolution of 300 dpi and submitted in a separate map.

When **citing papers in the text** with blue colour, only previously published papers should be mentioned. If authors consider it necessary, personal communication and unpublished papers may be cited in the paper, but in an appropriate manner, either as part of the text or in acknowledgements at the end of the paper. **References** include an alphabetical list of published papers that have been cited in the text. The **Harvard citation** and referencing style should be used.

If the paper is accepted for publication, the authors are obliged to harmonize the paper with the instructions given by the reviewers/editors. If the authors do not accept the reviewers'/editors' remarks or if they do not submit the corrected version of the paper within three months, the editorial board will deem that the authors have withdrawn their paper from the procedure and no longer wish to have it published.

Prior to its publication, the authors will receive the paper for inspection and final revision.

The paper which has been through all the phases of text preparation will first be published online, and then in the printed edition. Authors will receive a separate in pdf format as well as one copy of the journal in which the paper was published.