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Zagreb, Ksaverska c. 2

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JEDANAESTI HRVATSKI
ZNANSTVENO-STRUČNI SKUP

ZAŠTITA ZRAKA 2019

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Bol, 15. – 19. listopada 2019.

Pokrovitelji:
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Hrvatsko udruženje za zaštitu zraka nastavlja svoju dugogodišnju tradiciju organiziranja znanstveno – stručnog skupa na temu zaštite zraka. Ovogodišnji XI. skup „Zaštita zraka 2019“ s međunarodnim sudjelovanjem održava se po prvi put u Bolu, najstarijem gradiću na otoku Braču, poznatom po najatraktivnijoj plaži Jadrana Zlatni rat.

Veliki broj prijavljenih sudionika i 55 prijavljena izlaganja, prikazanih u ovom zborniku sažetaka pokazatelj su zainteresiranosti stručne javnosti, domaće i inozemne o sve prisutnijem problemu onečišćenja zraka koje ima štetan utjecaj na okoliš i ljudsko zdravlje.

Svakodnevne aktivnosti praćenja kvalitete zraka zahtijevaju znanje, iskustvo, odgovarajuću opremu, primjenu zakonske regulative... Na skupu „Zaštita zraka 2019“ sudionici će prezentirati svoja iskustva i probleme s kojima se susreću tijekom rada kroz slijedeće teme:

1. Upravljanje kvalitetom zraka – inspekcija i nadzor
2. Emisije onečišćenja u atmosferu
3. Onečišćenje vanjske atmosfere – imisije
4. Razvoj i provjera mjernih metoda
5. Procjena izloženosti onečišćenjima u zraku i učinci na zdravlje
6. Zaštita zraka u sustavu prostornog uređenja, graditeljstva i zaštite okoliša
7. EFCA sekcija “Ultrafine particles - air quality and climate: State of play related to scientific evidence and policy proposal”

Zadovoljstvo nam je najaviti EFCA sekciju, koja se po četvrti put organizira pod pokroviteljstvom Europske federacije udruženja za čisti zrak i zaštitu okoliša (European Federation of Clean Air and Environmental Protection Associations) na temu „Ultrafine Particles“.

Pozitivna iskustva prethodno održanih skupova daju nadu u uspješnost i ovog skupa. Svim sudionicima želimo uspješno izlaganje, korisne izmjene iskustva, plodonosne rasprave i ugodno druženje.

Jagoda Doko Jelinić i *Gordana Pehnec*

FOREWORD

The Croatian Air Pollution Prevention Association continues its longstanding tradition of organising scientific and professional conferences on air protection. The eleventh edition of Air Protection (2019) with international participation is held for the first time in Bol, the oldest town at island Brač, famous of the most attractive Adriatic beach Zlatni rat.

The large number of participants and the 55 submitted presentations in this Book of Abstracts clearly prove that both the international and domestic professional community are more than interested to learn about and discuss the ever-growing and threatening impact of air pollution on human health and the environment.

As we are all aware, the everyday activities of regular air quality monitoring require knowledge, experience, adequate equipment, good legislation, as well as many other factors to coincide and fall into place. The participants of the Air Protection 2019 conference will present their experiences and the issues they encounter in their work through the following topics:

1. Managing air quality – inspection and control
2. Atmospheric emissions of pollutants
3. Monitoring ambient air pollution
4. Developing and testing measuring methods
5. Estimating exposure to air pollutants and impact on health
6. Air Protection in physical planning, construction, and environmental protection
7. EFCA session "Ultrafine particles - air quality and climate: State of play related to scientific evidence and policy proposal"

It is our great pleasure to announce the EFCA session, organised for the fourth time under the auspices of the European Federation of Clean Air and Environmental Protection Associations (EFCA) with the topic „Ultrafine Particles".

Positive memories from previous conferences assure us that this year's edition will be just as successful. We wish all of the participants a fruitful professional stay and a lovely time in Bol.

Jagoda Doko Jelinić and *Gordana Pehnec*

Uvodna predavanja

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Bol, October 15-19, 2019
CAPPA

Selahattin Incecik[1], Abdurrahman Bayram[2], Tolga Elbir[2]

18TH WORLD CLEAN AIR CONGRESS, ISTANBUL-TURKEY

Keywords: *declaration, IUAPPA, TUNCAP*

18th World Clean Air Congress (www.wcac2019.org) organized by the Turkish National Committee for Air Pollution Research and Control (TUNCAP) and International Union of Air Pollution Prevention Associations (IUAPPA) was held from 23rd to 27th September 2019 in Istanbul Hilton Maslak.

The WCAC'19 in Istanbul whose main topic of the Congress was One Atmosphere: Air Pollution and Climate Interactions and Challenges is provided a worldwide platform for scientists, policymakers, and industrialists to discuss state-of-the-art scientific knowledge and latest progress and technical solutions in improving air quality throughout the week.

We believe that the aim of the Congress has been realized to a great extent. Throughout the week oral and poster papers presented by distinguished guests from 44 countries on five continents. 170 oral and 35 poster presentations were presented at the Congress, which had 298 participants.

The distinguished Key-Note Speakers in the Plenary Sessions presented specifically very attractive state-of-the-art topics each day. Dr.Tedros Ghebreyesus who is the Director-General of WHO was attended the first-day Plenary Session by a Video message. Furthermore, the international institutions and associations performed six highly interesting significant side events during the World Congress: Air Quality Management in Eastern Europe and West Asia by the World Bank, Ultrafine Particles by EFCA, Global Atmospheric Pollution Forum, Reducing Air Pollution in Asian Cities by the Clean Air Asia, Air Quality Strategy by the World Research Institute, and finally a Workshop on Health Impact Assessment and a Forum on Low Carbon Economy by the Malaysian Clean Air Society (MyCAS).

The Abstract Proceedings book was distributed before the Congress. Additionally, an e-Proceedings Book from the submitted full papers will be uploaded to the Conference Web Page soon. Besides, selected papers will be published in the Special Issues of the Elsevier journals as the Science of the Total Environment and Atmospheric Pollution Research. The declaration of the 18th World Clean Air Congress will be announced soon as well.

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[2] Dokuz Eylül University, Cumhuriyet Bulvarı No: 144 35210 Alsancak/İzmir, Turkey

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Paweł Ciećko[1]

THE REFORM OF AIR QUALITY MONITORING SYSTEM IN POLAND

Keywords: *air quality monitoring system, air quality modelling system, Poland*

The year 2019 is the year of transition of the air quality monitoring system in Poland. The act of 20th July 2018 on amendment of the act on Inspection of Environmental Protection and some other acts enabled to make substantial organisational changes in the Inspection of Environmental Protection. Previous environmental monitoring units and laboratories of Voivodship Inspectorates of Environmental Protection were joined as of 1st January 2019 with the Chief Inspectorate of Environmental Protection and became parts of it. That change allows to optimise air quality monitoring system in Poland. The Chief Inspectorate of Environmental Protection is now in the process of redesigning the air quality monitoring system after conducting in June 2019 the preliminary air quality assessment for 2014-2018. The management of the air quality measurement system can be performed more effectively now concerning the allocation of stations as regards to the needs and organisational and financial capabilities. National level public procurements for the air quality measurement, analytical and IT equipment as well as accompanying acquisitions result in cutting costs of the air quality monitoring system. Also, day-to-day management concerning maintaining the equipment and software can be done with better performance. At the same time the number of air quality stations is being increased and the new air quality modelling system is being implemented.

[1] Chief Inspectorate of Environmental Protection, Wawelska 52/54, 00-922 Warsaw, Poland

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Cleo Kosanović[1]

AIRQ – PROŠIRENJE I MODERNIZACIJA DRŽAVNE MREŽE ZA TRAJNO PRAĆENJE KVALITETE ZRAKA

Ključne riječi: *klimatske promjene, obuhvat podataka, upravljanje, praćenje i procjena kvalitete zraka*

Projekt „AIRQ – Proširenje i modernizacija državne mreže za trajno praćenje kvalitete zraka" ima cilj unapređenje sustava upravljanja i praćenja kvalitete zraka kako bi se postigla učinkovita kontrola i upravljanje kvalitetom zraka u urbanim sredinama, zonama i aglomeracijama. Namjera je pružiti potporu implementaciji zakonodavnog okvira u području zaštite kvalitete zraka i okoliša (Direktiva 2008/50 EZ, Zakon o zaštiti zraka NN 130/11, NN 47/14, NN 118/18) uključujući razvoj održivih integriranih strategija i projekata koji stvaraju preduvjete za adekvatnu ocjenu, planiranje i provođenje odgovarajućih mjera radi provođenja kontrole kvalitete zraka mjerenjem relevantnih parametara kako bi se poboljšao program za nadzor klimatskih onečišćujućih tvari kratkog vijeka (SLCF-short livedclimate forcers) i uvele klimatski osjetljive mjere protiv onečišćenja zraka.

Glavni korisnik projekta je Državni hidrometeorološki zavod (DHMZ), a partner na projektu je Institut za medicinska istraživanja i medicinu rada (IMI). Projekt je vrijedan 125.1 milijuna kuna, od čega je iz Europskog fonda za regionalni razvoj u sklopu Operativnog programa Konkurentnost i kohezija 2014.-2020 osigurano 85 % sufinanciranja ukupno prihvatljivih troškova, a 15 % nacionalnog učešća osigurava Fond za zaštitu okoliša i energetsku učinkovitost.

Ciljevi projekta AIRQ su: povećanje udjela stanovništva u Hrvatskoj obuhvaćenog podacima o kvaliteti zraka u urbanim područjima s 50 % na 100 %, 5 novoizgrađenih i 19 moderniziranih postaja za mjerenje kvalitete zraka u državnoj mreži za trajno praćenje kvalitete zraka, razvijen i funkcionalan model kvalitete zraka za procjenu prizemnih koncentracija onečišćujućih tvari za područja na kojima ne postoje mjerenja u Hrvatskoj, uspostavljen i funkcionalan kemijski laboratorij DHMZ-a za analizu kemijskog sastava oborine i zraka, uspostavljen i funkcionalan kemijski laboratorij IMI-ja za analizu kemijskog sastava lebdećih čestica, uspostavljen i funkcionalan umjerni laboratorij DHMZ-a za umjeravanje mjerila kvalitete zraka i vezanih mjernih veličina u svrhu osiguranja sljedivosti navedenih mjerenja do međunarodnih etalona te nadogradnja računalne infrastrukture DHMZ-a radi osiguranja brže i kvalitetnije dostupnosti informacija o kvaliteti zraka. Provedbom projekta AIRQ uspostavlja se cjelovit sustav mjerenja i kontrole kvalitete zraka u Hrvatskoj u svrhu zadovoljenja europskih i nacionalnih kriterija o očuvanju okoliša i zdravlja ljudi.

Prikazana je realizacija projekta AIRQ do danas kroz prikaz izvršenih javnih nabava i potpisanih ugovora.

[1] Državni hidrometeorološki zavod, Grič 3, Zagreb, Hrvatska

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AIRQ – EXPANSION AND MODERNISATION OF THE NATIONAL NETWORK FOR CONTINUOUS AIR QUALITY MONITORING

Keywords: *air quality management, monitoring and assessment, climate changes, data capture*

The purpose of the project "AIRQ – Expansion and Modernisation of the National Network for Continuous Air Quality Monitoring" is to improve and optimize the system for managing and monitoring air quality in urban areas, zones and agglomerations. The project aims to support the implementation of the legislative framework for air quality and environmental protection (Directive 2008/50/EC, Air Protection Act (Official Gazette 130/11, 47/14)). This entails developing integrated strategies and projects which enable the evaluation, planning and implementation of adequate procedures for controlling air quality by means of measuring relevant parameters. In the end, the project thus aims to improve the monitoring programme for short-lived climate forcers (SLCF) and introduce climate-sensitive measures against air pollution.

The main institution is the Meteorological and Hydrological Service of Croatia (DHMZ) and the Institute for Medical Research and Occupational Health (IMI) is the partner. The project will receive a grant in the amount of 125,1 million HRK (85 % funded by the European Regional Development Fund within Operational Programme Competitiveness and Cohesion 2014-2020, and 15 % by the Environmental Protection and Energy Efficiency Fund).

Objectives of the AIRQ project are: increasing the percentage of population covered by air quality data in urban areas, upgrading existing 19 air quality measurement stations and building 5 new ones, developing an operational model for the evaluation of ground-level pollutant concentrations, equipping the DHMZ laboratory for analysing the chemical composition of precipitation and air, equipping the IMI chemical laboratory for analysing the chemical composition of particulate matter, equipping the calibration laboratory for calibrating air quality standards and related measures, so as to ensure the traceability of the said measurements to international measuring standards, and upgrading the DHMZ computer infrastructure. The implementation of the project AIRQ establishes a comprehensive system of measurement and control of air quality in Croatia in order to meet the European and national criteria for the environment and human health.

The realization of the project will be displayed through the executed public procurement and contracts signed.

[1] Croatian Meteorological and Hydrological Service, Grič 3, Zagreb, Croatia

Tema 1
Upravljanje kvalitetom zraka – inspekcija i nadzor

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Zdenko Franić[1]

ISKUSTVA AKREDITACIJE VERIFIKACIJSKIH TIJELA ZA OCJENU PLANOVA PRAĆENJA I VERIFIKACIJU EMISIJA CO_2 U POMORSKOM PROMETU

Ključne riječi: *MRV propisi, pomorski promet, CO_2 emisije, klimatski i energetski paket*

Europska komisija (EK) u svom klimatskom i energetskom paketu zakona iz 2009. godine obrađuje problematiku CO_2 emisija u pomorskom prometu putem EU MRV (Monitoring, Reporting, Verification) regulative koja se efektivno primjenjuju od 1. siječnja 2018. godine. Ti propisi zahtijevaju da vlasnici i operateri brodova na godišnjoj razini tijekom svake plovidbe izvještavaju i verificiraju CO_2 emisije za sva plovila veća od 5.000 bruto tonaže (BT) koja pristaju u bilo kojoj EU i EFTA (Norveška i Island) luci. MRV propisi dizajnirani su tako da progresivno integriraju emisije u pomorskom prometu u EU politiku reduciranja domaćih emisija stakleničkih plinova (EU uredba 2015/757). Brodarske kompanije za svaki od brodova koji potpadaju pod MRV propise moraju pripremiti plan praćenja emisija CO_2. Propisano je da se prati i prijavi količina CO_2 koju emitiraju njihovi brodovi na putovanjima do, iz i između luka u EU, a također se moraju dati informacije o parametrima energetske učinkovitosti. Prikupljanje podataka za svaku plovidbu pokriva period od 1. siječnja do 31. prosinca. Akreditirana certifikacijska (verifikacijska) tijela, kao nezavisna treća strana, verificiraju podatke o emisijama CO_2 i ostalim zahtijevanim relevantnim informacijama, a koje za svaki brod vodi Europska agencija za pomorsku sigurnost (EMSA) putem Web aplikacije THETIS-MRV.

- *Prilikom verifikacijskog postupka, verifikacijska tijela verificiraju sljedeće parametre:*
- *Polaznu i dolaznu luku, uključujući datum i sat isplovljavanja i uplovljavanja*
- *Ukupnu količinu i emisijski faktor za svaku vrstu upotrijebljenog goriva,*
- *Emisiju CO_2,*
- *Prevaljenu udaljenost,*
- *Vrijeme provedeno u plovidbi,*
- *Teret koji se prevozi i*
- *Transportni rad kao produkt prevaljene udaljenosti i mase prevezenog tereta.*

Norma prema kojoj se provodi akreditacija verifikacijskih tijela za područje „Ocjena planova praćenja" i „Verifikacija emisija CO_2 u pomorskom prometu" je HRN EN ISO 14065:2013 (Stakleнički plinovi - zahtjevi za tijela koja provode validaciju i verifikaciju stakleničkih plinova za potrebe akreditacije ili drugih oblika odobrenja), dok EU uredbe br. 757/2015, br. 2071/2016 i br. 2072/2016 predstavljaju EU pravni okvir. Akreditacijski postupak uključuje ocjenu dokumentacije, znanja, i vještina osoblja verifikacijskog tijela (verifikatori) u njihovom sjedištu te ocjenu na licu mjesta (tzv. witness audit) kod brodara.

[1] Institut za medicinska istraživanja i medicine rada, Ksaverska cesta 2, 10000 Zagreb, Hrvatska

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EXPERIENCE OF ACCREDITATION OF VERIFICATION BODIES FOR ASSESSMENT OF MONITORING PLANS AND VERIFICATION OF CO_2 EMISSIONS IN MARITIME TRANSPORT

Keywords: *MRV regulation, maritime transport, CO_2 emissions, climate and energy package*

The European Commission (EC) in its 2009 climate and energy package covered CO_2 emissions from maritime transport through EU MRV (Monitoring, Reporting, and Verification) regulation that become fully effective on 1st January 2018. This regulation requires that ship owners and operators annually, on a per voyage basis, monitor, report and verify CO_2 emissions for vessels larger than 5,000 gross tonnage (GT) calling at any EU and EFTA (Norway and Iceland) port. The MRV regulation is designed to progressively integrate maritime emissions into the EU's policy for reducing domestic greenhouse gas emissions (EU regulation 2015/757). Shipping companies must for each of their ships that falls under the jurisdiction of MRV regulation prepare a monitoring plan. They have to monitor and report the verified amount of CO_2 emitted by their vessels on voyages to, from and between EU ports and are also required to provide information on energy efficiency parameters. For each voyage, data-collection covers period 1st January to 31st December. Accredited certification (verification) bodies, as an independent third-party organizations, verify data on CO_2 emissions and other required relevant information, that are for each vessel subsequently managed by the European Maritime Safety Agency (EMSA) through Web-based application THETIS-MRV.

- *During verification process, verification bodies verify the following parameters:*
- *Port of departure and port of arrival, including the date and hour of departure and arrival,*
- *Amount and emission factor for each type of fuel consumed in total,*
- *CO2 emitted,*
- *Distance travelled,*
- *Time spent at sea,*
- *Cargo carried and*
- *Transport work defined as the product of distance travelled and cargo mass transported.*

The standard for accreditation of verification bodies for the scope "Assessment of monitoring plans" and "Verification of CO_2 Emissions in Maritime Transport" is HRN EN ISO 14065:2013 (Greenhouse gases - requirements for greenhouse gas validation and verification bodies for use in accreditation or other forms of recognition), while EU regulations No. 757/2015, No. 2071/2016 and No. 2072/2016 create EU-wide legal framework. The accreditation process involves the assessment of the documentation, knowledge and skills of the verification body personnel (verifiers) at their headquarters and the on-the-spot audit ("witness audit") on the ship or in the premises of the shipping company.

[1] Institute for Medical Research and Occupational Health, Ksaverska c. 2, 10000 Zagreb, Croatia

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Vjeran Magjarević[1], Mario Pokrivač[1], Gordan Golja[1]

PROBLEMATIKA IZRADE AKCIJSKOG PLANA ZA POBOLJŠANJE KVALITETE ZRAKA

Ključne riječi: *akcijski plan, kvaliteta zraka, Velika Gorica, lebdeće čestice $PM_{2.5}$*

Odredbama članka 46. Zakona o zaštiti zraka (NN 130/1, 47/14, 61/17, 118/18) propisano je da ukoliko u određenoj zoni ili aglomeraciji razine bilo kojih onečišćujućih tvari u zraku prekoračuju bilo koju graničnu vrijednost ili ciljnu vrijednost, donosi se Akcijski plan za poboljšanje kvalitete zraka za tu zonu ili aglomeraciju kako bi se, u što je moguće kraćem vremenu, osiguralo postizanje graničnih ili ciljnih vrijednosti.

Obavezni sadržaj Akcijskog plana propisan je Prilogom 1. Pravilnika o uzajamnoj razmjeni informacija i izvješćivanju o kvaliteti zraka i obvezama za provedbu odluke komisije 2011/850/EU (NN 03/16), te stavkom 3. članka 46. Zakona o zaštiti zraka. Akcijski plan između ostalog mora sadržavati mjesto prekomjernog onečišćenja, vrstu i ocjenu onečišćenja, podrijetlo onečišćenja, analizu stanja, mjere za smanjivanje onečišćenja zraka, njihov redoslijed i rokove ostvarivanja kao i procjenu sredstava.

Prema članku 4. Uredbe o utvrđivanju popisa mjernih mjesta za praćenje koncentracija pojedinih onečišćujućih tvari u zraku i lokacija mjernih postaja u državnoj mreži za trajno praćenje kvalitete zraka (NN 65/16) mjerna postaja u Velikoj Gorici je jedna od 21 mjerne postaje koje čine državnu mrežu za trajno praćenje kvalitete zraka, te se koristi za potrebe izrade godišnjeg izvješća o kvaliteti zraka kao i za uzajamnu razmjenu informacija i izvješćivanja o kvaliteti zraka između Republike Hrvatske i Europske komisije.

Na mjernoj postaji u Velikoj Gorici srednja godišnja vrijednost lebdećih čestica $PM_{2.5}$ tijekom 2016. godine bila je prekoračena te je zrak na navedenoj mjernoj postaji ocjenjena kao II kategorije, zbog čega je Grad Velika Gorica bio u obavezi izrade Akcijskog plana za poboljšanje kvalitete zraka. Je li moguće i u kolikoj mjeri zadovoljiti propisani obavezni sadržaj Akcijskog plana u slučaju potrebe izrade istog, koliko su obvezujuće te kako i u kojem roku provesti mjere iz Akcijskog plana, na koji se način informacije iz Akcijskog plana šalju Europskoj komisiji - samo su neka od pitanja na koje izrađivač Akcijskog plana nailazi. Postoje li uopće precizni odgovori na sva postavljena pitanja razmatrat ćemo kroz primjer izrade Akcijskog plana za poboljšanje kvalitete zraka s obzirom na lebdeće čestice $PM_{2.5}$ na području grada Velike Gorice.

[1] Dvokut Ecro d. o. o., Trnjanska 37, Zagreb, Hrvatska

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ISSUES REGARDING THE AIR QUALITY ACTION PLAN

Keywords: *action plan, air quality, city of Velika Gorica, $PM_{2.5}$*

Article 46 of the Air Protection Act (OG 130/1, 47/14, 61/17, 118/18) stipulates that, if in any given zone or agglomeration the levels of (any) pollutants in air exceed any limit value or target value, the representative body of the local self-government unit competent for the zone or agglomeration shall adopt an air quality action plan (AQAP) for that zone and agglomeration, in order to achieve the limit values or target values as soon as possible.

The mandatory content of the AQAP, set out in Annex 1 of the Ordinance on reciprocal exchange of information and reporting on ambient air quality and commitments for implementation of Commission Decision 2011/850/EU (OG 3/16), demands establishing, inter alia, the identification of the region in which excessive pollution has appeared, pollution type and assessment, pollution origin, status analysis, air pollution abatement measures, their order and deadlines for realisation.

According to Article 4 of the Regulation on the establishment of a List of measurement sites for monitoring concentrations of certain pollutants in the air and locations for measurement stations in the national air quality monitoring network (OG 65/16), a total of 21 air quality monitoring stations in the Republic of Croatia comprise an air protection information system and the data from these stations are used for the purpose of producing the Annual Report on Air Quality, but also for the mutual exchange of information and reporting on air quality between the Croatian Ministry of Environmental Protection and Energy and the European Commission.

Is it possible to comply to the prescribed mandatory content of the AQAP, are the measures specified with Action plan mandatory and how and within what period to implement those measures, what is the procedure of information exchange between Croatia and European Commission - these are just some of the issues the Action Plan creator faces. Can we give precise answers to these and other questions is a matter discussed herein through the example of the AQAP for Velika Gorica with respect to $PM_{2.5}$.

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Tema 2
Emisije onečišćenja u atmosferu

ELEVENTH CROATIAN
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Bol, October 15-19, 2019
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IMPROVEMENT OF BLACK CARBON EMISSIONS AND MODELLED CONCENTRATIONS IN GERMANY

Keywords: *BC, GRETA, LOTOS-EUROS chemistry-transport model*

Black carbon (BC) acts as a short-lived greenhouse gas and is associated with enhanced morbidity, respiratory and cardiovascular disease. Thus, reducing BC emissions results in a win-win situation for both climate and health. However, uncertainties in BC emissions are still quite large. We provide a comparison between two detailed emission inventories for Germany: CAMS and GRETA. Differences in the BC inventories are found because of differences in PM emission factors for specific source sectors and differences in used BC fractions in PM composition splits that speciate the total reported PM into species. These are related to assumptions within each emission sector. The focus was on the residential heating sector (stoves) and the transport sector (e.g. diesel exhaust), which are the sectors that contribute most to BC. Differences were addressed based on literature reviews and a new consistent BC emission inventory was created.

Baseline GRETA emissions and the new emission set were used in the regional-scale LOTOS-EUROS chemistry-transport model to calculate BC ambient air concentrations over Germany, including labeling of source sectors and source areas. By making use of the labelled concentrations, the impact of increasing emissions from specific sources and areas can be explored quickly, allowing to give directions for further refinement of the emission inventory and emission distribution. Modelled concentrations were compared with observations of ambient BC concentrations from filter analysis and aethalometer data. Different types of locations (different regions, urban/rural) were used to evaluate the different aspects of the emission changes in detail. Our first findings suggest that emissions from agricultural machinery need redistribution in space by using a different proxy, that residential combustion emissions are still underestimated in some but not all parts of the country, and that contributions from road transport were still underestimated.

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BIOMASA KAO OBNOVLJIVI IZVOR ENERGIJE U EU ETS-U

Ključne riječi: *besplatna dodjela emisijskih jedinica, CO_2*

Biomasa je kao energent u sve većoj upotrebi u industriji 21. stoljeća. Prilikom korištenja biomase kao oblika obnovljive energije dolazi do ispuštanja CO_2 apsorbiranog tijekom rasta biljaka te emitiran natrag u atmosferu prilikom gorenja. Takav sustav se najčešće naziva „ugljik – neutralnim".

Svrha rada je prikazati prednosti korištenja biomase i njenu korist u sustavu praćenja emisije stakleničkih plinova te prednost pri besplatnoj dodjeli emisijskih jedinica za razdoblje 2021.-2030. sukladno Direktivi (EU) 2003/87 i Delegiranoj Uredbi Komisije (EU) 2019/331. Prikazano je korištenje biomase u različitim industrijskim djelatnostima, njena korist kao i energetska vrijednost različitih tipova biomase. Također, primjeri prikazuju dodjelu besplatnih emisijskih jedinica s korištenjem biomase i bez korištenja biomase u istim industrijskim djelatnostima. Iz primjera se vidi iznimna korist korištenja biomase što postaje sve značajnije u procesu trgovanja za razdoblje 2021.-2030. gdje se količina emisijskih jedinica linearno godišnje smanjuje uz faktor 2,2 %. Rad ujedno prikazuje i nedostatke korištenja biomase u smislu skladištenja, određivanja udjela biomase kod heterogenih smjesa i emisije krutih čestica u zrak. Ovime se želi ukazati na ulogu biomase u nacionalnom sustavu za praćenje provedbe politike, mjere i projekcije za smanjenje emisija stakleničkih plinova kao i stvarnu financijsku korist korištenja biomase u EU ETS (eng. European Union Emissions trading system) odnosno Europskom sustavu trgovanja emisijskim jedinicama stakleničkih plinova.

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BIOMASS AS A RENEWABLE ENERGY SOURCE IN EU ETS

Keywords: *free allocation emission unit, CO_2*

Biomass as an energy source is increasingly used in the industry of the 21st century. When using biomass, CO_2 emissions are absorbed during plant growth and returned to the atmosphere during burning. Such a system is commonly referred to as "carbon-neutral".

The purpose of this paper is to demonstrate the benefits of using biomass and its benefits in a greenhouse gas emission monitoring system and the free allocation of emission allowances for the period 2021-2030 in accordance with Directive (EU) 2003/87 and Delegated Commission Regulation (EU) 2019/331.

The paper presents the use of biomass in different industrial activities, benefits and net calorific values of different types of biomass. Also, examples are the allocation of free emission units with the use of biomass and without the use of biomass in the same industrial activities. The exceptional benefit of using biomass is visible, and it is becoming more and more significant in the trading phase for the period 2021-2030 where the amount of emission units decreases linearly annually with a factor of 2.2%. The paper also shows a lack of biomass use in terms of storage, determination of biomass fraction in heterogeneous mixtures and emission of particles matters into the air. We hereby point to the role of biomass in the national system for monitoring the implementation of policies, measures and projections for the reduction of greenhouse gas emissions as well as the real financial benefit of biomass use in the EU ETS (European Union Emissions Trading System) or the European Emission Trading System for Greenhouse Gas.

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UTJECAJ PROMJENA U ČETVRTOM RAZDOBLJU TRGOVANJA EMISIJSKIM JEDNICAMA STAKLENIČKIH PLINOVA NA ELEKROENERGETSKI SUSTAV

Ključne riječi: *trgovanje, emisijske jedinice, četvrto razdoblje, elektroenergetski sustav*

Cilj rada je dati prikaz promjena u četvrtom razdoblju europskog sustava trgovanja emisijskim jedinicama stakleničkih plinova (EU-ETS) koje će trajati od 2021. godine do 2030. godine te opisati utjecaj tih promjena na elektroenergetski sustav Hrvatske. Najznačajnija promjena u četvrtom razdoblju trgovanja je mogućnost korištenja sredstava iz Fonda za modernizaciju energetskog sektora. Sredstva iz ovog fonda mogu se koristiti za financiranje projekata koji imaju za cilj dekarbonizaciju elektroenergetskog sektora, povećanje energetske učinkovitosti u proizvodnji, prijenosu i distribuciji energije te povećanje udjela obnovljivih izvora energije u proizvodnom portfelju. Povećanje godišnjeg lineranog faktora s 1,74% na 2,2,% ukupnih emisijskih jedinica koje se uklanjaju s tržišta i poništavaju te mehanizam povlačenja jedinica u rezervu za postizanje stabilnosti tržišta (eng. Market Stability Reserve), uvode se s ciljem smanjenja viška emisijskih jedinica na tržištu, povišenja njihove cijene te poticanje emitera na smanjenje emisija. Prva velika promjena u cijeni emisijskih jedinica dogodila se u 23.8.2018. godine kada je cijena općih emisijskih jedinica (EUA) prvi puta u trećem razdoblju trgovanja prešla 20 eura po toni i od tada je u stalnom porastu, a za očekivati je da će i dalje rasti te imati sve većeg utjecaja na varijabilni trošak cijene energije. Unatoč prethodnim najavama da se u četvrtom razdoblju trgovanja neće dodjeljivati besplatne emisijske jedinice za proizvodnju toplinske energije koja se predaje u centralni toplinski sustav, ova mogućnost se zadržava i u razdoblju od 2021. do 2030. godine, no metodologija izračuna na temelju kojeg će se dodjeljivati besplatne emisijske jedince znano je postrožena. U pisanju rada korišteni su europski i hrvatski zakonski propisi iz područja zaštite zraka i klime te trgovanja emisijskim jedinicama stakleničkih plinova, analize i studije strukovnih udruženja i europskih tvrtki koje se bave analizama funkcioniranja sustava trgovanja i kretanju njihove cijene na tržištu. Sve promjene u europskoj politici vezanoj za smanjenje emisija stakleničkih plinova s naglaskom na sustav trgovanja emisijskim jedinicama stakleničkih plinova kao i odredbe Pariškog sporazuma imaju utjecaja na promjenu proizvodnog potrfelja u hrvatskom elektroenergetskom ustavu koji se okrenuo obnovljivim izvorima energije i e-mobilnosti te povećanju energetske učinkovitosti.

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IMPACT OF CHANGES IN THE FOURTH PERIOD OF EMISSION TRADING SYSTEM ON THE ENERGY SECTOR

Keywords: *emission trading, emission allowances, fourth period, energy sector*

The aim of this study is to present the changes in the fourth period of the European Emission Trading System (EU-ETS), which will last from 2021 to 2030 and describe the impact of these changes on the Croatian power system. The most significant change in the fourth trading period is the possibility of using funds intended for the modernization of the energy sector. Funds from this fund can be used to finance projects aimed at decarbonising the power sector, increasing energy efficiency in energy generation, transmission and distribution and increasing the share of renewable energy sources in the production portfolio. The increase in the annual linear factor from 1.74 to 2.2% of total emission allowances and the withdrawal mechanism of the allowances in the Market Stability Reserve are introduced with the intention to reduce the allowances surplus on the market, increase their prices, and encourage installations to reduce emissions. The first major allowances price change occurred on 23rd Aug 2018 when the price for the first time in the third trading year exceeded 20 euros per tonne and since then it has been steadily rising and is expected to continue to grow and have more and more influence on the variable cost of energy prices. Notwithstanding previous announcements that during the fourth trading period there will be no free emission allowances for heat production delivered to the central heating system, this option will be retained in the period between 2021 and 2030 but the calculation methodology will be stricter. European and Croatian legislation in the field of air and climate protection and greenhouse gas emission trading system are also discussed in the paper, dealing with the analysis of the functioning of the trading system and their market prices. All changes in the European greenhouse gas emission reduction policy with an emphasis on the greenhouse gas emission trading system as well as the provisions of the Paris Agreement have an impact on the Croatian power generation portfolio that revolves around renewable energy sources of energy, e-mobility and energy efficiency.

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UTJECAJ PRIJEDLOGA DIREKTIVE 2003/87/EC RADI POBOLJŠANJA TROŠKOVNO UČINKOVITIH SMANJENJA EMISIJA I ULAGANJA ZA NISKE EMISIJE UGLJIKA NA HEP

Ključne riječi: *koncentracije SO_2 u dimnim plinovima, VDI 3921*

Nakon rekonstrukcije regenerativnog rotacijskog izmjenjivača topline (REGAVO) obavljena su mjerenja emisijskih koncentracija SO_2 i O_2 dimnih plinova u dijelu sustava odvoda dimnih plinova koji su produkt izgaranja kamenog ugljena. Sustav je vezan za regenerativni izmjenjivač dimnih plinova i apsorber SO_2, prije odvoda u dimnjak. REGAVO služi za hlađenje dimnih plinova, prije ulaska u apsorber u kojem se korištenjem vapnenca uklanjaju spojevi sumpora u dimnim plinovima te za ponovno grijanje dimnih plinova, nakon izlaska iz apsorebera, a prije ulaska u dimnjak.

Izmjerene koncentracije SO_2, izražene su mg/m^3, preračunate na 6 % sadržaj kisika u dimnim plinova te svedene na normirane uvjete tlaka od 101325 Pa i temperature od 273,15 K, što su uobičajeni zahtjev za ložišta termoelektrana koja koriste ugljen kao gorivo. Mjerenje je obavljeno sa tri neovisna automatska mjerna sustava sa pripadajućim sustavima za pripremu plinova, primjenom HRN EN 14789 za mjerenje koncentracija O_2 i HRN ISO 7935 za mjerenje koncentracija SO_2. U svrhu utvrđivanja propuštanja SO_2, na REGAVO-u su obavljena mjerenja u 3 mjerne ravnine istovremeno. U svakoj mjernoj ravnini su izmjerene koncentracije SO_2 i O_2 u 30 mjernih točaka prema zahtjevu VDI 3921. Mjerenja su obavljena u mjernoj ravnini 1 u sirovom dimnom plinu ispred REGAVO ($SO_{2(1)}$), mjernoj ravnini 3 u čistom dimnom plinu ispred REGAVO ($SO_{2(3)}$) i mjernoj ravnini 4 u čistom dimnom plinu nakon REGAVO ($SO_{2(4)}$).

Propuštanje SO_2 je izraženu u % i definirano formulom:

ΔSO_2 (%) izmjereno = $[(SO_{2(4)} - SO_{2(3)}) / SO_{2(1)}] \cdot 100$

Prilikom mjerenja su osigurani zahtjevi projekta prema kojima je utvrđen:

- unos energije goriva u iznosu os 24,5- 29,3 GJ/t,
- maksimalno opterećenje kotlova uz proizvodnju pare od 670 t/h
- proizvodnja električne energije od oko 218 MWh
- korištenje kamenog ugljena sa udjelom sumpora od 0,3 do 1,4 %.

Provedena su dvodnevna garantna mjerenja u trajanju od 4 sata sa minimalnim trajanjem mjerenja od 5 minuta po mjernoj točki, što je zahtjev VDI 3921. Prosječan rezultat propuštanja SO_2 (ΔSO_2) je 0,865 %.

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LEAKAGE CHECK FOR SO_2 ON THE REGENERATIVE ROTATING CHANNEL OF HEAT EXCHANGER (REGAVO) IN THE HEP PROIZVODNJA D.O.O. – TE PLOMIN 2

Keywords: *SO_2 concentration in waste gases, VDI 3921*

After the reconstruction of the regenerative heat exchanger (REGAVO), the emissions of SO_2 and O_2 were measured in flue gases in the part of the flue gas system, which is the product of combustion of coal, connected to the regenerative flue gas exchanger and the SO_2 absorber, before chimney drainage. REGAVO is used for flue gas cooling before entering an absorber where smoke is smoked by flue gas, and for re-heating flue gas, after leaving the absorber, before entering the chimney.

The measured SO_2 concentrations, expressed in mg / m^3, are standardized to 6% smoke content in flue gases, 101325 Pa pressure and 273.15 K temperature, which is a common requirement for fuel cells of coal-fired power plants. The measurement was carried out with three independent automated measuring systems with associated gas preparation systems, using HRN EN 14789 for measuring the O_2 and HRN ISO 7935 concentrations for SO_2 concentration measurement. Due to the need to determine SO_2 leakage on the side of raw flue gas, REGAVO was measured in 3 measuring planes at the same time. In each measuring plane, SO_2 and O_2 concentrations were measured in 30 metering points according to VDI 3921. Measurements were made in: measuring plane 1 in raw waste gas in front of REGAVO ($SO_{2(1)}$), measuring plane 3 in clean waste gas in front of REGAVO ($SO_{2(3)}$) and measuring plane 4 in clean waste gas after REGAVO ($SO_{2(4)}$).

Leakage of SO_2 was expressed in % and defined by the formula:

$$\Delta SO_2\ (\%)\ measured = [(SO_{2(4)} - SO_{2(3)}) / SO_{2(1)}] \cdot 100$$

During the measurements, the project requirements were established as follows:

- *- Fuel intake in the amount of 24.5 to 29.3 GJ/t,*
- *- maximum boiler load, with steam production of 670 t/h,*
- *- Electricity production of about 218 MWh,*
- *- use of coal with sulphur content of 0.3 to 1.4%.*

Two-day guarantee measurements lasting 4 hours were performed with a minimum measurement time of 5 minutes per metering point, which is the VDI 3921 requirement. The average leakage rate of SO_2 (ΔSO_2) is 0.865 %.

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UPORABA ALTERNATIVNIH GORIVA U CEMENTNOJ INDUSTRIJI I SMANJENJE EMISIJA CO_2 NA PRIMJERU NAŠICECEMENTA D.D.

Ključne riječi: *cement, stakleнički plinovi, alternativne goriva, gorivo iz otpada*

Stakleнički plinovi su jedan od velikih izazova današnjeg doba. Svjedoci smo kontinuiranog truda na globalnoj razini da se ove emisije smanje i dovedu pod kontrolu. Pri tome najveći zagađivači snose i najveću odgovornost. Cementna industrija je materijalno i energetski intenzivna industrija koja doprinosi sa oko 4-5% emisija CO_2 na svjetskoj razini. U Republici Hrvatskoj taj udio je oko 10%. Emisije koje nastaju se mogu podijeliti na procesne emisije i emisije od sagorijevanja. Emisije od sagorijevanja čine oko 40 % udjela u ukupnim emisijama tvornice, a ovise o vrsti goriva koje se koristi. Ostalih 60 % su emisije iz procesa proizvodnje klinkera, koje su posljedice tipičnih kemijskih reakcija dekarbonatizacije sirovine.

Osnovni energenti u proizvodnji klinkera su prirodni plin, ugljen visoke kvalitete, petrolkoks te alternativna goriva: otpadne gume, otpadna ulja I. i II. kategorije i gorivo iz otpada. Tijekom 2018. u Našicecementu započelo se s doziranjem goriva iz otpada čime se znatno povećala supstitucija fosilnih goriva sa 6 na 16 %. Zamjena fosilnih goriva sa alternativnim gorivima u proizvodnji cementa je dugogodišnja praksa cementne industrije Europske Unije, a sve značajnija postaje i u Republici Hrvatskoj. Uzroka tome je više, od ekonomske do okolišne prirode. Fosilna goriva su ograničeni resursi i samim time njihova količina se vremenom smanjuje, a cijena raste te je opstanak proizvodnje povezan sa sposobnošću učinkovite zamjene fosilnih goriva alternativnim. Našicecement d.d. kao i cijela industrija proizvodnje cementa igra veliku ulogu u gospodarenju otpadom. Priroda procesa je takva da nema ostataka već se svi proizvodni produkti ugrađuju u klinker ili izlaze u obliku emisija u zrak van. Ovim načinom upotrebe otpada smanjuje se potreba za odlaganjem otpada te se doprinosi ostvarivanju ciljeva postavljenih kroz Direktivu 1999/31/EZ o odlagalištima otpada odnosno kroz Ugovorom o pristupanju Republike Hrvatske Europskoj uniji. Korištenjem alternativnih goriva smanjuju se i emisije stakleničkih plinova.

Gorivo iz otpada koje se upotrebljava u postrojenju proizvodi se u kontroliranim uvjetima i mora udovoljavati standardima opisanima u normi HRN EN ISO 15359:2012 da bi se uopće moglo koristiti kao zamjensko gorivo za dobivanje energije u industrijskim pogonima. Doziranje goriva iz otpada u postrojenju provodi se u kontroliranim uvjetima uz redovne analize ulaza otpada u pogonskom laboratoriju, a povremene analize provode se u vanjskom akreditiranom ispitnom laboratoriju. Vanjski ispitni laboratoriji u uzorcima goriva iz otpada određuje udio vode, donju ogrjevnu vrijednost, udio ugljika te udio biomase. Za određivanje biogenog udjela u gorivu iz otpada primjenjuje se metoda selektivnog raspadanja prema standardu HRN EN 15440:2011, a analize su pokazale da udio biogene komponente varira od 18 do 51%. što ovisi o vrsti goriva iz otpada. Navedeni izvor toka sadrži biomasu, a izvori emisija iz navedene biomase izvještavaju se kao jednaki nuli. Rezultati pokazuju značajne pozitivne utjecaje na emisije CO_2, ali i na proizvodnju i poslovanje.

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USE OF ALTERNATIVE FUELS IN THE CEMENT INDUSTRY AND CO_2 EMISSION REDUCTION IN NAŠICECEMENT D.D.

Keywords: *cement, greenhouse gases, alternative fuels, waste derived fuel*

Greenhouse gases are one of the greatest challenges of our age. We are witnessing continuous efforts on a global scale to reduce their emission and control them. With this in mind, the biggest polluters hold the biggest responsibility. The cement industry is an intense industry with regard to material and energy consumption which contributes 4 to 5% to total CO_2 emissions on the global scale. In Croatia, the cement industry contributes with around 10% to total national emissions. These emissions can be divided into process emissions and combustion emissions. Combustion emissions make about 40% of total facility emissions. They are dependent on the type of fuel used. The other 60% are emissions coming from the clinker production process resulting from typical chemical reactions of raw material decarbonisation. Replacing fossil fuels with alternative fuels in the cement industry has been a long standing practice of the cement industry in Europe and is becoming more significant in Croatia. The reasons vary from economic to environmental. Fossil fuels are limited resources and hence their amount decreases over time. Prices are rising and production survival is linked to the ability to effectively replace fossil fuels. Našicecement d.d. as well as the entire cement production industry plays a major role in waste management. The nature of the process is such that there are no residues, but all the production products are embedded in clinker or air emission outputs. This waste disposal method reduces the need for waste disposal and contributes to the achievement of the objectives set out in Directive 1999/31/EC on waste landfills through the Treaty of Accession of the Republic of Croatia to the European Union. Using alternative fuels reduces greenhouse gas emissions. Basic energy sources in clinker production are natural gas, steam coal, petroleum coke and alternative fuels: waste tires, waste oils of I and II categories and waste-derived fuel. The year 2018 saw the beginning of fuel filling from waste derived fuel, thus significantly increasing the substitution of fossil fuels from 6 to 16%. Waste-derived fuel used in the plant Našicecement is manufactured under controlled conditions and must meet the standards described in HRN EN ISO 15359:2012 to even be used as a replacement fuel for generating energy in industrial plants. Co-incineration of waste derived fuel into the plant is carried out under controlled conditions with regular analysis of waste inputs in the driving laboratory, while occasional analyses are carried out by an external accredited test laboratory. External test laboratory determines the water content, net calorific value, the carbon content, and the biomass fraction in waste-derived fuel samples. To determine the biogenic fraction in waste fuel, a selective decomposition method according to HRN EN 15440:2011 is used and analysis showed that the biogenic component content varies from 18 to 51% depending on the type of fuel from the waste. The mentioned source stream contains biomass, and where biomass is contained in a source stream, the emissions stemming from this biomass are reported as zero. The results show positive impact on CO_2 emissions and production and company business as well.

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Tema 3
Onečišćenje vanjske atmosfere – imisije

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SOURCE ATTRIBUTION OF PM FOR NORTHWESTERN EUROPEAN CITIES USING LOTOS-EUROS

Keywords: *source apportionment, air quality modelling, emission modelling*

Air Quality in northwestern Europe is a problem especially during winter episodes. During such episodes the buildup of pollutants released within a city is just one factor contributing to the high concentrations. During conditions with easterly winds and inversion situations with low planetary boundary layer heights pollutants produced in eastern Europe are adverted to Dutch and German cities. To support the development of the air quality plans the origin of the pollution for the annual mean and during episodes is required.

To be able to attribute the share of the overall pollution in cities for 2014-2017 to its origins the labelling approach incorporated in the Chemistry Transport Model (CTM) LOTOS-EUROS v2.1 is used. For the emission datasets used to drive the model, some specifications were done including emission dependencies on temperature (e.g. cold starts of engines and heating degree days for households). During winter episodes agriculture and residential combustion are the most important sectors, each contributing about 30% to $PM_{2.5}$ mass. Secondary contributions come from industry, energy production and traffic. The latter is the most important local source. Only during the highest episodes the Polish contribution to $PM_{2.5}$ exceeds that of Germany, whereas the Polish contributions are generally as high as the combined contribution of other eastern European countries. The model results are evaluated against the AirBase monitoring sites.

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KARAKTERIZACIJA I ODREĐIVANJE PORIJEKLA ČESTICA NAD SREDNJIM JADRANOM: PRIMJENA LOTOS-EUROS ATMOSFERSKOG MODELA

Ključne riječi: *lebdeće čestice, porijeklo onečišćenja PM, kemijski sastav PM, primjena atmosferskog modela, srednji Jadran*

Najveća nesigurnost u procjenama antropogenih klimatskih pritisaka povezana je s atmosferskim lebdećim česticama odnosno aerosolima (engl. particulate matter, PM) zbog nedovoljnog poznavanja njihovog porijekla, kemijskog sastava kao i atmosferskih (trans)formacija i taloženja. Jadransko more se nalazi pod kombiniranim utjecajem različitih lokalnih, regionalnih i dalekosežnih prirodnih i antropogenih izvora. Glavnina danas dostupnih podataka o kemiji atmosferskih aerosola i njihovim izvorima, odnose se na studije provedene na zapadnim i istočnim dijelovima Mediterana dok je samo limitirani broj studija proveden na području Jadranskog mora i one su ograničene na područje sjevernog Jadrana.

Tako, uz iznimku sjevernog Jadrana i područja u okolici Venecije, ne postoje detaljna istraživanja porijekla i sastavnica atmosferskih lebdećih čestica na području Jadranskog mora.

Primjena atmosferskog kemijskog modela LOTOS-EUROS omogućit će identifikaciju i kvantifikaciju glavnih izvorišnih područja i procesa koji imaju utjecaj i doprinose taloženju lebdećih čestica na područje srednjeg Jadrana u periodu eksperimentalnih mjerenja od veljače do srpnja 2019. godine.

Zahvala: Ovaj rad je financirala Hrvatska zaklada za znanost IP-2018-01-3105 projektom: Biokemijski odgovori površinskog sloja oligotrofnog područja Jadranskog mora na atmosfersko taloženje.

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CHARACTERIZATION AND SOURCE APPORTIONMENT OF PARTICULATE MATTER OVER THE MIDDLE ADRIATIC SEA: LOTOS-EUROS MODELLING STUDY

Keywords: *source apportionment, modelling study, Middle Adriatic, particle matter, characterisation of PM*

Atmospheric particulate matter (PM) has the highest uncertainty among the components contributing to anthropogenic climate forcing. This uncertainty is largely due to insufficient knowledge of aerosol sources, chemical composition as well as their atmospheric (trans)formation and removal. The Adriatic area is under the combined influence of local, regional and long-distance natural and pollution sources. While large efforts have been devoted to the investigation of the sources and chemical composition of PM in the western and eastern part of the Mediterranean basin, only a limited number of studies have been related to the Adriatic Sea sub-basin. Thus, with the exception of the northern part and the area in the vicinity of Venice, no extensive investigations discussing together the chemical composition and source apportionment of atmospheric PM have been conducted in the Adriatic Sea. In order to contribute to filling the gap of observations in the Mediterranean and gain more insight into atmospheric dynamical and chemical mechanisms, this work focused on the source apportionment of aerosol particles and its dominant constituents (e.g. nitrates) in the Middle Adriatic area. Application of the LOTOS-EUROS model will enable the identification and quantification of main source areas and processes contributing to the deposition of particulate matter over Middle Adriatic during the experimental period February-July 2019.

Acknowledgements: This work was supported by the Croatian Science Foundation under the IP-2018-01-3105 project: Biochemical responses of oligotrophic Adriatic surface ecosystems to atmospheric deposition inputs.

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INDOOR AND OUTDOOR PM CHARACTERIZATION AT HOMES AND SCHOOLS, IN LISBON, PORTUGAL

Keywords: *PM_{10}/$PM_{2.5}$, indoor-outdoor chemical composition, residences, schools*

The chemical composition of atmospheric particulate matter (PM) may provide insight into their emission sources and formation processes, as well as their health impact. In this framework, a comprehensive characterization of the ambient and indoor aerosol in micro-environments critical for children exposure (homes and schools) has been performed in Lisbon, Portugal. The obtained chemical composition database was used to assess the concentration levels of specific PM_{10} and $PM_{2.5}$ components and the relative contribution of indoor and outdoor sources. 40 residences and 5 schools, covering areas of the city with different characteristics, were studied for 5 consecutive days each. Indoor and outdoor $PM_{2.5}$ and $PM_{2.5-10}$ samples were simultaneously collected and analysed for major and trace elements and organic (OC) and elemental carbon (EC).

The observed concentration levels were typical of urban environment. The ambient concentrations of soil and road dust related elements were elevated at the school sites in comparison to homes, suggesting higher contribution from road traffic at the areas where the schools are located. Indoor aerosol at homes was significantly enriched in carbonaceous components and in smaller particle sizes, due to their more effective penetration indoors. Correlation between indoor and outdoor OC concentrations revealed the impact of both indoor and outdoor sources inside homes and significant impact of children's and teaching activities in schools. EC and most major and trace elements observed indoors were found to be of ambient origin; nevertheless, indoor coarse particle concentrations at schools were also affected by resuspension, due to children's intense activity.

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PREKORAČENJA DNEVNE GRANIČNE VRIJEDNOSTI KONCENTRACIJA PM_{10} NA GRADSKOJ POZADINSKOJ MJERNOJ POSTAJI U ZAGREBU TIJEKOM RAZDOBLJA 2001.-2018.

Ključne riječi: *PM_{10}, $PM_{2.5}$, prekoračenje, sezonska ovisnost*

Masene koncentracije frakcije lebdećih čestica PM_{10}, izmjerene na pozadinskoj gradskoj mjernoj postaji Ksaverska cesta u Zagrebu tijekom osamnaestogodišnjeg razdoblja (2001. – 2018. godina), obrađene su s obzirom na učestalost prekoračenja dnevne granične vrijednosti od 50 μg m^{-3} tijekom kalendarske godine, trend učestalosti tijekom mjernog razdoblja, sezonsku ovisnost, te ovisnost o koncentracijama pod-frakcija PM_{10} ($PM_{2.5}$ i $PM_{10-2.5}$ - coarse fraction). Prekoračenja su zabilježena u prosjeku 52 puta godišnje, odnosno u nešto više od 14% mjerenja. Polovina od ukupnog broja prekoračenja (938) odnosi se na koncentracije niže od 65 μg m^{-3}, dok je kod svega 12% prekoračnja izmjerena koncentracija PM_{10} viša od 100 μg m^{-3}. Vidljiv je opadajući trend broja prekoračenja od -2,8 god^{-1} što predstavlja značajan pad od približno 48 zabilježenih prekoračenja godišnje u posljednjoj u odnosu na prvu godinu mjernog razdoblja. Prekoračenja su zabilježena u prva tri i zadnja tri mjeseca kalendarske godine, dok je njihov broj tijekom ostatka godine bio zanemariv. Vidljivo je da koncentracije grube frakcije čestica ne koreliraju s koncentracijama prekoračenja, već slobodno variraju očito kao posljedica lokalnih izvora. Nasuprot tome koncentracije $PM_{2.5}$ u danima prekoračenja vrlo dobro koreliraju s koncentracijama PM_{10} (R=0,940) i njihov prosječan doprinos masi PM_{10} iznosi 90%, što je mnogo više nego u danima bez prekoračenja. Iz navedenog se može zaključiti da su izvori $PM_{2.5}$ tijekom hladnog razdoblja godine osnovni razlog prekoračenja dnevne granične vrijednosti PM_{10}. Razlika u dominantnim izvorima $PM_{2.5}$ određenim između dvije grupe podataka za dane s koncentracijama PM_{10} ispod s onima iznad granične vrijednosti od 50 μg m^{-3} ukazala bi na izvore prekomjernog onečišćenja, te na taj način posredno omogućila potrebne mjere za poboljšanje kvalitete zraka. Korekciju broja prekoračenja dnevne koncentracije PM_{10} nije preporučljivo izvoditi s obzirom na ukupni obuhvat podataka (dozvoljena granica od minimalno 90%), već ju treba provesti prilagođeno sezonskoj raspodjeli. No i taj način korekcije, s obzirom na trend smanjenja broja prekoračenja godišnje postaje upitan, odnosno nepotreban pri jednoliko raspoređenim izostancima mjerenja tijekom godine.

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EXCEEDANCES OF PM_{10} DAILY LIMIT VALUE AT AN URBAN BACKGROUND STATION IN ZAGREB 2001-2018

Keywords: *PM_{10}, $PM_{2.5}$, exceeding, seasonal dependence*

Mass concentrations of the PM_{10} particle fraction measured at the urban background station Ksaverska cesta in Zagreb during the 2001-2018 period were analysed with regard to the frequency of exceedances of the daily limit value (50 μg m^{-3}), trend of occurrence for the measuring period, seasonal dependence and its relation to PM_{10} sub-fractions ($PM_{2.5}$ and $PM_{10-2.5}$ CF-coarse fraction). On average, 52 excess values were measured in one year (14% of total samples). One half of exceeding concentrations (938) were lower than 65 μg m^{-3}, while only 12% were higher than 100 μg m^{-3}. A descending trend of -2.8 $year^{-1}$ was detected, which means that the yearly number of excess concentrations dropped for 48 during the measuring period. Exceedances occurred mainly during the first three and last three months of the year, while their number in the rest of the year was negligible. Coarse fraction concentrations varied freely and did not show any correlation with exceeding PM_{10} concentrations, obviously originating from local sources. $PM_{2.5}$ concentrations for days with exceeding PM_{10} concentrations showed a strong correlation with PM_{10} concentrations (R=0.940) and represent in average 90% of its mass. The difference in source apportionment results for PM_{10} in two separate groups of results (days with and without exceeding PM_{10} concentration values) could point to specific $PM_{2.5}$ sources and thereby enable measures for air quality improvement. Corrections of the total number of excess concentrations should not be based on data capture rate (90% minimum), but rather rely on the observed seasonal distribution. However, even this type of correction is questionable with regard to the descending trend, especially if the days with exceeding concentrations are spread uniformly over the year.

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RAZINE MASENIH KONCENTRACIJA U VODI TOPLJIVIH KOMPONENTI U $PM_{2,5}$ FRAKCIJI LEBDEĆIH ČESTICA U ZRAKU ZA RAZDOBLJE 2014. – 2018.

Ključne riječi: *onečišćenje zraka, anioni, kationi, ionska kromatografija*

Prikazani su rezultati kontinuiranih mjerenja sadržaja u vodi topljivih komponenti anioni (Cl^-, NO_3^-, SO_4^{2-}) i kationi (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) u $PM_{2,5}$ frakciji lebdećih čestica u zraku za razdoblje 2014. - 2018. godine.

Uzorci čestica sakupljani su na dvije pozadinske mjerne postaje i to: urbana mjerna postaja (UMP) u sjevernom dijelu Zagreba i ruralna mjerna postaja (RMP) Plitvička jezera tijekom 24-satnih razdoblja od 01. siječnja 2014. do 31. prosinca 2018. godine (UMP) te od 17. srpnja 2014. do 31. prosinca 2018. godine (RMP). Uzorci su sakupljani sukladno normama HRN EN 14907:2006 (EN 14907:2005) i HRN EN 12341:2014 (EN 12341:2014). Masena koncentracija čestica određena je gravimetrijski sukladno zahtjevima normi. Sadržaj u vodi topljivih komponenti aniona (Cl^-, NO_3^-, SO_4^{2-}) i kationa (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) u $PM_{2,5}$ frakciji čestica nakon otapanja na ultrazvučnoj kupelji određen je ionskom kromatografijom na uređaju Thermo Scientific – ICS 5000 Capillary.

Razine masenih koncentracija mjerenih onečišćujućih tvari pokazuju značajnu prostornu i vremensku ovisnost s višim vrijednostima određenim na pozadinskoj urbanoj mjernoj postaji (UMP). Za promatrano razdoblje mjerenja srednje godišnje vrijednosti masenih koncentracija $PM_{2,5}$ frakcije čestica izmjerene su u rasponu od 18,6 μg m^{-3} do 22,7 μg m^{-3} na pozadinskoj urbanoj mjernoj postaji (UMP), dok su za ruralnu postaju (RMP) izmjerene vrijednosti u rasponu od 7,5 μg m^{-3} do 9,4 μg m^{-3}.

Srednje godišnje vrijednosti masenih koncentracija mjerenih iona na UMP postaji slijedile su niz $SO_4^{2-} > NO_3^- > NH_4^+ > K^+ > Ca^{2+} > Cl^- > Na^+ > Mg^{2+}$, a njihov ukupni doprinos masi $PM_{2,5}$ frakcije lebdećih čestica bio je u rasponu od 26,5% do 31,5%, dok je za RMP postaju taj niz bio $SO_4^{2-} > NH_4^+ > NO_3^- > K^+ > Ca^{2+} > Na^+ > Mg^{2+} > Cl^-$, a ukupni doprinos masi $PM_{2,5}$ frakcije lebdećih čestica u rasponu od 31,4% do 39,2 %.

Srednje godišnje vrijednosti omjera masenih koncentracija nitrata i sulfata (NO_3^-)/(SO_4^{2-}) u $PM_{2,5}$ frakciji lebdećih čestica bile su u rasponu od 0,76 do 1,07 na pozadinskoj urbanoj mjernoj postaji (UMP), dok su za ruralnu postaju (RMP) izmjerene vrijednosti bile u rasponu od 0,19 do 0,35, što upućuje na dominantnost mobilnog izvora (prometa) za postaju UMP.

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LEVELS OF MASS CONCENTRATIONS OF WATER–SOLUBLE COMPONENTS IN $PM_{2.5}$ PARTICLE FRACTION IN AIR FOR THE PERIOD 2014 – 2018

Keywords: *air pollution, anion species, cation species, ion chromatography*

Daily $PM_{2.5}$ samples were taken over five years 2014 – 2018 at two measuring sites classified as urban background site (UBS) in northern part of Zagreb, and rural background site (RBS) at Plitvice Lakes. Samples were analysed for water-soluble anion species (Cl^-, NO_3^-, SO_4^{2-}) and cation species (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}), to investigate the relationship between pollutant mass concentrations, contribution of measured species to $PM_{2.5}$ mass and prediction of the pollutant sources.

Mass concentrations of $PM_{2.5}$ particle fraction were determined by gravimetry according to the standard HRN EN 14907:2006 (EN 14907:2005) and HRN EN 12341:2014 (EN 12341:2014). Water-soluble ionic species were analysed using Thermo Scientific – ICS 5000 Capillary ion chromatography.

Mass concentrations of measured pollutants were significantly influenced by the season and the location of sampling sites, reaching their high values at UBS. Annual average $PM_{2.5}$ mass concentration ranged from 18.6 μg m^{-3} to 22.7 μg m^{-3} at UBS and from 7.5 g m^{-3} to 9.4 μg m^{-3} at RBS, respectively.

The annual average ion mass concentrations at UBS and RBS followed the order $SO_4^{2-} > NO_3^- > NH_4^+ > K^+ > Ca^{2+} > Cl^- > Na^+ > Mg^{2+}$ and $SO_4^{2-} > NH_4^+ > NO_3^- > K^+ > Ca^{2+} > Na^+ > Mg^{2+} > Cl^-$, respectively, contributed from 26.5% to 31.5% and from 31.4% to 39.2% to the overall $PM_{2.5}$ mass, respectively.

Annual average mass ratios of $(NO_3^-)/(SO_4^{2-})$ obtained in $PM_{2.5}$ ranged from 0.76 to 1.07 at UBS and from 0.19 to 0.35 at RBS, respectively, indicating that mobile source emission was an important contributor to particle mass at UBS.

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FRAKCIJE LEBDEĆIH ČESTICA U ATMOSFERI GRADA RIJEKE

Ključne riječi: *kaskadni impaktor, metali, ioni ,WSOC*

Kao nastavak MED projekta POSEIDON, koji se bavio utjecajem emisija iz pomorskog prometa na onečišćenje atmosfere u Rijeci, u INTERREG IT-HR projektu ECOMOBIITY, nastavljeno je s karakterizacijom frakcija lebdećih čestica sakupljenih 10-stupanjskim kaskadnim impaktorom nominalnih «cut-off» veličina od 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10 i 0.056 μm u razdobljima: 16.10.-10.12.2018 i 26.03.-21.05.2019. U tom je razdoblju sakupljeno po osam 7-dnevnih uzoraka. U prvom tjednu uzorkovanja sakupljeni su uzorci lebdećih čestica čije su koncentracije bile višestruko više od koncentracija u narednim tjednima. Masena koncentracija čestica u tom tjednu iznosila je 143 μg/m^3, dok su se u ostalim tjednima ti prosjeci kretali u rasponu 9,0-37,4 μg/m^3. Raspodjela masenih koncentracija lebdećih čestica po veličini pokazuje bimodalnu krivulju s maksimumom u frakciji S4 (raspon promjera čestica d = 1,8-3,2 μm) i S8 (d=0,18-0,32 μm). Raspodjela masenih koncentracija čestica po veličini za uzorak sakupljan prvi tjedan se ponešto razlikuje, te je pored sekundarnog maksimuma u S4 zabilježen i primarni maksimum u S6 (d= 0,56-1,0 μm) te treći u S10 (d=0,056-0,10 μm). Raspodjela masenih koncentracija čestica po veličini s tri maksimuma tipična je za pojavu pustinjskog pijeska u atmosferskim česticama. Pojava saharskog pijeska povećala je i udio nanočestica (d<1 μm) u uzorku, iako je najveći porast udjela nanočestica u uzorku uslijed izgaranja u kućnim ložištima. Kemijska analiza uzoraka je pokazala da su u uzorcima sa saharskim pijeskom višestruko povišene koncentracije sekundarnih anorganskih aerosola (SIA - sulfata i amonijevog iona) te u vodi topivih organskih tvari (WSOC, odnosno sekundarnih organskih aerosola - SOA) u finijim frakcijama S9-S6 (d= 0,10-1,0 μm). Za razliku od sulfata i amonijevog iona, nitrat je dominantan ion u grubljoj (coarse) frakciji, što potvrđuje intruziju NOx u morske aerosole. Prema literaturi, ova je pojava karakteristična za onečišćene atmosfere priobalnih područja, i u postupku pridruživanja izvora Positive Matrix Factorization (PMF) metodom svrstava nitrat ne u sekundarne anorganske (SIA), već u morske aerosole

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FRACTIONS OF AIRBORNE PARTICULATES IN THE URBAN ATMOSPHERE OF RIJEKA

Keywords: *cascade impactor, metals, ions, WSOC*

Based on the results from the previous MED project POSEIDON, which dealt with the impact of maritime traffic on air quality in Rijeka, one of the aims of the INTERREG IT-HR project ECO-MOBILITY is to further characterize the physical and chemical properties of 11 fractions of airborne particulates collected with a 10-stage cascade impactor with nominal cut-off sizes of: 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10 and 0.056 μm. The two sampling campaigns were autumn, in the period from 26th Oct to 10th Dec 2018, and spring, in the period from 26th Mar to 21st May 2019. Eight 7-day samples were collected in each campaign. The overall average mass/concentration varied between 9 and 37.4 μg/m³, except for the first week of monitoring when the average was 134.6 μg/m³. The distribution of airborne fractions showed a bimodal curve with two maxima: S4 (particle diameter range d=1.8-3.2 μm) and S8 (d=0.18-0.32 μm) fractions. The size distribution of particulate mass concentrations differed for the first week; except for a secondary peak at S4, there was a primary one at S6 (d=0.56-1.00 μm) and tertiary at S10 (d=0.56 –1.00 μm). Three peak mass distribution is characteristic for desert dust. The sample with Saharan sand showed a higher content of nanoparticles (d<1 um), although the highest contribution of nanoparticles stemmed from domestic heating that began in mid-November. Chemical analyses showed that multiple higher mass/concentrations of secondary inorganic aerosols (SIA) sulphate and ammonium were found in fine fractions S9-S6 (d=0.10-1.0 μm) of the sample with Saharan sand, thus indicating atmospheric gas chemistry as their sources. The same was found for WSOC (or SOA) in the same fine fractions. Unlike sulphate and ammonium, maximum nitrate was found in the coarse fractions S4-S6 (d=0.56-3.2 μm) suggesting a well-known intrusion of NOx in marine aerosols. The same phenomenon is the reason why nitrate is classified within marine, and not SIA aerosols in source apportionment techniques like Positive Matrix Factorization (PMF).

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MJERENJE PARAMETARA ONEČIŠĆENJA ZRAKA NA POSTAJI PUNTIJARKA

Ključne riječi*: Puntijarka, obarina, lebdeće čestice, policiklički aromatski ugljikovodici*

Državni hidrometeorološki zavod sudjeluje u programu suradnje za praćenje i procjenu daljinskog prijenosa atmosferskog onečišćenja u Europi (EMEP program) od 1981. godine koji je uspostavljen u okviru Konvencije o dalekosežnom prekograničnom onečišćenju zraka (CLRTAP). Postaja Puntijarka dio je EMEP mreže postaja i kao pozadinska postaja reprezentativna je za praćenje prekograničnog prijenosa atmosferskih onečišćenja te praćenje učinkovitosti provođenja međunarodnih sporazuma o smanjivanju emisija.

Praćenje i analiza kemijskog sastava oborine i zraka omogućuje razumijevanje i povezivanje izvorišnih područja emisija s atmosferskim procesima i putanjama prijenosa onečišćujućih tvari te razlučivanje lokalnih i regionalnih utjecaja na kvalitetu zraka.

Analizirani su podaci za oborinu i lebdeće čestice aerodinamičkog promjera 2.5 μm ($PM_{2.5}$) i 10 μm (PM_{10}) s mjerne postaje Puntijarka za 2017. i 2018. godinu. Dnevni uzorci oborine prikupljani su otvorenim polietilenskim lijevcima s rezervoarom (bulk uzorkivač), a uzorci lebdećih čestica LVS uzorkivačima te su analizirani u skladu s važećim normama. Kiselost oborine određena je pH-metrom, koncentracije glavnih iona u oborini i $PM_{2.5}$ frakciji (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+} i Mg^{2+}) određene su ionskim kromatografom, a koncentracije policikličkih aromatskih ugljikovodika (benzo(a)pirena, krizena, benzo[a]antracena, benzo[b]fluorantena, benzo[j]fluorantena, benzo[k]fluorantena, dibenzo[a,h]antracena, indeno[1,2,3-cd]pirena i benzo[ghi]perilena) u frakciji lebdećih čestica PM_{10} određene su plinskom kromatografijom spregnutom s masenim spektrometrom (GC-MS). Masena koncentracija $PM_{2,5}$ i PM_{10} frakcije određena je gravimetrijskom metodom.

Praćenjem kvalitete oborine dokazana je mala prisutnost štetnog kiselog taloženja tvari iz atmosfere putem oborine. Ukupno godišnje taloženje kiselih komponenti je ispod granice štetnog utjecaja na okoliš. Masene koncentracije policikličkih aromatskih ugljikovodika u PM_{10} frakciji su više u zimskim mjesecima što upućuje na lokalni izvor tih onečišćenja prvenstveno uzrokovan povećanim emisijama iz ložišta.

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MEASUREMENT OF AIR POLLUTION PARAMETERS AT THE PUNTIJARKA STATION

Keywords*: Puntijarka, wet precipitation, particulate matter, polycyclic aromatic hydrocarbons*

The Croatian Meteorological and Hydrological Service has participated in the the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) since 1981, established under the Convention on Long-range Transboundary Air Pollution (CLRTAP). The Puntijarka station is part of the EMEP Measurement Network and as a background station is representative for monitoring the long-range transboundary transport of atmospheric pollution and monitoring the effectiveness of implementing international emission reduction agreements.

The monitoring and analysis of the chemical composition of wet precipitation and air enables understanding and linking emission sources with atmospheric processes and pathways of pollutants, and the discernment of local and regional impacts on air quality.

In this paper, the data for wet precipitation and particulate matter with aerodynamic particles of 2.5 μm ($PM_{2.5}$) and 10 μm (PM_{10}) for the Puntijarka station for 2017 and 2018 were analysed. Daily precipitation samples were collected through open polyethylene funnels with tank (bulk sampler), $PM_{2.5}$ and PM_{10} samples with LVS samplers, and all analysed in accordance with standard procedures. Precipitation acidity was determined by a pH meter, the concentration of the ions in the precipitation and $PM_{2.5}$ (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) were determined by ion chromatography. Polycyclic aromatic hydrocarbon concentrations in PM_{10} fraction (benzo[a]pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perilene) were determined by gas chromatography-mass spectrometry (GC-MS). The mass concentration of the $PM_{2.5}$ and PM_{10} fraction was determined by gravimetric method.

Through monitoring the precipitation quality, a small amount of harmful acid deposition of the substance from the atmosphere through the precipitate has been demonstrated. Total annual acidic components deposition was below the limit of adverse environmental impacts. The mass concentrations of polycyclic aromatic hydrocarbons in the PM_{10} fraction were higher in winter indicating a local source of these pollutants primarily caused by increased emissions from combustion.

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MASENE KONCENTRACIJE METALA U PM_{10} FRAKCIJI ČESTICA NA PODRUČJU SARAJEVA

Ključne riječi: *arsen, kadmij, nikal, olovo, zrak*

S ciljem karakterizacije organskih i anorganskih onečišćenja zraka na području grada Sarajeva i njegove okolice, u razdoblju od 4. prosinca 2017. do 14. ožujka 2018. godine, proveden je projekt SAFICA (eng. Sarajevo Canton Winter Field Campaign 2018) u sklopu kojeg su uzorkovane lebdeće čestice aerodinamičkog promjera manjeg od 10 μm (PM_{10}) na više mjernih postaja u Kantonu Sarajevo u Bosni i Hercegovini (BIH). U ovom radu prikazani su rezultati analize arsena, kadmija, nikla i olova prikupljeni na mjernim postajama Federalnog Hidrometeorološkog Zavoda BIH u gradu Sarajevu (lokacija Bjelave) te na planinskom prijevoju Ivan Sedlo, oko 45 km jugozapadno od Sarajeva. Uzorci PM_{10} sakupljani su uređajem za prosisavanje velikih volumena zraka na kvarcne filtre, a za analizu metala odvojen je dio filtra (20% od uzorka). Lebdeće čestice razorene su dušičnom kiselinom uz mikrovalove na povišenoj temperaturi i tlaku, a sadržaj metala određen je spektrometrijom masa uz induktivno spregnutu plazmu. Rezultati pokazuju da su srednje vrijednosti masenih koncentracija metala u promatranom razdoblju na mjernoj postaji u Sarajevu iznosile 2,13 ng/m^3 za arsen, 0,36 ng/m^3 za kadmij, 0,72 ng/m^3 za nikal i 8,48 ng/m^3 za olovo. Nađena je statistički značajna korelacija između masenih koncentracija arsena, kadmija i olova u PM_{10} frakciji lebdećih čestica. Rezultati pokazuju i značajnu razliku između mjernih postaja, pri čemu su vrijednosti masenih koncentracija metala na mjernoj postaji Ivan Sedlo, u istom razdoblju uzorkovanja bile tri do šest puta manje.

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MASS CONCENTRATIONS OF METALS IN PM_{10} PARTICULATE MATTER IN THE SARAJEVO REGION

Keywords: *arsenic, cadmium, nickel, lead, air*

The aim of the SAFICA project (Sarajevo Canton Winter Field Campaign 2018) was to characterise the organic and inorganic pollutants in the city of Sarajevo and its surroundings. The project took place from 4 December 2017 to 14 March 2018. Samples of PM_{10} particulate matter were collected at several sampling sites within the Sarajevo Canton, Bosnia and Herzegovina. This paper presents results of arsenic, cadmium, nickel and lead analysis from samples collected at Sarajevo (location Bjelave) and at the sampling site Ivan Sedlo, mountain pass located about 45 km south-west from Sarajevo. Samples of particulate matter were collected using high volume sampler on quartz filter and an aliquot of 20% of filters was cut for determination of metals. Particulate matter was digested with nitric acid and microwaves at high temperature and pressure and metallic content was determined using inductively coupled plasma mass spectrometry. The results show that the average mass concentrations at the Sarajevo sampling site were 2.13 ng/m^3 for arsenic, 0.36 ng/m^3 for cadmium, 0.72 ng/m^3 for nickel and 8.48 ng/m^3 for lead. A significant correlation was found between mass concentrations of arsenic, cadmium and lead in the PM_{10} particle fraction. Concentrations significantly differed between sampling sites, showing three to six time lower values at Ivan Sedlo.

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METALI U PM_{10} I PM_1 FRAKCIJI LEBDEĆIH ČESTICA U ZRAKU ZAGREBA

Ključne riječi: *arsen, ICP MS, kadmij, lebdeće čestice, nikal, olovo*

Lebdeće čestice važno su atmosfersko onečišćenje. Imaju značajan utjecaj na kvalitetu zraka, ljudsko zdravlje, atmosfersku vidljivost i klimatske promjene. Urbane lebdeće čestice složena su smjesa raznih tvari poput elementarnog ugljika, sulfata, nitrata, organskih spojeva i metala. Finije frakcije, kao što je PM_1 (čestice s aerodinamičkim promjerom manjim od 1 μm), najopasnije su jer mogu prodrijeti u pluća i krvotok uzrokujući dišne i kardiovaskularne probleme i preuranjenu smrt, ali i razne bolesti koje nisu nužno vezane uz respiratorni i kardiovaskularni sustav. U Hrvatskoj je propisano praćenje masenih koncentracija nikla (Ni), arsena (As), kadmija (Cd) i olova (Pb) u PM_{10} frakciji (čestice s aerodinamičkim promjerom manjim od 10 μm) lebdećih čestica te se stoga ovi metali određuju u okviru mjernih mreža za praćenje kvalitete zraka. Kao istraživački projekt tijekom 2016. godine na mjernoj postaji u sjevernom dijelu Zagreba sakupljeni su uzorci PM_1 frakcije lebdećih čestica kako bi se odredio sadržaj metala u istim. Dnevni uzorci lebdećih čestica sakupljeni su prosisavanjem približno 55 m^3 zraka na kvarcne filtre. Tako prikupljeni uzorci lebdećih čestica pripremljeni su mikrovalnom razgradnjom pod povišenim tlakom i temperaturom uz dodatak dušične kiseline. Sadržaj metala određen je masenom spektrometrijom induktivno spregnute plazme (ICP MS). Srednje godišnje vrijednosti u PM_{10} frakciji lebdećih čestica bile su 0,45 ng m^{-3} za Ni, 0,35 ng m^{-3} za As, 0,14 ng m^{-3} za Cd i 5,40 ng m^{-3} za Pb te 0,14 ng m^{-3} za Ni, 0,23 ng m^{-3} za As, 0,13 ng m^{-3} za Cd i 4,49 ng m^{-3} za Pb u PM_1 frakciji lebdećih čestica. Prosječne godišnje masene koncentracije svih određivanih metala nisu prelazile granične vrijednosti, a okolni zrak je bio 1. kategorije kvalitete na mjernoj postaji u sjevernom dijelu grada. Dobiveni rezultati pokazuju da se 36,7% nikla nalazi u PM_1 u odnosu na nikal u PM_{10} frakciji lebdećih čestica. Zbog niskih vrijednosti nikla, veliki broj uzoraka bio je ispod granice kvantifikacije te to bi mogao biti razlog za niži postotak nikla u PM_1 frakciji u usporedbi s PM_{10} frakcijom lebdećih čestica. Arsena u PM_1 česticama ima 64.0 % u odnosu na arsen u PM_{10} česticama. Kadmij se nalazi u 73.2 % u PM_1 česticama u odnosu na kadmij u PM_{10} lebdećih česticama. Olova u PM_1 frakciji ima 64.6 % u odnosu na olovo sadržano u PM_{10} frakciji lebdećih čestica.

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METALS IN PM_{10} AND PM_1 FRACTIONS IN ZAGREB AIR

Keywords: *arsenic, cadmium, ICP MS, nickel, lead, particulate matter*

Particulate matter (PM) is an important atmospheric pollutant. It has substantial impacts on air quality, human health, atmospheric visibility and climate change. Urban particulate matter is a complex mixture of different chemicals like elemental carbon, sulphates, nitrates, organic compounds and metals. The finer fractions, such as PM_1 (particulate matter with an aerodynamic diameter less than 1 μm), are the most dangerous as they can penetrate into the lungs and bloodstream causing respiratory and cardiovascular problems and premature death, as well as various diseases not necessarily related to the respiratory and cardiovascular system. In Croatia, the monitoring of mass concentrations of nickel (Ni), arsenic (As), cadmium (Cd) and lead (Pb) in the PM_{10} fraction (particles with an aerodynamic diameter less than 10 μm) of particulate matter is regulated and therefore these metals are determined within the air quality monitoring network. Within a research project, samples of PM_1 fraction of particulate matter were collected at a monitoring station in the northern part of Zagreb during 2016 to determine their metal content. Daily samples of particulate matter were collected from approximately 55 m^3 of ambient air on quartz filters. The collected samples of particulate matter were prepared with nitric acid by microwave digestion under elevated pressure and temperature. Metal content was determined by inductively coupled plasma mass spectrometry (ICP MS). The mean annual values in the PM_{10} fraction of particulate matter were 0.45 ng m^{-3}, 0.35 ng m^{-3}, 0.14 ng m^{-3} and 5.40 ng m^{-3} for Ni, As, Cd and Pb, respectively, and 0.14 ng m^{-3}, 0.23 ng m^{-3}, 0.13 ng m^{-3}, and 4.49 ng m^{-3} in the PM_1 fraction of the particulate matter for Ni, As, Cd and Pb, respectively. The mean annual mass concentrations of all determined metals in PM_{10} did not exceed limit values and the ambient air was of the 1st quality category at the monitoring station in the north part of the city. The obtained results show that, compared to nickel in PM_{10} particles, 36.7 % was found in PM_1 particles. Due to the low values of nickel, a large number of samples were below the limit of quantification and that could be the reason behind a lower percentage of nickel found in PM_1 particles compared to PM_{10}. Compared to arsenic in PM_{10} particles, 64.0 % was found in PM_1 particles; to cadmium in PM_{10} particles, 73.2 % was found in PM_1 particles and compared to lead in PM_{10} particles, 74.6 % was found in PM_1 particles.

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UTJECAJ EL-TO NA KVALITETU ZRAKA U SJEVERNOM DIJELU ZAGREBA U RAZDOBLJU VELJAČA 2014. - VELJAČA 2018.

Ključne riječi: *HEP, EL-TO, kvaliteta zraka, lebdeće čestice, sumporov dioksid, okoliš*

Sanacijskim programom smanjenja emisije krutih čestica iz Elektrane-toplane EL-TO Zagreb utvrđena je potreba praćenja njezinog utjecaja na kvalitetu zraka. Istom studijom procijenjeno je da je taj utjecaj najizraženiji u sjevernom dijelu Zagreba te je iz tog razloga na tom području postavljena mjerna postaja Bijenik koja je započela s radom u veljači 2014. godine. Postaja je bila smještena na 264 nadmorske visine u sjever-sjeverozapadnom dijelu grada Zagreba, na hrptu obronka Medvednice u rezidencijalnoj četvrti s obiteljskim kućama, udaljena dvadesetak metara od lokalne ceste s prometom slabog intenziteta i minimalno 3 kilometra od većih prometnica. Postaja je po tipu industrijska te je bila udaljena 4,5 km sjeverno (350°) od EL-TO te u vizualnom kontaktu sa EL-TO.

U razdoblju od četiri godine na postaji su provedena mjerenja sumporovog dioksida (SO_2) referentnom automatskom metodom te mjerenja PM_{10} frakcije lebdećih čestica automatskom metodom i referentnom gravimetrijskom metodom. Mjerenja su provodili akreditirani laboratoriji Ekonerg laboratorij za zrak (SO_2 i PM_{10} automatskom metodom) i Institut za medicinska istraživanja i medicinu rada (PM_{10} referentnom gravimetrijskom metodom). U svrhu ocjene onečišćenja zraka obrađeni su i analizirani rezultati praćenja kvalitete zraka za sve mjerene onečišćujuće tvari u razdoblju od veljače 2014. do veljače 2018. godine.

Cilj analize bio je na temelju mjernih podataka ocijeniti kvalitetu zraka u okolici mjerne postaje Bijenik te uz pomoć općih znanja iz područja zaštite zraka procijeniti utjecaj EL-TO na kvalitetu zraka.

Koncentracije SO_2 (1-satne i 24-satne vrijednosti) u cijelom razdoblju mjerenja bile su vrlo niske, nisu zabilježena prekoračenja granične vrijednosti (GV) te je zrak s obzirom na SO_2 bio prve kategorije kvalitete u cijelom promatranom razdoblju. Dnevna granična vrijednost koncentracije PM_{10} nije prekoračena više od dozvoljenih 35 puta niti jedne godine (zabilježen je broj prekoračenja od 11 do 30 puta), a srednja godišnja granična vrijednost u istom razdoblju nije prekoračena niti u jednoj godini te je zrak s obzirom na PM_{10} bio prve kategorije kvalitete u cijelom promatranom razdoblju (mjereno s obje metode).

Koncentracije PM_{10} uspoređene su i sa koncentracijama PM_{10} sa ostalih mjerenih postaja u Gradu Zagrebu u istom razdoblju te se pokazalo da je jedino na mjernoj postaji Bijenik broj dana prekoračenja dnevne granične vrijednosti bio manji od dozvoljenog u sve četiri promatrane godine, a srednje godišnje koncentracije na mjernoj postaji Bijenik bile su najniže na cijelom mjernom području Grada Zagreba.

Kako je kvaliteta zraka u okolini mjerne postaje Bijenik prve kategorije te je time po definiciji zrak čist ili neznatno onečišćen možemo zaključiti da EL-TO Zagreb svojim radom ne utječe na prekomjerno onečišćenja zraka s SO_2 i PM_{10} na tom području sukladno regulativi RH.

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IMPACT ANALYSIS OF EL-TO ON AIR QUALITY IN NORTHERN ZAGREB FROM FEBRUARY 2014 TO FEBRUARY 2018

Keywords: *HEP, EL-TO, air quality, particulate matter, sulfur dioxide, environment*

The remediation program for the emission reductions of solid particles from EL-TO Zagreb identified the need to monitor the impact of Power and heating plant (EL-TO) Zagreb on air quality. It was found that the influence of EL-TO Zagreb was most pronounced in the northern part of Zagreb. Because of that, measuring station Bijenik was set up there and measuring started in February 2014. The station was situated in the north-northwestern part of Zagreb on the hillside of the Medvednica mountain in a residential neighbourhood with family houses, about 20 meters away from a local road with low intensity traffic and at least 3 kilometres from major roads at 264 meters above sea level. The station was industrial by type and was situated 4.5 km north (350°) from the EL-TO with visual contact between the station and EL-TO.

During the four-year period, sulphur dioxide (SO_2) measurements were carried out using a reference automatic method and measurements of the PM_{10} fraction of suspended particles were carried out by automatic method and reference gravimetric method. The measurements were carried out by the accredited laboratories Ekonerg Air Laboratory (SO_2 and PM_{10} automatic method) and the Institute for Medical Research and Occupational Health (PM_{10} reference gravimetric method).

The aim of the analysis was to assess air quality near the measuring station Bijenik on the base of measurement data and assess the influence of EL-TO on air quality. Air quality monitoring results were analysed as an air pollution indicator for all measured pollutants in the period from February 2014 to February 2018.

SO_2 concentrations (hourly and daily) throughout the four-year measurement period were very low and did not exceed the limit value (LV) a single time, whereas the air quality was of the first category throughout the entire observed period. Daily concentrations of PM_{10} did not exceed the limit value more than the allowed 35 times per year (the number of exceedances was 11 to 30 per year) and the annual mean value did not exceed the LV in any one year. Considering PM_{10}, the air quality was of the first category in the entire observed period (measured by both methods).

PM_{10} concentrations were compared with the PM_{10} concentrations for other measuring stations in the city of Zagreb during the same period. The number of days of exceedances was less than allowed in all four of the observed years only on the Bijenik measuring station and the annual mean concentrations at Bijenik were lowest in the entire area of the city.

From this analysis we can conclude that the air quality is the of first category near the measurement station Bijenik and thus by definition, the air is clean or negligibly polluted, and EL-TO Zagreb does not have an excessive influence on the air pollution above regulated levels for SO_2 and PM_{10} in this area.

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KONCENTRACIJE DUŠIKOVOG DIOKSIDA U ZRAKU ZAGREBA U RAZDOBLJU OD 2009. DO 2018. GODINE

Ključne riječi: *granična vrijednost, NO_2, trend srednjih godišnjih koncentracija, urbane postaje*

Dušikov dioksid (NO_2) je onečišćujuća tvar koja nastaje izgaranjem tekućih fosilnih goriva (dizela i benzina), gorenjem ugljena i zemnog plina te u raznim industrijskim procesima pa su stoga razine NO_2 često povišene u urbanim sredinama. Prema podacima Europske agencije za okoliš za 2015. godinu 9 % urbanog stanovništva Europske unije živjelo je u području s koncentracijom NO_2 višom od propisane godišnje granične vrijednosti (40 μg/m^3), a kao jedan od glavnih izvora onečišćenja smatra se cestovni promet.

Koncentracije dušikovog dioksida prate se kontinuirano u gradu Zagrebu od 1994. godine. Dosadašnja mjerenja su pokazala da je na većini mjernih postaja u Zagrebu dolazilo do prekoračenja propisane godišnje granične vrijednosti od 40 μg/m^3, a najviše koncentracije izmjerene su u pravilu na lokacijama u blizini opterećenih prometnica. Ranija istraživanja, provedena za razdoblje 1995.-2009. na šest mjernih postaja u Zagrebu pokazala su vrlo blagi rastući trend koncentracija, osim na mjernom mjestu u industrijskom dijelu grada. U ovom istraživanju promatrane su masene koncentracije NO_2 u razdoblju 2009.-2018. na tri lokacije različitih karakteristika: u sjevernom, stambenom dijelu grada s umjerenom gustoćom prometa, u centru grada s visokom gustoćom prometa te u istočnom, industrijskom dijelu grada. U promatranom desetogodišnjem razdoblju srednje godišnje vrijednosti NO_2 kretale su se između 17 μg/m^3 i 54 μg/m^3 u sjevernom dijelu grada, između 39 μg/m^3 i 52 μg/m^3 u centru grada te između 25 μg/m^3 i 35 μg/m^3 u istočnom dijelu grada. Granična vrijednost bila je prekoračena u centru grada tijekom devet godina, u sjevernom dijelu grada tijekom četiri godine, a u istočnom niti jednom. Na sve tri lokacije u razdoblju od 2009. do 2018. godine koncentracije NO_2 pokazale su padajući trend, koji je bio najviše izražen na mjernoj postaji u sjevernom dijelu grada te nešto slabije u istočnom dijelu grada. Padajući trend u centru grada nije pokazao statistički značajan.

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CONCENTRATIONS OF NITROGEN DIOXIDE IN ZAGREB AIR FOR THE PERIOD 2009 - 2018

Keywords: *limit value, NO_2, annual average concentration trend, urban stations*

Nitrogen dioxide (NO_2) is a pollutant formed by the combustion of liquid fossil fuels (diesel and gasoline), during coal and natural gas burning, as well as in various industrial processes. For that reason, NO_2 levels are often elevated in urban environments. According to the European Environment Agency's data for the year 2015, 9% of the urban population of the European Union lived in an area with NO_2 concentrations above the prescribed annual limit value (40 μg/m^3). Road traffic has been identified as one of the main sources of pollution.

Concentrations of nitrogen dioxide have been measured continuously in the city of Zagreb since 1994. Previous measurements in Zagreb have shown that at most monitoring stations NO_2 concentrations exceeded the prescribed annual limit value of 40 μg/m^3, and the highest concentrations were generally measured at locations near frequent roads. The research carried out for the period 1995 - 2009 at six measuring stations in Zagreb showed a very slight increasing trend of NO_2 concentrations, except for the measuring station located in the industrial part of the city. This study analysed the NO_2 data collected for the period 2009-2018 at three locations with different characteristics: in the northern residential part of the city with moderate traffic, in the city centre with high traffic density and in the eastern, industrial part of the city. During the observed ten-year period, the mean annual NO_2 values ranged between 17 μg/m^3 and 54 μg/m^3 in the northern part of the city, between 39 μg/m^3 and 52 μg/m^3 in the city centre and between 25 μg/m^3 and 35 μg/m^3 in the eastern part of town. In the centre of the city, the annual limit value was exceeded for nine years, in the northern part of the city for four years and in the east not even once. For the period 2009 – 2018, NO_2 concentrations at all three locations showed a decreasing trend, which was the most pronounced at the monitoring station in the northern part of the city, and less pronounced in the eastern part of the city. The decreasing trend in the city centre was not statistically significant.

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Tema 4
Razvoj i provjera mjernih metoda

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SENZORI – BUDUĆNOST MJERENJA KVALITETE ZRAKA?

Ključne riječi: *među-laboratorijska usporedba rezultata, senzori za praćenje kvalitete zraka*

Cilj rada je prikazati način rada senzora za praćenje kvalitete zraka, njihov povijesni razvoj te ukazati na njihove prednosti i mane. Rad prikazuje rezultate među-laboratorijske usporedbe senzora u sklopu istraživanja provedenog u trajanju od 6 tjedana (od početka siječnja do sredine veljače 2018. godine) od strane Francuskog središnjeg laboratorija za praćenje kvalitete zraka (LCSQA) u Lillu. U sklopu usporednog mjerenja sudjelovalo je 16 sudionika iz 7 zemalja (iz Francuske, Nizozemske, Ujedinjenog Kraljevstva, Španjolske, Italije, Poljske i Sjedinjenih Američkih Država) sa 44 seta senzora za mjerenje kvalitete zraka grupiranih u 17 različitih izvedbi. Predmet istraživanja bili su NO_2, O_3, $PM_{2,5}$ i PM_{10} kao dominantni predstavnici onečišćenja u urbanim sredinama. Rezultati mjerenja dobivenih senzorima uspoređivani su s rezultatima referentnih automatskih metoda za plinovita onečišćenja te sa automatskim sustavima za mjerenje masenih koncentracija lebdećih čestica u zraku (BAM, Thermo i FIDAS). Rezolucija mjerenja koncentracija onečišćujućih tvari u zraku za referentne metode je iznosila jedan sat, dok se prosječna satna vrijednost rezultata dobivenih senzorima određivala iz minutnih vrijednosti. Rezultati usporednih mjerenja prikazani su samo za NO_2 i $PM_{2,5}$ s obzirom da rezultati za O_3 i PM_{10} još nisu obrađeni. Vidljive su velike razlike u točnosti mjerenja koncentracija senzorima različitih proizvođača, kao i pri uporabi istog tipa uređaja ali s različitim elektrokemijskim ćelijama. Za NO_2 najbolji koeficijent determinacije R^2 je 0,87, a najlošiji 0,34. Za $PM_{2,5}$ najbolji R^2 iznosi 0,64 dok je najlošiji 0,00 što ukazuje na postojeće probleme korištenja senzora pri rutinskom praćenju kvalitete zraka.

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AIR QUALITY SENSORS – THE FUTURE OF AIR QUALITY MEASUREMENT?

Keywords: *inter-laboratory comparison, air quality sensors*

The aim of the paper is to show the how the air quality sensor work, their historical development and their advantages and disadvantages. The paper covers results of inter-laboratory comparison of the sensors conducted by the French Central Air Quality Monitoring Laboratory (LCSQA) for 6 weeks (from the beginning of January to mid of February 2018) in Lille. As part of the parallel measurement, 16 participants from seven countries (from France, the Netherlands, the United Kingdom, Spain, Italy, Poland and the United States) participated with 44 sets of air quality sensors grouped in 17 different performances and design. The subjects of the study were NO_2, O_3, $PM_{2.5}$ and PM_{10} as the dominant pollutants in urban environments. The measurement results of the sensors were compared with the results of the reference automated methods for gaseous pollutants and with automated systems for mass concentration of particle matter in the air (BAM, Thermo and FIDAS). The airborne pollutant measurement resolution for the reference methods was one hour, while the average hourly value of the results obtained by sensors was determined by minute values. The results of the parallel measurements are shown for NO_2 and $PM_{2.5}$ only, as the results for O_3 and PM_{10} have not been processed yet. There are great differences in the accuracy of sensor measurements between different manufacturers as well as large differences in measuring accuracy with the same type of device but with different electrochemical cells. For NO_2 the best coefficient of determination R^2 is 0.87 and the worst 0.34. For $PM_{2.5}$, the best R^2 is 0.64 while the worst 0.0 indicates the problem with the sensor work.

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OSIGURANJE KVALITETE PODATAKA KOD PRAĆENJA KVALITETE ZRAKA MALIM ELEKTROKEMIJSKIM SENZORIMA

Ključne riječi: *mali elektrokemijski senzor, kvaliteta podataka, skaliranje, regresijska analiza*

Prednosti malih senzora za praćenje kvalitete zraka u odnosu na konvencionalne (referentne) metode su definitivno njihova cijena i dimenzije. Zbog toga, mali senzori omogućuju praćenje kvalitete zraka na puno više lokacija. Međutim, postavlja se pitanje mogu li oni osigurati istu ili barem približno jednaku kvalitetu podataka kao i postaje koje prate kvalitetu zraka referentnim metodama. Kako bi se osigurala što bolja kvaliteta podataka mali senzor je potrebno postaviti na referentnu postaju. Postavljenjem senzora na referentnu postaju dobivaju se informacije potrebne za izračunavanje varijabli skaliranja, nagiba i pomaka. Skaliranje osigurava povećanu razinu točnosti na temelju lokalnih okolišnih uvjeta i načina na koji senzori reagiraju na okruženje. Varijable skaliranja izračunavaju se za određeno vremensko razdoblje. Nakon velike promjene u okolišnim uvjetima, npr. promjena prosječne temperature za 10 °C ili više, potrebno je ponovno izračunati varijable skaliranja. Primjenom tako izračunatih varijabli za nagib i pomak mogu se dobiti najbolji mogući rezultati tijekom istog perioda. Postupak skaliranja senzora može se podijeliti u četiri osnovna koraka. Prvi korak je regresijska usporedba malog senzora s referentnom metodom. Regresijska analiza može se izvršiti pomoću programa Microsoft Excel, MathCad ili sličnih matematičkih programa. U drugom koraku uklanjaju se potencijalno pogrešni podaci i pronalazi se jednadžba pravca. U trećem koraku regresijskom analizom dobivene varijable skaliranja, nagib i pomak primjenjuju se na cijeli skup podataka sa senzora, uključivo i pogrešne podatke. U četvrtom koraku vrijednosti varijabli skaliranja, nagiba i pomaka učitavaju se u online aplikaciju. Senzor koji je prošao ovakav postupak skaliranja može se dalje koristiti za validaciju ostalih senzora u mreži senzora. Iako se u trenutnom stupnju razvoja malim senzorima i dalje ne može dobiti ista kvaliteta podataka kao mjerenjima referentnim metodama, ovim postupkom skaliranja dobivaju se podaci koji se za pojedine plinove znatno ne razlikuju od podataka dobivenih mjerenjem referentnim metodama.

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QUALITY ASSURANCE OF AIR QUALITY MONITORING WITH LOW COST ELECTROCHEMICAL AIR POLLUTION SENSORS

Keywords: *low-cost electrochemical air pollution sensor, data quality, scaling, regression analysis*

Low-cost air pollution sensors are attracting more and more attention. They offer air pollution monitoring at a lower cost than conventional methods, theoretically making air pollution monitoring possible at many more locations. However, the question is whether they can provide the same or at least approximately the same data quality as conventional methods. In order to provide the greatest degree of accuracy, a low-cost air pollution sensor needs to be co-located with the reference station. This will provide the information necessary for calculating scaling variables: offset and slope. Scaling provides an increased level of accuracy, based on the local environmental conditions and how the used low-cost air pollution sensors react to that environment. Scaling values are calculated over a specific time period and as such are based on the environmental conditions on site over this period. After a major change in environmental conditions, e.g. a change in average temperature of 10 °C or more, scaling variables have to be re-calculated. Using the calculated offset and slope variables, the best possible results can be obtained during the same period. The scaling process of a low-cost air pollution sensor can be divided into four basic steps. The first step is the regression comparison of low-cost air pollution sensor with a reference method. Regression analysis can be completed using Microsoft Excel, MathCad or similar mathematical programs. The second step is removal of potential erroneous data points and finding a Cartesian equation for a linear trend line. In the third step, the offset and slope variables obtained by regression analysis are applied to the entire data set from the low-cost air pollution sensor (including erroneous data points). In the fourth step, offset and slope variables are uploaded to the online application. A low-cost air pollution sensor that has passed this scaling process can be further used to validate other low-cost air pollution sensors in the sensor network. Although in the current stage of development, low-cost air pollution sensors still cannot obtain the same quality data as with reference methods, this scaling procedure yields data that for certain gases are not significantly different from the data obtained with reference methods.

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PREGLED STUDIJA EKVIVALENCIJE AUTOMATSKIH MJERNIH SUSTAVA ZA ODREĐIVANJE MASENIH KONCENTRACIJA LEBDEĆIH ČESTICA

Keywords: *PM_{10}, $PM_{2.5}$, korekcijske funkcije*

U skladu s europskim direktivama (2008/50/EC i 2018/1480) i zakonodavstvom RH, gravimetrijska metoda predstavlja referentnu metodu određivanja masenih koncentracija frakcija lebdećih čestica PM_{10} i $PM_{2.5}$ u zraku. Automatski mjerni sustavi za određivanje masenih koncentracija čestica vrlo su rašireni s obzirom na to da omogućuju praćenje trenutnih vrijednosti koncentracija i ne zahtijevaju dodatne analitičke postupke. Automatski sustavi instalirani na području Republike Hrvatske nad kojima je provedena studija ekvivalencije koriste mjerni princip autenacije ß zračenja na 7 mjernih postaja, ortogonalnog svjetlosnog raspršenja (omogućuje istovremeno praćenje trenutnih koncentracija više frakcija lebdećih čestica) na 8 mjernih postaja te princip oscilirajuće mikro-vage na dvije mjerne postaje. Paralelnim mjerenjem koncentracija čestica automatskim mjernim sustavom i referentnom metodom određuju se sezonske i/ili godišnje korekcijske funkcije ili korekcijski faktori. Korekcijski faktor uključuje samo korekciju nagiba regresijskog pravca dok korekcijska funkcija uključuje korekciju nagiba regresijskog pravca i odsječka na y-osi. Nakon korekcije rezultata određuju se statistički parametri za ocjenu kvalitete zraka i uspoređuju sa statističkim parametrima određenim referentnom metodom. Zamijećeno je bolje slaganje parametara pri provedbi korekcije korekcijskim funkcijama. Također je zamijećeno da ne postoji velika razlika u statističkim parametrima ako se provodi sezonska ili godišnja korekcija rezultata. Provedbom velikog broja studija ekvivalencije zamijećena je značajna ovisnost korekcijskih funkcija o tipu mjerne postaje, o sezoni te o korištenom mjernom principu automatskog sustava. Koncentracije određene automatskim sustavima koji koriste mjerni princip ortogonalnog svjetlosnog raspršenja u prosjeku su više, dok su koncentracije određene automatskim sustavima koji koriste mjerni princip autenacije ß zračenja u prosjeku niže od koncentracija određenih referentnom metodom. Rezultati koncentracija lebdećih čestica bez provedene studije ekvivalencije mogli bi navoditi na krive zaključke o kvaliteti zraka na pojedinim područjima, a time posredno i na planiranje i provođenje mjera za očuvanje/poboljšanje kvalitete zraka u RH.

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A REVIEW OF EQUIVALENCY STUDIES ON AUTOMATIC MEASURING SYSTEMS FOR ATMOSPHERIC PARTICULATE MATTER MASS CONCENTRATION DETERMINATION

Keywords: *PM_{10}, $PM_{2.5}$, correction functions*

In accordance with European Directives (2008/50/EC and 2018/1480) and the legislation of the Republic of Croatia, the gravimetric method is the reference method for determining the mass concentrations of PM_{10} and $PM_{2.5}$ particle fractions in the air. Automatic measuring systems for the determination of mass concentrations of particles are very widespread in that they allow the monitoring of current concentration values and do not require additional analytical procedures. The automatic systems installed on the territory of Croatia use the measurement principle of ß radiation at 7 measuring stations, orthogonal light scattering (allowing simultaneous monitoring of the current concentrations of multiple fractions) at 8 measurement stations and the principle of tapered element oscillating microbalance (TEOM) at two measuring stations. The parallel measurement of particle concentrations by automatic measuring and a reference method determines seasonal and/or annual correction functions or correction factors. The correction factor includes only the slope correction of regression line, while the correction functions involves the slope and intercept correction. After the correction of results, the statistical parameters for air quality assessment are determined and compared with the statistical parameters determined by the reference method. Better agreement of parameters was recorded by correction with the correction function rather than the correction factor. It was been noted that there is no big difference in statistical parameters if a seasonal or annual correction of the results is carried out. Significant dependence of correction functions on the type of measuring station, season and used automatic system was recorded for a large number of equivalence studies. Concentrations determined by automatic systems using the orthogonal light scattering principle are on average higher, while the concentrations determined by automatic systems using the ß radiation measurement principle are on average lower than the concentrations determined by the reference method. Particle concentrations obtained without a conducted equivalence study could point to wrong conclusions about air quality in certain areas, and consequently to the planning and implementation of measures for preservation / improvement of air quality in the Republic of Croatia.

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INTERFERENCIJA SO_2 U METODI ZA AUTOMATSKO MJERENJE H_2S

Ključne riječi: *SOx odstranjivač, mjerenje sumporovodika*

Cilj rada je pokazati kolika je vjerojatnost pozitivne interferencije sumporovog dioksida (SO_2) na mjerenje sumporovodika (H_2S) metodom kojom se koristi velika većina laboratorija za kvalitetu zraka u Republici Hrvatskoj (RH).

Gotovo svi laboratoriji u RH za mjerenja H_2S-a koriste prilagođenu metodu za SO_2 - HRN EN 14212:2012. U navedenoj metodi svi sumporovi oksidi (SOx) uklanjaju se pomoću odstranjivača-scrubbera. H_2S se nakon toga u pretvaraču prevodi u SO_2 kojeg analizator mjeri i prikazuje kao H_2S. Iz navedenog opisa metode jasno je kako interferencije SOx (u zraku je to uglavnom SO_2) ovise o učinkovitosti odstranjivača. Ukoliko se kapacitet vezanja SO_2 odstranjivača prekorači doći će do pozitivne interferencije na način da će sav nevezani SO_2 proći u mjerni sustav te se prikazivati kao H_2S.

Prema podatcima proizvođača za tip analizatora koji koristimo, kapacitet odstranjivača je 42 000 µg SOx, a redovna izmjena istoga predlaže se jednom godišnje. Kako bismo procijenili postoji li mogućnost da se ovaj kapacitet u 12 mjeseci (period između dvaju izmjena odstranjivača) prekorači u okolnostima (onečišćenost zraka s SO_2) u kojima se obavljaju mjerenja H_2S obradili smo podatke o mjerenjima SO_2 na postajama gdje se paralelno obavljaju mjerenja SO_2 i H_2S. Istu analizu proveli smo i za tipičnu urbanu postaju u Zagrebu i dvije postaje u neposrednoj blizini rafinerije i termoelektrane gdje je najveća mogućnost visokih koncentracija SO_2 u zraku. Za izračun opterećenja odstranjivača sumporovim dioksidom koristili smo srednje godišnje koncentracije SO_2 izmjerene na gore spomenutim postajama u razdoblju od 2014. do 2018. godine. Korišteni su podatci iz godišnjih izvješća za ove postaje. Opterećenje odstranjivača izračunato je za godinu s najvećom srednjom godišnjom koncentracijom u navedenom razdoblju za svaku postaju. Zabilježeni su rasponi koncentracija od 947 µg na postaji u Zagrebu do 6000 µg SO_2 na postajama smještenim u blizini rafinerije i termoelektrane. Budući da se opterećenje odstranjivača određeno na ovaj način kreće od 2,26% do 14,29% od ukupnog kapaciteta SOx odstranjivača, zaključili smo kako je zanemariva vjerojatnost pozitivne interferencije SO_2 na mjerenja H_2S-a metodom koju smo testirali. Kako bi se potvrdile ove tvrdnje odlučili smo kroz nastupajući period između izmjena odstranjivača napraviti testiranje interferencije poznatom koncentracijom SO_2 u našem umjernom laboratoriju. Testiranje će se obavljati prije godišnjeg servisa instrumenata i izmjene odstranjivača.

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SO_2 INTERFERENCE IN AUTOMATIC METHOD FOR H_2S

Keywords: *SOx scrubber, the measurement of hydrogen sulphide*

The aim of this paper is to show the likeliness of a positive interference of sulphur dioxide (SO_2) on the measurement of hydrogen sulphide (H_2S) measured with the method used by the vast majority of laboratories for air quality in the Republic of Croatia.

Almost all laboratories in Croatia use the customized method HRN EN 14212:2012 for measurements of H_2S. In this method, all sulphur oxides (SOx) are removed by an SOx scrubber before it reaches the measuring system. After that, H_2S in the air in converter is converted into SO_2 which then is measured by an instrument and displayed as H_2S. Even from this short description of methods it is clearly visible that SOx interference (in the air, most SOx is in fact SO_2) depends on the efficiency of the scrubber. If the capacity of the scrubber to bound SO_2 is exceeded, there will be a positive interference and all of the unbound SO_2 that passes further into the measuring system will be shown as H_2S.

According to data from the manufacturer, the scrubber capacity is 42 000 µg of SO_2 and a regular exchange of scrubber is proposed once a year. To assess whether there is a possibility that in 12 months this capacity (the period between the two change of scrubber) is exceeded in circumstances (pollution of air with SO_2) in which measurements of H_2S are carried out, we processed information about measurements of SO_2 at stations where SO_2 and H_2S were measured simultaneously. The same analysis was performed for a typical urban station in Zagreb and two stations in the immediate vicinity of the refinery and power plant where there was the biggest possibility of a high concentration of SO_2 in the air. For the calculation of the scrubber upload of SO_2 in one year, we used the highest annual average concentrations of SO_2 measured on the above mentioned stations for the period from 2014 up to 2018. Data from official annual reports for this stations were used. Scrubber upload was calculated for the year with the highest annual average concentration in this period for each station. The results ranged from 947 µg on the station in Zagreb up to 6000 µg of SO_2 upload on the station next to the refinery and power plant. Whereas the scrubber upload calculated in this manner ranged from 2.26 to 14.29% of the total scrubber capacity, we concluded that the probability of a positive interference of SO_2 on measurement of H_2S performed with the method that we tested was negligible. To confirm these conclusions, we decided to perform a test of SO_2 interference with known SO_2 concentrations on all instruments for H_2S that will come in our service in a one-year period. The test will be performed prior to the annual service of the instruments (and exchange of scrubber) in our calibration laboratory.

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OPTIMIZIRANJE POSTUPKA PRIPRAVE UZORAKA PRI ODREĐIVANJU POLICIKLIČKIH AROMATSKIH UGLJIKOVODIKA VEZANIH NA LEBDEĆE ČESTICE U ZRAKU

Ključne riječi: *ASE, ekstrakcija, uparavanje, PAU*

Policiklički aromatski ugljikovodici (PAU) zbog svog štetnog kancerogenog i mutagenog djelovanja na ljudsko zdravlje predstavljaju važan dio organskog onečišćenja koji se veže na lebdeće čestice u zraku. Ubrzana ekstrakcija otapalima (ASE) uz povišeni tlak i temperaturu je tehnika koja se u novije vrijeme sve više koristi za pripravu uzoraka prilikom određivanja organskih analita u uzorcima okoliša. Ovom tehnikom omogućena je brza ekstrakcija (~20 min) u zatvorenom i inertnom sustavu, pod visokim tlakom (3,3-20,3 MPa) i temperaturom (40-200 °C). Visoki tlak omogućava otapalu dublje prodiranje u matricu uzorka te pospješujući time ekstrakciju analita. Istovremeno, na povišenoj temperaturi povećava se topljivost analita te prijenos tvari postaje brži. Također, visoka temperatura smanjuje viskoznost otapala i površinsku napetost čime se povećava prodiranje otapala u matricu uzorka.

Kako bi se ispitala djelotvornost ASE pri ekstrakciji organskih onečišćujućih tvari vezanih na lebdeće čestice priređeni su modelni uzorci na način da su se na filtar od kvarcnih vlakana nakapale točno određene količine certificiranih standardnih otopina policikličkih aromatskih ugljikovodika (PAU). Kod priprave uzoraka lebdećih čestica u ekstrakcijsku ćeliju (10 mL) stavio se filtar s uzorkom te se ćelija napunila do vrha adsorbensom (dijatomejska zemlja) koji pospješuje učinkovitost same ekstrakcije. Ćelija s uzorkom se direktno zagrijavala u pećnici, a sama ekstrakcija se provodila izravnim kontaktom uzorka s vrućim otapalom na dva načina, statički i dinamički. Nakon završetka ekstrakcije uzorak je sakupljen u bočice za ekstrakt te je uparen do suhog u uparivaču (Rocket, Genevac). Nakon otapanja uzoraka u acetonitrilu, uzorci su analizirani tekućinskom kromatografijom visoke djelotvornosti uz fluorescentni detektor promjenjivih valnih duljina ekscitacije i emisije. Određeni su sljedeći PAU: fluoranten, piren, benzo(a)antracen, krizen, benzo(j)fluoranten, benzo(k) fluoranten, benzo(b)fluoranten, benzo(a)piren, dibenzo(ah)antracen, benzo(ghi)perilen i indeno(1,2,3,cd)piren. U ovom istraživanju ispitivan je volumen otapala potreban za ekstrakciju kao i broj ciklusa ekstrakcije (2 ili 3 ciklusa). Volumen otapala s kojim se vršila ekstrakcija bio je 60, 70, 80 i 90 % od volumena ćelije. Zadovoljavajuća djelotvornost dobivena je, za sve PAU, uz volumen otapala koji je iznosio 70 % od volumena ćelije, i iznosila je više od 97 % za sve PAU (osim za fluoranten i piren, za koje je djelotvornost bila oko 83 %). U ekstraktu iz trećeg ciklusa zaostalo je oko 3 % koncentracije analita.

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OPTIMIZATION OF DIFFERENT SAMPLE PREPARATION PROCEDURES FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS BOUNDED ON PARTICLE FRACTIONS IN THE AIR

Keywords: *ASE, extraction, evaporation, PAH*

Polycyclic aromatic hydrocarbons (PAH), due to its harmful carcinogenic and mutagenic effects on human health had an important role of organic pollutant in the air. The Accelerated Solvent Extraction (ASE) system at high temperature and pressure is a technique increasingly used to prepare samples for determining organic pollutions in environmental samples. This technique enables rapid extraction (~ 20 min) in closed and inert systems, under high pressure (3.3-20.3 MPa) and temperature (40-200 °C). High pressure allows the solvent to penetrate deeper into the sample matrix, enhancing the analytic extraction. At elevated temperatures, analytical solubility and transfer of substance increases and becomes faster. Also, high temperature affects solvent viscosity and surface tension by reducing them and thereby increasing the penetration of a solvent into the sample matrix.

In order to investigate ASE's efficacy in extracting organic pollutants bounded to the particle fraction, model samples were prepared by spike with known concentrations of a certificate standard of polycyclic aromatic hydrocarbon (PAH). Quartz fiber filters were put in the extraction cell (10 mL) and filled to the top with an adsorbent (diatomaceous earth) that enhances the efficiency of the extraction itself. The cells with the sample were directly heated in the oven, and the extraction was carried out by direct contact with the hot solvent sample in two ways: statically and dynamically. After the extraction was complete, the sample was collected in the extract vials and was ready for evaporation in the Rocket evaporator, Genevac. They were then re-dissolved in acetonitrile and all samples were analyzed by high performance liquid chromatography with fluorescence detection and changeable excitation and emission wavelength. Samples were analyzed for the following PAHs: fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chry), benzo(j)fluoranthene (BjF), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(ah) anthracene (DahA), benzo(ghi)perylene (BghiP), and indeno(1,2,3-cd)pyrene (IP).

In this study, the volume of solvent required for extraction as well as the number of extraction cycles (2 or 3 cycles) were studied. The volume of the solvent represented the extracted were 60, 70, 80 and 90 % of cell volume. Satisfactory recoveries for all PAHs were obtained with a volume of 70 % of the cell volume, and they were more than 97 % for all PAHs, except for fluoranthene and pyrene (83 %). The extract from the third cycle contained about 3 % of the PAH concentration.

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Tema 5
Procjena izloženosti onečišćenjima u zraku i učinci na zdravlje

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POJAVNOST SIMPTOMA SINDROMA BOLESNE ZGRADE U ZAPOSLENIKA TRGOVAČKIH CENTARA

Ključne riječi: *trgovački centri, sindrom bolesne zgrade, zdravlje*

Sindrom bolesne zgrade (SBS) skup je simptoma povezanih s kvalitetom zraka u zatvorenom prostoru, koji utječe na kožu, živčani i dišni sustav. Najčešći simptomi koji su javljaju su glavobolja, vrtoglavica, umor, kašalj, kihanje, iritaciju očiju i kože. Cilj ovog istraživanja bio je ispitati pojavnost simptoma SBS-a i povezane rizične čimbenike među zaposlenicima trgovačkih centara na području grada Zagreba.

Tijekom 2018. godine provedeno je presječno istraživanje korištenjem upitnika koji se odnosi na SBS i kvalitetu zraka u zatvorenom prostoru. U istraživanju je sudjelovalo 363 zaposlenika (55/15,2% muškaraca i 308/84,8% žena). Upitnik se sastojao od pitanja o demografskim karakteristikama, stručnoj osposobljenosti, dužini radnog iskustva, navikama i uvjetima na radnom mjestu te pitanjima u učestalosti pojavljivanja pojedinih simptoma SBS-a. S obzirom na njihovo zdravstveno stanje, zaposlenici su mogli prijaviti od 1 do 22 simptoma. Uočene razlike između skupina analizirane su Mann-Whitney U testom sa statističkom značajnošću $P<0.05$.

Među ispitanicima, njih 96.1% (97,7% žena i 83,3% muškaraca) imalo je jedan ili više simptoma SBZ-a. Najčešći simptomi bili su: glavobolja (58,5%), umor (56,7%), problemi s gornjim dišnim sustavima (kašalj, kihanje) (56,5%), problemi s kožom (suha koža, svrbež i osip) (43,5%). nedostatak koncentracije (32,5%) i svrbež očiju (32,2%). Prosječan broj uočenih simptoma značajno se razlikovao između žena (Mdn=6) i muškaraca (Mdn=3), $P <0,001$, međutim pojavnost simptoma nije razlikovala između muškaraca i žena ovisno o godišnjem dobu. Nije uočena razlika u pojavnosti simptoma između pušača i nepušača. Najveći broj ispitanika 252 (69.4%) radilo je na radnom mjestu prodavač, u dobi od 21-40 godine, a 294 (81.0%) njih s radnim iskustvom manjim od 5 godina. Zaposlenici koji su radili više od 10 godina imali su 6.9 6.9 ± 5.0 SBS-a. 93,1% ispitanika radilo je klimatiziranim prostorima tijekom cijele smjene, pod umjetnim izvorima svjetla (fluorescentne cijevi) i pri temperaturi zraka od 20-24°C. Na ometajuću buku žalilo se 120(33.1%) ispitanika.

Iz navedenoga može se zaključiti da simptomi SBS-a se često javljaju među zaposlenicima u trgovačkim centrima, što ugrožava njihovo zdravlje, smanjuje produktivnost i povećava odsutnost s radnog mjesta. Poboljšanjem radnih uvjeta i radnog okruženja, kao što su snižavanje razine intenziteta buke, osiguravanje toplinske udobnosti i odgovarajuće osvjetljenje i ventilacija radnog mjesta, moguće je na kraju smanjiti učestalost simptoma SPS-a i poboljšati zdravlje zaposlenika trgovačkih centara.

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THE PREVALENCE OF SICK BUILDING SYNDROME SYMPTOMS AMONG SHOPPING MALL EMPLOYEES

Keywords: *shopping malls, sick building syndrome, health*

Sick building syndrome (SBS) is an indoor air quality-related disease that affects the skin, nervous and respiratory system and includes headaches, dizziness, nausea, sore throat, cough, sneezing, itchy eyes and various levels of skin inflammation. The aim of this study was to investigate the prevalence of SBS symptoms and associated risk factors among shopping mall employees in Zagreb, Croatia.

A cross-sectional study was conducted among employees working in four shopping malls in Zagreb using a questionnaire related to SBS and indoor air quality. This study covered 363 employees (55/15.2% males and 308/84.8% females). The questionnaire consisted of information on demographic characteristics (sex, age and education level), job characteristics (professional qualification and length of work experience) and personal habits (smoking status). Regarding their health status, the employees could report 1 to 22 suggested SBS symptoms. The observed differences between groups were analysed using the Mann-Whitney U test with the statistical significance $P<0.05$.

The prevalence of participants who reported 1 or more SBS symptoms was 96.1% (97.7% in women and 83.3% in men). The most common symptoms reported in the questionnaire were headache (58.5%), fatigue (56.7%), upper respiratory system problems (cough, sneezing) (56.5%), skin problems (dry skin, itching and a rash) (43.5%), lack of concentration (32.5%) and itchy eyes (32.2%). The average number of observed symptoms significantly differed between women (Mdn=6) and men (Mdn=3), $P<0.001$, while the occurrence of symptoms did not differ through all the seasons of the year. As many as 81.9% of them were 21-40 years old and 78.2% of them reported a work experience shorter than five years. The group of employees with up to 10 years of the work experience had the highest risk of SBS development. They reported 6.9 ± 5.0 SBS symptoms. There was no significant difference in the appearance of these symptoms between smokers and non-smokers. A total of 93.1% of participants worked in air-conditioned areas during their entire shift, under artificial light sources (fluorescent tubes) and at an air temperature of 20-24°C. Finally, 120 (33.1%) respondents complained about disturbing noise.

Symptoms of SBS often occur among shopping mall employees, which compromises their health, reduces productivity and increases absence from the workplace. By improving working conditions and the working environment, such as lowering noise intensity levels, ensuring thermal comfort and adequate light and ventilation, it is possible to reduce the frequency of SBS symptoms and ultimately improve the health of shopping mall employees.

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MEHANIZAM DJELOVANJA LEBDEĆIH ČESTICA NA KARDIOVASKULARNI SUSTAV

Ključne riječi: *lebdeće čestice, zagađenje zraka, kardiovaskularne bolesti, čimbenici rizika.*

Tradicionalni čimbenici rizika za kardiovaskularne bolesti kao što su: spol, dob, hipertenzija, povećane razine kolesterola u krvi, pušenje i dr. čine oko 50% kardioloških događaja. Ostali čimbenici kao primjerice zagađen zrak, mogu djelovati nezavisno, a zajedno s prethodnim dovode do razvoja kardiovaskularnih bolesti. Akutna i kronična izloženost lebdećim česticama dovodi do povećanja broja hospitalizacija zbog kardiovaskularnih bolesti i do povećanja smrtnih ishoda. Američko udruženje za srce (AHA - American Heart Association) zaključuje da izloženost povećanim koncentracijama $PM_{0,1}$ u zraku kroz nekoliko sati tjedno može biti okidač smrtnoga ishoda kod srčanih bolesnika, te tako i smanjenja očekivanog trajanja života.

Cilj rada je prikazati mehanizam djelovanja povećanih koncentracija lebdećih čestica na kardiovaskularni sustav. Udisanje $PM_{0,1}$ u povećanim koncentracijama djeluje na kardiovaskularni sustav na tri načina: sistemskom upalom, translokacijom u krv i direktnim i indirektnim učinkom na autonomni živčani sustav. Oksidativni stres koji se pri tom pojavljuje, djeluje na stanice endotela krvnih žila, protrombinske procese, elektrofiziologiju srca i metabolizam lipida. Udisanjem povećane koncentracije lebdećih čestica dolazi do klinički značajnih kardiovaskularnih efekata kao što su akutni koronarni sindrom, uključujući i nestabilnu anginu pektoris, aritmija, kronično smanjenje srčane funkcije, srčani udar i iznenadna smrt. Ovakvi učinci posljedica su akutnog izlaganja povišenim koncentracijama lebdećih čestica, dok kronično izlaganje dovodi do pojave ubrzane ateroskleroze i smanjenja očekivanog trajanja života.

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MECHANISM OF ACTION OF AIRBORNE PARTICLES ON THE CARDIOVASCULAR SYSTEM

Keywords: *particulate matter, air pollution, cardiovascular diseases, risk factors.*

Traditional risk factors for cardiovascular disease, such as: gender, age, hypertension, increased blood cholesterol levels, and smoking account for about 50 percent of cardiac events. Other factors as polluted air, can act independently and, together with the previous ones, lead to the development of cardiovascular diseases. Acute and chronic exposure to airborne particles has been shown to increase the risk of hospitalizations for cardiovascular conditions and mortality. American Heart Association (AHA), concluded both that exposure to increased concentrations of $PM_{0.1}$ in the air over a few hours to weeks can trigger cardiovascular disease-related mortality and decreases life expectancy.

The aim of the paper is to demonstrate the mechanism of action of increased concentration of airborne particles on the cardiovascular system. Inhalation of $PM_{0.1}$ in increased concentrations affects the cardiovascular system through three primary pathways: systemic inflammation, translocation into the blood and direct and indirect effects on the autonomic nervous system. The oxidative stress that occurs upon it acts on blood vessel endothelial cells, pro-thrombotic processes, electrophysiology of the heart, and lipid metabolism. Inhalation of increased concentration of particles results in clinically significant cardiovascular effects such as: acute coronary syndrome, including unstable angina, arrhythmia, chronic heart failure, stroke and sudden cardiac death. Such effects can be measured after acute exposure, and there is accumulating evidence that chronic exposure accelerates atherosclerosis and reduces life expectancy.

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OCJENA KVALITETE ZRAKA U HRVATSKOJ NA OSNOVI REZULTATA MJERENJA I MODELIRANJA U RAZDOBLJU 2011.-2015. S OBZIROM NA ONEČIŠĆENJE SUMPOROVIM DIOKSIDOM, SUMPOROVODIKOM I AMONIJAKOM

Ključne riječi: *ozon, gradijent, Riječki zaljev, respiratorne bolesti*

Ozon je sekundarna onečišćujuća tvar koja nastaje iz dušikovih oksida (NOx) i u zraku prisutnih hlapivih ugljikovodika (VOC) pri povišenim temperaturama (>20°C) i djelovanjem sunčeva zračenja. Kao posljedica pojave globalnog zagrijavanja, očekuje se i porast troposferskog ozona. Analiza troposferskog ozona u Riječkom zaljevu za razdoblje 1999.-2007. pokazala je trend smanjenja, ali se od 2009. godine trend mijenja u uzlazni. Tijekom čitavog perioda zabilježena su mnogobrojna prekoračenja ciljne vrijednosti za ozon (8-satni pomični prosjek) na svim stanicama. Nadalje, zbog kompleksne orografije i kružnog kretanja zračnih masa, u Riječkom zaljevu dolazi do formiranja gradijenta ozona s porastom koncentracija prema većim visinama. Često prekoračenje ciljnih vrijednosti za ozon tijekom ljeta postavlja pitanje mogućeg utjecaja na zdravlje populacije. S tim ciljem pregledani su zdravstveni kartoni školske djece i mladeži za 229 učenika sa područja Viškova, područja povišenog ljetnog ozona, te paralelno anketirani roditelji tih istih učenika. U ukupnom uzorku nađeno je samo 2% djece s bolestima dišnog sustava koje imaju alergijsku podlogu što je u skladu s učestalošću takvih bolesti kod djece iz zapadnog dijela grada Rijeke (Zamet, Kantrida). Roditelji navode da su bolesti aktivnije u doba zime vezano uz akutne respiratorne infekte te u proljeće kod djece s alergijama vezanim uz pelud. Svaki od navedenih učenika imao je dobro kontroliranu bolest zbog koje uz dobru suradnju s odabranim pedijatrima i specijalistima alergolozima nije imao potrebe za intenziviranjem terapije. To je u skladu s izmjerenim razdobljima povećanih koncentracija ozona (>160 μg/m³) u razdoblju 2016.-2018. koje, premda mogu djelovati na promjenu plućnih funkcija, s obzirom da su promjene reverzibilne pitanje koliko uistinu utječu na pojavu simptoma respiratornih bolesti. U buduća istraživanja valjalo bi uključiti roditelje na način da tijekom cijele godine prate i bilježe stanje svoje djece i njihove bolesti, a tek onda retrogradno usporediti s pojavom povišenih koncentracija.

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OZONE AIR POLLUTION IN RIJEKA BAY AND ITS POSSIBLE IMPACT ON HUMAN HEALTH

Keywords: *ozone, gradient, Rijeka Bay, respiratory illness*

Ozone (O_3) is secondary pollutant generated by NOx and volatile organics (VOC) in the atmosphere at higher temperatures (>20°C) and insolation. As a results of global warming, the increase of tropospheric ozone is expected. Evaluation of airborne ozone in the Rijeka Bay area showed a declining temporal trend for the period of 1999-2007, followed by an increased trend since 2009. In spite of the declining trend in the first decade, the high number of 8-h moving average exceedances were observed at most stations. Furthermore, the complex orography and circular air mass circulation in the area were responsible for the formation of an O_3 gradient, with concentrations rising with altitude. Frequent exceedances of target values for ozone in summer raise the question of possible impact on human health. Therefore, health records of 229 schoolchildren and youngsters living in the Viškovo area, often affected by high ozone in summer, were examined. An inquiry regarding children's health status was also carried on among their parents. Only 2% of the children were found to suffer from respiratory diseases originating from allergies, which does not differ from the data for children living in the western part of the city (Zamet, Kantrida). Parents reported that acute conditions appeared mostly in winter due to respiratory infections and in spring because of pollen allergy. The children's diseases were well-controlled, and their allergists and paediatricians did not have need to change their therapy because they communicated well. This finding is in agreement with a few elevated concentrations of ozone (>160 μg/m³) measured in the period 2016-2018. Such a high ozone concentrations might affect the pulmonary functions of the exposed population, but these changes are reversible and it is still unclear if they could promote the acute phase of respiratory diseases. To answer that question, another study that would involve parents is necessary. The parents would have to take records of their children's health conditions on a day-to-day basis and subsequently their records would be compared with periods of elevated ozone concentrations.

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PROCJENA AEROBIOLOŠKE KVALITETE ZRAKA U ZATVORENIM PROSTORIMA DJEČJIH VRTIĆA NA PODRUČJU GRADA ZADRA

Ključne riječi: *aerobiologija, spore, kvaliteta zraka u zatvorenim prostorima, Zadar*

Različite vrste peludnih zrnaca kao i spore gljivica koje se nalaze slobodno raspršene u zraku smatraju se najsnažnijim prirodnim alergenima te mogu izazivati zdravstvene probleme posebice u dječjoj dobi. Djeca u vrtićima provode veći dio dana u zatvorenom prostoru, koji se najčešće slabo prozračuje. Podaci o vrstama alergija kod djece na području grada Zadra su oskudni i nedovoljno istraženi. Cilj istraživanja bio je utvrditi koncentracije alergenih peludnih zrnaca i spora u zatvorenim prostorima, te procijeniti aerobiološku kvalitetu zraka u dječjim vrtićima na području grada Zadra.

Istraživanje se provodilo jednom mjesečno tijekom školske godine 2015./2016. u devet objekata gdje borave djeca vrtićke i predškolske dobi na području grada Zadra. Uzorkovanje je provedeno pomoću volumetrijskog uzorkivača tipa Burkard. Prilikom svakog uzorkovanja bilježila se temperatura i relativna vlaga zraka. Uzorci su pripremljeni pomoću Gelvatola obojanog fuksinom te pregledani direktnom mikroskopijom pri povećanju 400x. Osim mjerenja koncentracija peludnih zrnaca određivana je i koncentracija patogenih spora Alternaria spp., Aspergillus/Penicillium, Cladosporium spp., Epicoccum spp. i Torula spp. Voditeljima dječjih vrtića dostavljen je upitnik kako bi se ustanovio broj djece i osoblja koje boravi u objektima kao i udio djece i osoblja koje ima dijagnosticirane alergološke smetnje. Upitnikom su prikupljeni i podaci o vrtićima (godina izgradnje, godina posljednje adaptacije, vrsta podne podloge, godina posljednjeg bojenja zidova i brušenja/ lakiranja parketa, vrsta prozora, način provjetravanja, sustav grijanja) kako bi se ispitala razina održavanja pojedinog objekta.

Rezultati dobiveni ovim istraživanjem ukazali su na sezonsku varijaciju peluda i spora, te razlike u izmjerenim koncentracijama po objektima. Izmjerene koncentracije peluda i ukupnih spora u zatvorenim prostorima su uglavnom niže od onih izmjerenih u vanjskom zraku (0/m^3- 5322/m^3). Koncentracije patogenih spora u pojedinim objektima su povremeno bile više od onih izmjerenih u vanjskom zraku (22/m^3- 611/m^3). Prema EU standardima izmjerene koncentracije patogenih spora su većinom niske (< 200 spora/m^3 zraka) ili niske do srednje koncentracije (200- 1000 spora/m^3 zraka). Rezultati mjerenja pokazuju da je aerobiološka kvaliteta zraka u ispitivanim objektima zadovoljavajuća. Iz podataka dobivenih upitnikom može se zaključiti da su objekti u dobrom stanju i redovito se održavaju.

Sve veća prisutnost aerobioloških zagađenja u zatvorenim prostorima, te porast broja alergija na aerobiološke čestice ukazuje na potrebu daljnjih sustavnih ispitivanja kvalitete zraka u prostorima u kojima borave djeca kao i redovito praćenje kemijskih štetnosti koji mogu ugroziti zdravlje najmlađih.

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AN ASSESSMENT OF AEROBIOLOGICAL INDOOR AIR QUALITY IN ZADAR KINDERGARTENS

Keywords: *aerobiology, spore, indoor air quality, Zadar*

Apart from different pollen types that are considered the most powerful natural allergens, health problems can also be caused by various fungus spores freely dispersed in the air.

Children in kindergartens spend most of the day in indoor areas, which are often poorly ventilated. Statistical data on children allergies in the Zadar area are scarce and insufficiently explored. The aim of this study was to determine the concentrations of allergenic pollen grains and spores in kindergarten indoor areas and assess the aerobiological air quality in kindergartens in the Zadar area.

The study was implemented once a month during the school year 2015-2016 in nine different kindergarten facilities in the city of Zadar. Sampling was carried out using a personal Burkard volumetric sampler. At each sampling, the temperature and relative humidity of the air were recorded. Samples were prepared using a fuchsine coloured Gelvatol and examined by direct microscopy at 400x magnification. In addition to the pollen grains, the focus of this study was to determine the concentrations of the pathogenic spores (Alternaria spp., Aspergillus / Penicillium, Cladosporium spp., Epicoccum spp. and Torula spp.). Kindergarten teachers filled out a questionnaire on the number of children and staff in the facility, their allergic health problems and on the maintenance requirements of a particular facility.

The results showed seasonal variation of pollen and pathogenic spore concentrations, and differences between facilities was also observed. Measured indoor pollen concentrations and total spores are generally lower than those measured in the outdoor air (0 /m^3 - 5322 /m^3). Concentrations of pathogenic spores in some facilities were occasionally higher than those measured in the outer air (22 /m^3- 611 /m^3). According to EU standards, the measured indoor concentrations of pathogenic spores were mostly low (<200 spores /m^3 air) or low to medium (200 to 1000 spores /m^3 air). The aerobiological indoor air quality in the kindergartens that participated in this study can be considered to be good. The data obtained from the questionnaire indicated that the facilities were in good condition and regularly maintained.

The increasing presence of indoor aerobiological pollutants and the increase of the aerobiological allergies point to the need for further systematic air quality researches in children's living spaces as well as regular monitoring of chemical hazards that can endanger the health of the youngest members of the population.

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PELUDNA SEZONA AMBROZIJE U HRVATSKOJ TIJEKOM 2018. GODINE

Ključne riječi: *pelud, ambrozija, kontinentalna i mediteranska Hrvatska, peludni kalendar*

Ambrozija, Ambrosia artemisiifolia L., je invazivna korovna biljka porijeklom iz Sjeverne Amerike. Sredinom prošlog stoljeća započelo je njezino intenzivno širenje u Europi. Rod Ambrosia sadrži oko 50 vrsta i nekoliko podvrsta. Samo jedna vrsta, A. maritima L., porijeklom je iz Europe i zabilježena je na području mediteranske Hrvatske, iako novija istraživanja dovode u sumnju njezinu prisutnost. Prve zapise o njenim nalazištima na našem području nalazimo 1842. godine, u djelu „Flora Dalmatica" Roberta de Visianija koji je opisuje kao biljku rasprostranjenu na pješčanim morskim obalama oko Dubrovnika i na otocima. U Europi su tri velika područja zaražena ambrozijom: Karpatski bazen/Panonska nizina, Francuska regija Rona-Alpe i sjeverna Italija. Hrvatska, osobito njen kontinentalni nizinski dio, u epicentru je širenja ambrozije. Posljednjih dvadesetak godina ambrozija je predmet brojnih istraživanja mnogih znanstvenih disciplina u Hrvatskoj. Uz navedeno, razlog tome je i činjenica da pelud ambrozije ima izuzetno visok alergeni potencijal i uzrokuje alergijske reakcije kod sve većeg broja ljudi. Javnozdravstveno značajna, A. artemisiifolia, raste na pjeskovitom, nedovoljno obrađenom i šljunčanom tlu te je lako prilagodljiva širokom rasponu kiselosti tla. Nalazimo je u monokulturi čime znatno utječe na smanjenje prirodne raznolikosti. Širenje staništa ambrozije prvenstveno se uočava duž komunikacijskih linija, u novosagrađenim naseljima, okućnicama i ostalim nepoljoprivrednim površinama. Uočavanjem javnozdravstvenog

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problema uzrokovanog peludom ambrozije 2001. godine u Osijeku je postavljena prva mjerna postaja za praćenje koncentracije alergene peludi u zraku. U sklopu nadležnosti županijskih zavoda za javno zdravstvo uspostavljena je mreža mjernih postaja u kontinentalnom i mediteranskom dijelu zemlje.

U ovom istraživanju, po prvi puta su objedinjeni aerobiološki podaci o polinacijskoj sezoni ambrozije za čitavu Hrvatsku. Prikazana je polinacijska sezona ambrozije tijekom 2018. godine na svim mjernim postajama (Osijek, Beli Manastir, Đakovo, Našice, Virovitica, Slavonski Brod, Sisak, Kutina, Popovača, Varaždin, Koprivnica, Karlovac, Zagreb, Rijeka, Pula, Labin, Pazin, Zadar, Šibenik, Split, Metković, Dubrovnik). Prikazan je početak i kraj polinacijske sezone, trajanje polinacije, prosječna maksimalna dnevna koncentracija, peludni indeks, alergijski potencijal i alergijski rizik. Na temelju dobivenih rezultata napravljen je peludni kalendar za svaki grad. Prikazani podaci temelj su za daljnja postupanja u svrhu primjena mjera iskorjenjivanja i informiranja javnosti o dnevnoj dinamici peludi ambrozije u zraku. Također, sustavno praćenje širenja i rasprostranjenosti ambrozije u obalnim dijelovima Hrvatske smanjilo bi njezino napredovanje na južnije dijelove i otoke.

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RAGWEED POLLEN SEASON IN CROATIA IN 2018

Keywords: *pollen, ragweed, continental and Mediterranean Croatia, pollen calendar*

Ragweed, Ambrosia artemisiifolia L., is an invasive weed plant that originates from North America. Its intensive expansion across Europe began in the middle of the previous century. The genus Ambrosia includes about 50 species and several subspecies. Only one species, A. maritima L., originates from Europe and was recorded for the Mediterranean part of Croatia, although recent studies indicated doubts about its presence. The first data about its distribution in Croatia were recorded in 1842 by Robert de Visiani, in his monograph "Flora Dalmatica". He noted that the plants were found on sandy beaches around Dubrovnik and on some islands.

In Europe, three major areas are infected by ragweed: the Carpathian basin/Pannonian lowlands, the Rona-Alps region of France and northern Italy. Croatia, especially its continental lowland part, is located in the epicentre of ragweed spread. For the past twenty years, ragweed has been the topic of numerous researches of many scientific disciplines in Croatia. In addition, the reason for this is the fact that ragweed pollen has an extremely high allergenic potential and causes an allergic reaction to an increasing number of people. A. artemisiifolia grows on sandy, insufficiently treated and gravel soil and is easily adaptable to a wide range of soil acidity. It can be found in monoculture, which greatly contributes to the reduction of natural diversity. The spread of ragweed habitats is primarily observed along communication lines, in newly built settlements, gardens and other non-agricultural areas.

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Recognizing the public health problem caused by ragweed pollen resulted in the establishment of the first measurement station for monitoring allergenic pollen the air in Osijek (2001). Under the jurisdiction of County Public Health Institutes, the network of measuring stations was established in both the continental and Mediterranean parts of the country. In this study, for the first time we united aerobiological data on ragweed pollination season for the whole territory of Croatia. The pollination season of ragweed was analysed during 2018 at all of the measuring stations (Osijek, Beli Manastir, Đakovo, Našice, Virovitica, Slavonski Brod, Sisak, Kutina, Popovača, Varaždin, Koprivnica, Karlovac, Zagreb, Rijeka, Pula, Labin, Pazin, Zadar, Šibenik, Split, Metković, Dubrovnik). The start and end of the pollination season, pollination duration, average maximum daily concentration, pollen index, allergenic potential and allergy risk are presented. Based on the obtained results, a pollen calendar was created for each city. In order to implement measures for eradication and inform the public about the daily dynamics of ragweed pollen in the air, the obtained data represent an important and valuable basis. Moreover, the systematic monitoring of the spread and prevalence of ragweed in the Croatian coastal parts might reduce its progress to the south and islands.

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USPOREDNA AEROBIOLOŠKA STUDIJA SVOJTE OLEA EUROPAEA L. U DALMACIJI

Ključne riječi: *aerobiologija, pelud, maslina, Dalmacija, rizik od alergija*

Zbog visokog alergijskog potencijala pelud masline se ubraja među najznačajnije uzročnike alergija dišnog sustava na području Mediterana. Hrvatska, velikim dijelom mediteranska zemlja, ima iznimno povoljne prirodne uvjete i dugu tradiciju uzgoja masline. Maslina je najzastupljenija poljoprivredna kultura u regiji Jadranska Hrvatska, a više od ¾ ukupng broja stabala maslina je na području Dalmacije.

Cilj ovoga istraživanja je utvrditi obilježja glavnih peludnih sezona masline na području četiriju dalmatinskih gradova (Zadar, Split, Dubrovnik i Metković) u šestogodišnjem razdoblju (2013.-2018.). Aerobiološka baza podataka, na kojoj je istraživanje temeljeno, dobivena je primjenom metodologije po Hirst-u. Klase peluda određene su prema pragovima za pojavu alergijskih reakcija po preporuci španjolske aerobiološke mreže (REA), prilagođeno lokalnim uvjetima. Glavna peludna sezona definirana je za dane s 95% ukupnog godišnjeg peluda. Proučena su i kolebanja među sezonama i lokacijama. Određen je početak, kraj i trajanje glavne peludne sezone, datum vršnih vrijednosti koncentracija te klase peludi masline. Izrađeni su peludni kalendari za sve istraživane lokacije.

Istraživanje je pokazalo da su peludne sezone masline na istraživanom području bile relativno kratke i trajale prosječno 34 dana. Na području Splita i Metkovića peludna je sezona uglavnom počinjala u drugoj polovinci travnja, a na dubrovačkom i zadarskom području, u prvoj polovici svibnja. Peludne sezone završavale su u lipnju, ovisno o lokaciji. Najintenzivnije i najdulje peludne sezone bile su na splitskom području gdje su zabilježene najviše vrijednosti peludnih indeksa i najviše vršne vrijednosti koncentracija peludi masline. Peludne sezone bile su najslabijeg intenziteta na području Metkovića. U Zadru i Dubrovniku peludne sezone masline bile su sličnog intenziteta i sličnih značajki. Dvogodišnja izmjena visokih i niskih vrijednosti godišnjih peludnih indeksa (karakteristično za pelud masline) uočena je samo na području grada Zadra.

Dobiveni rezultati od velike su važnosti za osobe alergične na pelud masline i imat će primjenu u planiranju preventivnih alergoloških i javnozdravstvenih mjera. Temelj su za daljnja istraživanja u kojima će baza aerobioloških podataka biti upotpunjena meteorološkim podacima.

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COMPARATIVE AEROBIOLOGICAL STUDY OF OLEA EUROPEA L. POLLEN IN DALMATIA

Keywords: *aerobiology, Olea pollen, Dalmatia, allergy risk*

Olea pollen is considered one of the main causes of allergic respiratory diseases in the Mediterranean region because of its high allergenic potential. Croatia, as part of the Mediterranean, has favourable natural conditions and a long tradition of growing olives. Olive is the most abundant cultivated arboreal taxa on the Croatian Adriatic Coast, with more than ¾ of the total number of olive trees widespread throughout Dalmatia. The aim of this study was to determine the characteristics of the main pollen seasons of Olea pollen in four Dalmatian cities (Zadar, Split, Dubrovnik and Metković) during a six-year period (2013-2018). The aerobiological data for this research were obtained following Hirst's methodology. The pollen classes for causing allergic reactions were determined using a threshold system according to the Spanish Aerobiology Network (REA) and adapted to local conditions. The main pollen season was defined as the period with 95% of the total annual index. The start, end and duration of the main pollen season, the daily maximum pollen concentrations and the classes of the Olea pollen type were determined, as well as seasonal and spatial oscillations. The fluctuations between seasons and locations were studied and pollen calendars were created for each location. The research showed that the Olea pollen season was relatively short and lasted on average 34 days. In the cities of Split and Metković, Olea pollen season mainly started in the second half of April, in the cities of Dubrovnik and Zadar in the first half of May, and lasted until mid-June. The most intensive and the longest pollen seasons were recorded in the city of Split with the highest values of the annual pollen index and the highest values of the daily maximum pollen concentrations. In the city of Metković, pollen seasons had weak intensity, while pollen seasons in the cities of Zadar and Dubrovnik had medium intensity and similar characteristics. Biannual exchange of high and low annual pollen index (characteristic for Olea pollen) was visible only in the Zadar area.

The results obtained in this aerobiological study are of great importance for people allergic to Olea pollen and may be applied in planning preventive allergology and public health activities. This paper will be the basis for further research in which the aerobiological database will be supplemented with meteorological data.

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Tema 6
Zaštita zraka u sustavu prostornog uređenja, graditeljstva i zaštite okoliša

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PRISUTNOST AZBESTNIH VLAKANA U ZRAKU U GRADOVIMA REPUBLIKE HRVATSKE

Ključne riječi: *PLM, azbest u zraku, mikroskopija, membranska filtracija*

Azbest je prirodni silikatni mineral koji se zbog svojih „čudotvornih" svojstava ugrađivao u više od 3000 proizvoda (npr, žbuka, krovni pokrov, betonske ploče i cijevi, protupožarna izolacija, konopi i dr.). Krizotil, amozit, krocidolit, temolit, aktinolit i antofilit su komercijalno najčešće korišteni azbesti. Iako je uvoz i proizvodnja materijala koji sadrži azbest zabranjena u Hrvatskoj, azbest je prisutan na cijelome teritoriju RH. Cilj rada je bio procijeniti koncentracije ukupnih i azbestnih vlakana u zraku na odabranim mjernim mjestima na području grada Zagreba, Karlovca, Splita i Ploča.

Uzorkovanja zraka su provedena pri ugodnom, suhom i sunčanom vremenu bez oborina na visini zone disanja računajući od podloge. Koncentracija ukupnih i azbestnih vlakana određena je korištenjem metode membranske filtracije. Uzorci su analizirani korištenjem mikroskopa s polarizacijskim svjetlom (PLM). Analizom pomoću PLM-a, za razliku od mikroskopije s faznim kontrastom (PCM), moguće je ustanoviti karakteristične osobine azbestnih vlakana; anizotropija, morfologija, reljef, oblik, sjaj, dvolom, polarizacija i boja. Rezultati analiza su pokazali prisustvo ukupnih vlakna respirabilne veličine u zraku na svim mjernim mjestima. Raspon izmjerenih koncentracija ukupnih vlakana u zraku u Zagrebu kretao se od 0,001 do 0.003 vl/cm^3, Splitu 0.007 do 0.001 vl/cm^3, Karlovcu 0,009 vl/cm^3 i Pločama 0.001 do 0.003 vl/cm^3. Koncentracija azbestnih vlakna u zraku na širem području Splita (Vranjic) iznosila je od 0,001 do 0,002 vl/cm^3 i Ploča od 0,001 do 0,003 vl/cm^3. u područjima gdje je bila proizvodnja azbesta i proizvoda koje sadrže azbest.

U Hrvatskoj nema Pravilnika koji propisuje maksimalno dozvoljene vrijednosti za respirabilne veličine azbestnih vlakana u zraku općeg okoliša, jer azbestnih vlakana na bi smjelo ni biti u zraku. Pravilnik o zaštiti radnika od rizika zbog izlaganja azbestu NN 40/07, Zakona o zaštiti na radu (NN 59/96; 94/96, 114/03 i 100/04) propisuje maksimalno dopustivu koncentraciju (članak 9) azbestnih vlakana za osmosatnu izloženost na radnom mjestu od 0,1 vl/cm^3.

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THE PRESENCE OF ASBESTOS FIBRES IN THE AIR AT THE CITIES OF CROATIA

Keywords: *PLM, asbestos in air, microscopy, membrane filter method*

Asbestos, or "miracle fiber", is a naturally occurring silicate mineral that has been incorporated into more than 3000 products (e.g., plaster, roof covering, concrete slabs and pipes, fireproofing, ropes, etc.). Chrysotile, amosite, crocidolite, temolite, actinolite and anthophyite are commercially the most commonly used asbestos materials. Although the import and production of asbestos-containing material is prohibited in Croatia, asbestos is present throughout the territory of the Republic of Croatia. In order to determine concentrations of total and asbestos fibres in the air, air was sampled at measurement points in Zagreb, Karlovac, Split and Ploče. The sampling was conducted during dry, stable and sunny weather without precipitation. Samples of air were taken at the height of the breathing zone starting from the ground. The concentration of total and asbestos fibres was determined using membrane filter method. Samples were analysed by means of polarized light microscopy (PLM). By PLM analysis, unlike microscopy with phase contrast (PCM), it is possible to establish characteristic traits of asbestos fibres; anisotropy, morphology, relief, shape, shine, twist, polarization and colour. The analysis showed the presence of total breathable airborne fibres at all measuring stations. The concentration range of the total fibre in the air in Zagreb was from 0.001 to 0.003 vl/cm^3, Split 0.007 to 0.001 vl/cm^3, Karlovac 0.009 vl/cm^3, and Ploče 0.001 to 0.003 vl/cm^3. Asbestos fibres were found in the area of Split from 0.001 to 0.002 vl/cm^3 and Ploče from 0.001 to 0.003 vl/cm^3. Asbestos fibres were found in areas where an asbestos production factory was present. In Croatia, allowable values of respirable size of asbestos fibres in the air in the general environment are not prescribed. However, the Croatian Occupational Safety and Health Act (OG 59/96, 94/96, 114/03 and 100/04), and the Risks Related to Exposure of Workers to Asbestos Ordinance (OG 40/07), where Article 9 stipulates that the eight-hour time-adjusted average single worker is allowed to be exposed to a concentration of asbestos in the air no higher than 0.1 fibres per cm^3.

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TREND TALOŽENJA ATMOSFERSKOG ONEČIŠĆENJA NA PODRUČJU HRVATSKE (1981.-2018.)

Ključne riječi: *kvaliteta oborine, taloženje, modelirane vrijednosti koncentracija, dugoročni trend*

Doprinos atmosferskog taloženja oborinom prati se u Hrvatskoj na postajama Državnog hidrometeorološkog zavoda od 1981. godine. Iz dnevnih uzoraka oborine određuje se njena kiselost i koncentracije glavnih iona. Iako se općenito, smatralo se da je atmosferski doprinos oborinom relativno mali u usporedbi onim koji je praćen u industrijskim zemljama Zapadne Europe, skandinavskim zemljama i zemljama Srednje Europe, mjerenja su pokazala da je bio značajan kao pokazatelj daljinskog, prekograničnog prijenosa onečišćenja te kao indikator i mjerilo uspješnosti provođenja zajedničke politike smanjivanja emisija onečišćujućih tvari na području Europe u posljednjih 30 godina.

U ovome radu prikazane su prostorne i vremenske promjene kemijskog sastava oborine na 18 mjernih postaja u razdoblju od 1981.-2016. godine. Izrađena je analiza sezonskih i godišnjih trendova primjenom neparametarskog Mann-Kendall-ovog testa jačine trenda i Sen's-ovog estimatora nagiba trenda.

Rezultati analize pokazuju da su se koncentracije iona sulfata i nitrata u oborini, komponenata najzaslužnijih za procese eutrofikacije i zakiseljivanja okoliša, postepeno smanjivale tijekom razmatranog razdoblja, osobito u središnjem dijelu i na jugu Hrvatske. Najveći trend smanjenja uslijedio je sredinom 90-tih godina prošloga stoljeća. Središnji i južni dijelovi Hrvatske gdje je trend statistički značajan pokazuju i slična obilježja s obzirom na jačinu i nagib trenda dok je u području Panonske Hrvatske trend blaži i slabe je statističke značajnosti. Zbog toga možemo zaključiti da su se okolnosti prijenosa onečišćujućih tvari na područje Hrvatske promijenile, da nisu jedinstvenog predznaka u svim regijama i da ih treba dovoditi u vezu s redistribucijom glavnih emisijskih područja u Europi i našem neposrednom okruženju. Dok su se emisije u zemljama zapadne Europe značajno smanjile (više od 80% u slučaju sumporovih oksida) emisije u zemljama istočne Europe i zemljama Balkana i dalje se zasnivaju na ugljenu kao sirovini npr. u energetskom sektoru. Nakon ekonomske krize 2008. godine kućanstva su također postala značajniji izvor onečišćenja budući da se prešlo na loženje drvnom masom kao jeftinijim gorivom. Posljedice ovih promjena u ponašanju i navikama postale su mjerljive i u kemijskom sastavu oborine tako da se Panonsko područje počelo izdvajati kao područje najvećeg opterećenja taloženjem iona sulfata i nitrata.

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ATMOSPHERIC DEPOSITION TRENDS IN CROATIA (1981-2018)

Keywords: *precipitation quality, deposition, model calculations, long-term trends*

The contribution of atmospheric input to the overall deposition of pollutants through precipitation has never been considered a serious problem in Croatia. Relatively low emission rates of pollutants, especially when compared to ones of industrially developed European countries, created an impression that this region could not be dramatically affected by pollution of atmospheric origin. Nevertheless, atmospheric deposition monitoring programme has been established and operationally run within regular meteorological observational network since 1981. Chemical composition of precipitation, sampled on a daily basis, has been used as a valuable indicator for regional and long-range transport of pollutants and matrix for successfulness of emission reduction policies in Europe over the last 30 years.

Spatial, temporal and trend changes in precipitation chemistry over the period 1981-2018 were analysed using the data from 18 sampling sites spatially distributed over Croatian territory. Volume weighted average concentrations of major ions in precipitation samples (sulphate, nitrate, chloride, ammonium, calcium, magnesium, sodium, potassium) and acidity (pH) are calculated for each year and season. The trend analysis was performed and tested by nonparametric Mann-Kendall test and Sen's slope estimator.

Results showed that sulphate and nitrate ion concentrations significantly decreased for majority of sites in central and southern regions of Croatia. The main decline of sulphate ion concentration occurred after 1990. Changes in anthropogenic sulphur emission patterns over Europe in the last two decades resulted in different acidity and sulphate ion concentrations in relation to particular sector compared to earlier times. In additions, precipitation chemistry is influenced by geographical and climatological diversity. While central and southern parts of Croatia exhibit similar trend behaviour (trend slope and significance level), results for Pannonian region show a much slower decrease without statistical significance. Therefore it cannot be assumed that decline of atmospheric deposition of pollutants is significant. Main reasons could be related to the fact that in most neighbouring countries (Slovenia, Serbia, Bosnia and Herzegovina, and Bulgaria) locally mined coal with higher content of sulphur is used in industry and electrical power generation as major fuel. This became much more pronounced since 2008 with economic crisis that also reversed the trend of cleaner fuel usage for residential heating. Due to the lower prices households started to use again cheaper solutions for burning, like wood or coal, instead of already installed natural gas option. Effects of these behavioural changes are therefore measurable in precipitation chemistry parameters of the last decade in Croatian regions.

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ATMOSFERSKO TALOŽENJE ONEČIŠĆUJUĆIH TVARI NA ŠIBENSKOM PODRUČJU JADRANSKOG MORA

Ključne riječi: *BC, EC, OC, PAT, PM_{10}*

Procjenjuje se da bi kompleksna međudjelovanja mora i oceana, atmosfere i klime mogla postati još značajnija u budućim klimatskim scenarijima toplije atmosfere i povećanih emisija i brzina taloženja prirodnih i antropogenih aerosola. Stoga je za očekivati kako će utjecaj atmosfere, kao značajnog vanjskog izvora hranjivih soli ali i zagađivala za površinske oligotrofne vode, u budućnosti rasti, a doseg njezina utjecaja moguće je procijeniti samo kroz cjelovita istraživanja koja obuhvaćaju različite okolišne sastavnice. Stoga je provedena kampanja sakupljanja morskih i atmosferskih uzoraka na postaji Martinska (Šibenik) koja ima za cilj po prvi puta procijeniti koncentracije i izvore atmosferskih sastavnica te dobiti uvid u prirodu obogaćenja površinskih slojeva mora tvarima atmosferskog porijekla na području srednjeg Jadrana - ključnog područja za istraživanja biokemijskih učinaka atmosferskog taloženja na području Jadranskog mora. U razdoblju od veljače do srpnja 2019. godine provodilo se sakupljanje dvotjednih uzoraka ukupnog i mokrog atmosferskog taloženja te dvodnevnih uzoraka lebdećih čestica promjera manjeg od 10 μm (PM_{10}). Prvi rezultati ukazuju na porast temperature od 4,3 °C do 33,5 °C, te promjenu relativne vlažnost između 36,5 % i 86,5 %. U frakciji čestica PM_{10} određene su masene koncentracije elementnog (EC) i organskog (OC) ugljika metodom termičko-optičke transmisije. Također su i procijenjene masene koncentracije crnog ugljika (BC) čije su vrijednosti bile u rasponu od 0,2 μg m^{-3} do 5,7 μg m^{-3} pomoću koeficijenta apsorpcije svjetlosti. U razdoblju mjerenje prosječne masene koncentracije PM_{10}, TC, OC i EC su iznosile 25,6 μg m^{-3}, 5,3 μg m^{-3}, 4,9 μg m^{-3} i 0,42 μg m^{-3}. Prosječni udjeli OC i EC iznosili 19 % i 2 %. Sadržaj ugljika i površinski aktivnih tvari (PAT) određen je u topivom i netopivom dijelu u uzorci ukupnog atmosferskog taloženja kao i uzorci mokrog atmosferskog taloženja. Taložni tokovi atmosferskog otopljenog organskog ugljika (DOC) i čestičnog organskog ugljika (POC) su veći u uzorcima ukupnog atmosferskog taloženja u odnosu na uzorke mokrog taloženja. Isto je zamijećeno i za površinski aktivne tvari. Udio topljivih površinski aktivnih tvari u ukupnim površinski aktivnim tvarima u uzorcima ukupnog i mokrog atmosferskog taloženja veći je od 50 %. Cjeloviti podaci za ispitivano razdoblje biti će prezentirani i diskutirani.

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ATMOSPHERIC DEPOSITION OF POLLUTANTS IN THE SEA SURROUNDING ŠIBENIK, CROATIA

Keywords: *BC, EC, OC, PM_{10}, SAS*

The complex mutual interactions between seas and oceans, atmosphere and climate should become even more important in a future scenario of a warmer atmosphere with increased natural and anthropogenic aerosol emissions and deposition rates. Hence, the impact of the atmosphere as a significant external source of nutrients, as well as pollutants, for surface oligotrophic waters is expected to increase in the future. Thus, an integral scientific approach considering different environmental compartments is crucial. For the first time, an interdisciplinary campaign at Martinska (Šibenik) was conducted to evaluate concentrations, sources and deposition fluxes of atmospheric constituents, and to get insight into the nature of enrichments of atmospheric constituents within the sea surface layers of the middle Adriatic-a «hotspot» area to study the biochemical effects of atmospheric deposition to the Adriatic Sea. In the period from February to July 2019, the collection biweekly samples of total and wet atmospheric deposition and two-day samples of airborne particles with a diameter less than 10 μm (PM_{10}) was conducted. The first results collected until April 2019 indicated a rise in temperature ranging from 4.3 ° C to 33.5 ° C, and a relative humidity changed between 36.5% and 86.5%. The mass concentrations of elemental (EC) and organic (OC) carbon in particle fraction of PM_{10} were determined by the thermal-optical transmission method (TOT). Black carbon (BC) mass concentrations, whose values ranged from 0.2 μg m^{-3} to 5.7 μg m^{-3} were estimated by light absorption coefficient. During the examined period, the average mass concentration of PM_{10}, TC, OC and EC were 25.6 μg m^{-3}, 5.3 μg m^{-3}, 4.9 μg m^{-3}, and 0.42 μg m^{-3}, respectively. The average mass fraction of OC and EC to the total mass of PM_{10} were 19 % and 2 % respectively. Carbon content and surface-active substance (SAS) content were analyzed in the soluble and insoluble part of biweekly samples of total atmospheric deposition as well as samples of wet atmospheric deposition. The atmospheric deposition rates of dissolved organic carbon (DOC) and particulate organic carbon (POC) are higher in total atmospheric deposition samples relative to wet deposition samples. The same was observed for surface-active substances. The ratio of soluble atmospheric surfactants and total surfactants in the samples of total and wet atmospheric deposition was higher than 50%. The full data for the measured period will be presented and discussed.

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ATMOSFERSKO TALOŽENJE ONEČIŠĆUJUĆIH TVARI NA PODRUČJU SREDNJEG JADRANA: VREMENSKA VARIJABILNOST I GLAVNE PUTANJE PRIJENOSA

Ključne riječi: *atmosfersko taloženje, kemijski model LOTOS-EUROS, srednji Jadran*

Atmosferski prijenos nije samo značajan, već često i dominantan put kojim se prirodne i antropogene tvari prenose s kopna na morsko područje. Jednom uneseni, putem procesa suhog i mokrog taloženja, aerosoli postaju vanjski izvor hranjivih, ali i toksičnih tvari koje imaju negativan učinak na funkcioniranje morskih organizama. Sjeverni Jadran jedno je od najeutrofnijih područja Mediterana, pod snažnim utjecajem riječnih donosa i atmosferskog taloženja uslijed sagorijevanja fosilnih goriva, naftne industrije te donosa sa sjevera Italije i drugih europskih industrijskih područja. Međutim, zbog intenzivnih obalnih i riječnih unosa, u ovom području atmosfersko taloženje ima slab utjecaj na primarnu produkciju tijekom cijele godine. Za razliku od sjevernog Jadrana, u oligotrofnim područjima srednjeg i jugoistočnog Jadrana riječni su donosi slabi, te bi donos materijala atmosferskog taloženja iz raznih izvora sagorijevanja mogao značajno utjecati na biologiju mora. Također, ovo područje je pod utjecajem sušnog Mediterana, a tijekom ljetnog razdoblja, posebno je srednji Jadran trajno izložen visokim do vrlo visokim rizicima od požara te ima dugu povijest ekstremnih šumskih požara. Gledajući u cjelini, nepoznati su učinci donosa atmosferskog materijala putem atmosferskog taloženja na oligotrofne površinske vode Jadrana. Ovaj rad pružit će prvi uvid u vremensku varijabilnost taloženja proračunatu pomoću atmosferskog numeričkog modela LOTOS-EUROS u svrhu kvantificiranja i ocjene utjecaja vremenske varijabilnosti atmosferskog taloženja Srednjeg Jadrana na morske ekosustave te njihovu produktivnost. Promatrat će se putanje atmosferskog donosa i taloženje onečišćenja u razdoblju povezanim s uspostavom oligotrofnih uvjeta u površinskom sloju mora (od veljače do srpnja 2019. godine) te njihova povezanost s unosom nutrijenata i drugih elemenata koji imaju utjecaj na funkcioniranje morskog ekosustava.

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IMPACT OF ATMOSPHERIC DEPOSITION ON THE CENTRAL ADRIATIC SEA: TEMPORAL VARIABILITY AND MAIN POLLUTANT PATHWAYS, MODELLING STUDY

Keywords: *atmospheric deposition, LOTOS-EUROS model, Central Adriatic*

The atmosphere is not only a signifcant but in some cases the dominant pathway by which both natural and anthropogenic materials are transported from continents to both coastal and open seas. Once deposited through dry and wet processing, aerosols become an external source of nutrients for ecosystems, but they are also sources of toxic substances that have a negative impact on marine ecosystem functioning. The northern Adriatic is one of the most eutrophic areas of the Mediterranean. It is under the strong infuence of river sediment and atmospheric depositions originating from fossil fuel combustion, oil and petroleum industry and transport from the north of Italy and other European industrial areas. However, throughout the whole year, due to intense coastal and river inputs to this area, the atmospheric deposition has a low infuence on primary productivity. This is in contrast with the central and south-eastern oligotrophic Adriatic regions which are under low river inputs. Atmospheric deposition, from various combustion sources, could here significantly affect marine biology. This area is also affected by arid Mediterranean conditions. During summer, the central Adriatic is especially exposed to permanently high and very high fire risks, and has a long history of extreme forest fires. The effects of atmospheric deposition inputs to oligotrophic surface waters of the Adriatic are generally unknown. This work will provide the first insight into the temporal variability of the deposition fluxes of atmospheric constituents calculated by the LOTOS-EUROS atmospheric numerical model with to the aim of evaluating temporal dynamics and the enrichment processes of atmospheric constituents within the surface layers of the central Adriatic and their potential to synergistically contribute to and/or affect marine biology. For the experimental measurement period related to the retrieval of sea surface oligotrophic conditions (February-July 2019), the main pathways and deposition fluxes of atmospheric aerosols will be examined and its connection with the input of nutrients and other constituents that have a synergistic impact on marine ecosystem functioning will be evaluated.

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Tema 7

EFCA sekcija: "Ultrafine particles - air quality and climate: State of play related to scientific evidence and policy proposal"

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UFP-INTEGRATING ACTION FOR CLEANER AIR AND CLIMATE PROTECTION

Keywords: *air quality, climate changes, particulate matter, ultrafine fraction*

Combustion of all kinds produces particulate matte (PM) pollution, including its ultrafine fraction (UFP) of less than 1 micron. This contributes greatly to forming SMOG. On the other side, carbonacerous particles in form of Black Carbon (BC) and Organic Aerosols (OA) are of particular concern as the climate change is concerned. Also UFPs are formed as secondary pollutants, including its precursors as Non-CO_2 Greenhouse Gases.

Targeting UFPs properly can be important in formulating policy to reduce emissions of toxic air pollution and climate forcers as well. Moreover, present policies to decrease exposure to particulate matter make use of the mass-balanced metrics for fractions $PM_{2,5}$ and PM_{10}, which do not properly represent all risks for human health. There are considerable differences in the toxic potency of UFPs from various sources when using mass as unifying metric.

Therefore European Federation of Clean Air and Environmental Protection Associations (EFCA) is in favour of developping fraction-by-fraction approach on PM both with respect to size and chemical composition and why not the particulate concentration. Also EFCA strongly supports the role of integrated policy as opposed the current practice of separate sectoral policies in combatting air pollution and mitigating climate change.

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MANAGING LARGE SOURCES OF ULTRA-FINE PARTICULATES: EMISSION REDUCTIONS FROM SHIPPING

Keywords: *UfP, sources of pollution, shipping emissions*

UfP (Ultra-fine Particles, particles less than 0.1 μm or 100 nm in diameter) pollution is an important fraction in atmospheric aerosol, arising from natural processes and human activity. Anthropogenic sources include transport, industrial combustion, domestic heating, cooking and a range of manufacturing processes. UfP pollution has consequences both for the global climate system and for human health, and although the pathways are complex, a consensus is emerging about the nature and scale of effects. EFCA, the European Federation of Clean Air Association has, in series of Symposia, explored the scientific aspects of UfP pollution, and in the most recent Symposium concluded that there is now sufficient evidence of harm on the climate systems and on health to begin the process of policy development to reduce impacts. Studies of emission from transport suggest that road transport, aviation and shipping all make contributions to overall exposure. Shipping emissions are of special concern as ship engines have long in-service lifetimes and use poor quality fuel. However, regulation of shipping emissions now coming into force will, although aimed mainly at sulphur dioxide, also have consequences for UfP emission. This presentation will consider current UfP emissions and how they might be affected by current emission controls. It will suggest further measure to maximise UfP reductions.

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RESULTS OF THE 7TH EFCA SYMPOSIUM ON ULTRAFINE PARTICLES - AIR QUALITY AND CLIMATE

Keywords: *UFP, NOx, $PM_{2.5}$*

Seventy-three experts from 13 different countries participated in the 7th symposium on ultrafine particles (UFP) to discuss UFP sources, ambient UFP measurements, urban UFP, UFP toxicity and epidemiology, and integrating actions in 10 sessions. The symposium was completed by a panel discussion on policy follow up on ultrafine particle regulation. The symposium started with a keynote lecture illustrating the role of black carbon particles in cloud formation depending on its organic carbon content, chemical aging and pore structure. UFP especially from aviation emissions around airports represent a substantial source of high numbers of very small particles (~20 nm). About 90 % of these particles are related to emissions of the aircraft's main engines. However, it remains uncertain to what extend these particles are volatile. Further studies of particle transformation processes are required to improve corresponding dispersion models. The airport related aerosol particles showed similar toxic properties as particles from urban traffic. Major sources for UFP in the lower troposphere are emissions from power plants and ships as their emissions have changed to higher particle numbers with smaller sizes. However, there is also evidence for significant contributions of new particle formation to UFP. The second keynote lecture demonstrated the significant progress made in development and airborne application of compact UFP measurement techniques allowing a better understanding of especially vertical aerosol distributions throughout the planetary boundary layer. More and more UFP instruments are also used in air quality monitoring networks e.g. for source identification. In metropolitan areas, still the largest mass fractions of soot particles (e.g. 65-90% in Brussels) are related to traffic emissions while their peak concentrations are governed by meteorological conditions. While $PM_{2.5}$ and precursors of secondary aerosol particles could be reduced during the past decade in some metropolitan areas (e.g. Mexico City or Beijing) this is not the case for UFP. Recently, also the development of high-resolution transport models makes great progress and especially their combinations with networks of low cost and reference instruments seem very promising for exposure prediction and the development of effective abatement strategies. The third keynote lecture requested internationally standardized UFP measurements before UFP limit values should be implemented. While traffic related particle mass and soot emissions have been reduced substantial in Europe this is not the case for UFP and NOx. Scientists should stand up against "fakes, hypes, fabricated doubts" and support long-term solutions including control policies to abate manipulation and fraud. The WHO air quality guidelines values should be the point of reference for national directives and regulations. It was shown that periodic technical inspections of vehicles; including e.g. particle number measurements, have the potential to ensure compliance with emission regulations. Exposure of humans to indoor UFP from common sources causes similar health effects as exposure to outdoor particles. The cardiovascular diseases may not be adequately explained by exposure to aerosol particle mass but requires inclusion of the UFP. It was declared that the European Federation of Clean Air and Environmental Protection Associations supports direct regulation of black carbon, UFP standards based on size and number, and regulating shipping as well as non-combustion sources.

During the concluding panel discussion, it became evident that $PM_{2.5}$ and UFP act both but differently on human health and thus both need to be regulated.

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FINE AND ULTRAFINE PARTICLE NUMBER SIZE DISTRIBUTION STATISTICS AT URBAN, SUBURBAN BACKGROUND AND REMOTE SITES IN GREECE

Keywords: *NPF, CCN, chemical aerosol characterisation*

Intensive microphysical and chemical aerosol characterisation measurements were conducted in urban (Patra City Center), urban background (Demokritos Athens/ ICE–HT Patra/ Thessaloniki) and regional background (Finokalia Crete) sites in Greece during the summer period. Their variability and dependence on airmass origin was examined. Particle size distributions were obtained by Scanning Mobility Particle Sizers and subsequently divided into 1-4 modes (the same algorithm was used for all measurements). Then, the acquired modes were separated into 6 categories, depending on their geometric mean diameter. The dry aerosol size distribution at Finokalia regional background site displays a peak approximately at 100 nm and the lowest particle number concentration values compared with all other stations. At Demokritos Athens, ICE–HT Patra and Thessaloniki Urban Background stations, size distributions display a peak approximately at 100 nm dry diameter also, but the number concentration is almost twice as high as at Finokalia. Patra City Center urban site demonstrates geometric mean dry diameter peak below 100 nm and has the highest concentration peak values. Nucleation events were identified at DEM station, where the newly formed particles accounted for 4% of the total particle concentration for the measurement period in the size range 10-20 nm, EPT, where they accounted for 12%, and FIN, where they accounted for 1%, respectively. NPF events contribution during summer to Condensation Cloud Nuclei were therefore found to be insignificant in the Eastern Mediterranean.

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MICROPHYSICAL AND SELECTED CHEMICAL PROPERTIES OF FINE AND ULTRAFINE PARTICLES AT A SUBURBAN ENVIRONMENT AND THEIR DEPENDENCE ON AIR CIRCULATION PATTERNS

Keywords: *UFP, SOC, OC, Sf, ρeff*

This study aimed at investigating the major microphysical and chemical properties of fine and ultrafine particles at a suburban background site, typical for a Mediterranean atmospheric environment. The parameters investigated included Number (NCtotal) and Fuchs surface (Sf) aerosol concentrations and size distributions, Elemental (EC), Organic (OC) and Secondary Organic (SOC) carbon concentrations, as well as particle effective density (ρeff). The 24-h and seasonal variability of these microphysical and chemical parameters exhibited strong dependence on the traffic-related emissions, long-range transport and local wind circulation patterns. A major mode in the accumulation region of the size distributions surface area accounted for more than 70% of the total Sf. This mode appeared to have the minimum diameter in the early-morning, while an average increase of 12% occurred during the day (maximum diameter at midday). The surface concentration levels varied strongly within during the day, whereas the structure of the size distributions exhibited less significant variability. Photochemical particle formation consisted a major formation mechanism, enhanced under intense sunlight, resulting in increased Nuclei (NCN) and Aitken (NCAt) particle concentrations at midday. Atmospheric stability may contribute to increased levels of both Aitken particles and particles in the accumulation mode, mainly in the evening. The OC/EC ratios, OC, SOC and Sf concentrations indicated that the study area was strongly influenced by secondary organic aerosol formation, with the latter occurring on the increased available surface area. The long-range transport and the evolution of specific local circulation patterns (i.e. sea breeze, katabatic winds) strongly affected the physicochemical properties of fine and ultrafine particles.

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Posteri

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ZNANSTVENO-STRUČNI SKUP
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TREND TALOŽENJA DUŠIKOVIH I SUMPOROVIH SPOJEVA IZNAD HRVATSKE U RAZDOBLJU 1981.-2018.

Keywords: *taloženje dušikovih spojeva, taloženje sumporovih spojeva*

Oborina je jedna od neophodnih komponenti života. Ima utjecaj na vegetaciju, životinjski svijet te ljude. Mokrim i suhim taloženjem razne vrste onečišćenja mogu utjecati na ekosustave. Pored emisija, geografski položaj, klima te biljni pokrov imaju važnu ulogu u ukupnom iznosu koncentracije i taloženja onečišćujućih tvari. Pretjerano zagađivanje dovodi do acidifikacije i eutrofikacije, propadanja zdravlja i raznolikosti ekosustava te utječe na regionalnu i globalnu klimu.

Kako bi se zadovoljile potrebe za globalnim praćenjem kvalitete zraka i oborine, prema uputama Svjetske meteorološke organizacije, Državni hidrometeorološki zavod (DHMZ) uspostavio je u kasnim 70-ima mrežu postaja koja je obuhvaćala gotovo 30 mjernih mjesta. Tijekom godina, broj mjernih postaja se mijenjao (20-26). Nakon optimizacije mreže 2010. godine, u funkciji je ostalo 14 mjernih postaja koje su dio mreže dugotrajnog kontinuiranog praćenja taloženja. Dvije postaje (Puntijarka i Zavižan) uključene su u EMEP program praćenja i procjene LRTAP konvencije.

U ovom istraživanju analizirana je prostorna i vremenska raspodjela te promjene trendova u kemijskom sastavu oborine i ukupnom taloženju na 14 mjernih postaja. Dnevni uzorci oborine prikupljeni su prema protokolima mjerenja oborine Svjetske meteorološke organizacije i EMEP-a. Prikazane su godišnje raspodjele ukupnog taloženja sulfata, nitrata i amonij iona. Rezultati mjerenja uspoređeni su s ukupnim taloženjem procijenjenim modelom kemijskog transporta. Proračun modela potvrđuje dugotrajan padajući trend u taloženju iznad cijele Hrvatske, ali je također vidljivo podcjenjivanje vrijednosti u odnosu na mjerenja. Dodatno, kako bi se proučio utjecaj klimatskih promjena, proučene su godine koje se prema meteorološkim uvjetima značajno ističu (izrazito kišna godina nasuprot sušne).

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NITROGEN AND SULPHUR DEPOSITION TRENDS OVER CROATIA DURING THE PERIOD 1981-2018

Keywords: *nitrogen deposition, sulphur deposition*

Precipitation is one of the indispensable life components. It has impact on vegetation, wildlife and humans. All kinds of contamination can affect ecosystems through wet and dry deposition. Beside emission, geographical location, climate and land cover play a huge role in the overall concentration and deposition levels of pollutants. Excessive pollution leads to acidification and eutrophication, deterioration of the ecosystem health and diversity, and influences regional and global climate.

To meet the needs for global air and precipitation monitoring based on WMO recommendations, the Meteorological and Hydrological Service of Croatia (DHMZ) established a precipitation monitoring network in the late 1970s, which encompassed nearly 30 sites. The number of sites varied from 20-26 until 2010 and finally, after optimisation of the network, settled at fourteen sites currently representing a long-term continuous deposition monitoring network. Two of these sites (Puntijarka and Zavižan) are included in the EMEP monitoring and evaluation programme of the LRTAP Convention.

In this study, we analysed the spatial and temporal distribution and trend changes in precipitation chemistry and deposition from 14 sampling sites. The daily bulk precipitation samples were collected according to the WMO and EMEP precipitation measurement protocol. Annual distributions of total deposition of sulphate, nitrate and ammonium ions were presented and compared with chemical transport model total deposition calculations. Model calculations confirmed a downward long-term deposition trend over the whole territory of Croatia but showed underestimation compared to observations. In addition, years with meteorological conditions considerably different from average climate conditions (excess precipitation vs. lack of precipitation) were examined in order to address possible influences of climate change.

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PRIZEMNI OZON U HRVATSKOJ 2007. – 2017.: MJERENJA I MODELIRANJE

Ključne riječi: *onečišćenje ozonom, mjerenja ozona, AOT40 parametar, kemijski transportni model, trendovi*

Onečišćenje ozonom predstavlja velik problem u mnogim Europskim zemljama, pogotovo onima na Mediteranu. Klimatske promjene te uranjeni i produljeni ljetni periodi donose dodatni stres na ekosustav i zdravlje ljudi.

U ovom istraživanju analizirane su vrijednosti prizemnog ozona tijekom razdoblja 2007. – 2017. na temelju dostupnih mjerenja i rezultata modela. Trenutno se ozon u Hrvatskoj, u sklopu Državne mreže za trajno praćenje kvalitete zraka i lokalne mreže, mjeri na 9 gradskih i 12 pozadinskih postaja koje su prostorno raspoređene po cijelom teritoriju Republike Hrvatske, obuhvaćajući tri velike cjeline: kontinentalni, planinski i priobalni dio, uključujući otoke. Kako su na početku promatranog razdoblja postojale samo dvije mjerne postaje u urbanim područjima, za računanje onečišćenja ozonom tijekom dužeg perioda nužna je upotreba kemijskih transportnih modela. U tu svrhu korišteni su EMEP i LOTOS – EUROS kemijski transportni modeli. Rezolucija EMEP modela je 50 km x 50 km, dok je rezolucija LOTOS – EUROS modela 25 km x 25 km. Oba modela imaju široku primjenu uključujući znanstvena istraživanja, regulatorne svrhe te buduće procjene prizemnih koncentracija onečišćujućih tvari u zraku.

Cilj istraživanja bio je usporediti izmjerene i proračunate vrijednosti prizemnog ozona te izračun dugogodišnjih trendova kako bi se ispitala učestalost pojave visokih koncentracija prizemnog ozona koje mogu štetno utjecati na zdravlje ljudi i ekosustav.

Uredbom o razinama onečišćujućih tvari u zraku (NN 117/2012) propisane su ciljne vrijednosti i dugoročni ciljevi za prizemni ozon s obzirom na zaštitu zdravlja ljudi, kao i za AOT40 parametar koji se računa od svibnja do srpnja u svrhu proučavanja utjecaja prizemnog ozona na vegetaciju.

Utvrđeno je da su prekoračenja ciljne vrijednosti i dugoročnog cilja prizemnog ozona, kao i AOT40 parametra, veća u priobalju te da je broj dana s prekoračenjima, kako ciljne vrijednosti tako i dugoročnog cilja prizemnog ozona, uobičajeno veći početkom promatranog razdoblja. Modeli dobro reprezentiraju distribuciju broja dana s prekoračenom ciljnom vrijednošću i dugoročnim ciljem prizemnog ozona te srednje godišnje vrijednosti AOT40 parametra (izračunate od svibnja do srpnja). Tijekom analiziranog razdoblja model precjenjuje izmjerenu srednju godišnju vrijednost prizemnog ozona na mjernim postajama u Zagrebu, Rijeci i Humu.

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GROUND-LEVEL OZONE IN CROATIA 2007-2017: MEASUREMENTS AND MODELLING

Keywords: *ozone pollution, ground – level ozone concentration, chemical transport model, trends*

Ozone pollution represents a serious problem in many European countries, especially in countries of the Mediterranean region. Changing climate circumstances, early and prolonged summer periods, and changing weather circulation patterns bring additional stress to the environment ecosystems and human health.

In this study, ground-level ozone trends over the period 2007-2017 based on available measurements and regional air quality modelling results were analysed. Ozone measurements within the State Air Quality Monitoring Network of Croatia and local network are currently performed at 9 urban and 12 rural stations spatially distributed over the country to encompass three distinctive areas of Croatia: continental, mountainous and Adriatic, including islands. Nevertheless, at the beginning of the analysed period there were only two measurement sites in urban areas. Therefore, to assess the ozone pollution in Croatia over a longer period, it was necessary to utilise air quality transport models. For that purpose, we used EMEP and LOTOS-EUROS CTM models. As ozone is largely a regional scale pollutant, the resolution scale used for calculation by the EMEP model is 50 km x 50 km. The default model resolution of LOTOS-EUROS model is 25 km x 25 km. Both models are open-source chemical transport models used for a wide range of applications supporting scientific research, regulatory purposes and air quality forecasts.

The purpose of the work was twofold: to compare model outputs with measurements and to establish longer term trends of ground-level ozone based on model calculations in order to assess environmental and health related impacts of high ozone concentrations.

The Ordinance on Levels of Air Pollutants (OG 117/2012) prescribes the exceedances of the target value and the long-term objective of ground-level ozone for the protection of human health, as well as the AOT40 value, which is calculated from May to July for the purpose of studying the impact of ground-level ozone on vegetation.

This includes the number of days on which the target value and the long-term objective of ground-level ozone was exceeded, as well as the AOT40 value. They are usually higher in the coastal part of Croatia and the number of days on which the target value of ground-level ozone was exceeded are usually higher at the beginning of the observed period. Models successfully represent the distribution of the numbers of days on which the target value of ground-level ozone was exceeded and the AOT40 mean annual value. Over the whole analysed period, the modelled mean annual values of ground-level ozone overestimated measurements at sites in Zagreb, Rijeka and Hum.

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RAZINE KLORIDA, NITRATA I SULFATA U UKUPNOJ TALOŽNOJ TVARI NA DVIJE MJERNE POSTAJE U ZAGREBU ZA RAZDOBLJE 2014.–2018.

Ključne riječi: *UTT, trend, kisele komponente*

Ukupnu taložnu tvar (UTT) čini ukupna masa onečišćujućih tvari koja se prenosi iz zraka na površine (tlo, vegetacija, voda, građevine i drugo) po površini kroz određeno razdoblje i najčešće je izražena u mg/(m^{2}d). UTT mjerilo je vidljivog onečišćenja okoliša, narušava njegovu kvalitetu, a može nepovoljno djelovati na sve njegove elemente. Ukupno atmosfersko taloženje jedno je od glavnih mehanizama uklanjanja onečišćujućih tvari iz zraka, a odvija se putem suhog i mokrog taloženja uslijed gravitacije i ispiranja s oborinama.

Prikazani su rezultat kontinuiranih mjerenja kiselih komponenti klorida, nitrata i sulfata u ukupnoj taložnoj tvari (UTT) u zraku Zagreba za razdoblje 2014. – 2018. godine na dvije mjerne postaje: mjerna postaja u centru grada s gustim prometom (C) i mjerna postaja na rubnom zapadnom dijelu grada s industrijskim objektima (Z). Mjesečni uzorci (30 ± 2 dana) ukupne taložne tvari sakupljani su Bergerhoff-ovim sakupljačem. Količina UTT određena je gravimetrijski, dok je sadržaj klorida, nitrata i sulfata u UTT određen ionskom kromatografijom.

Za promatrano razdoblje mjerenja na postaji (C) srednje godišnje vrijednosti količine UTT kretale su se u rasponu od 50 mg/(m^{2}d) do 111 mg/(m^{2}d), količine kiselih komponenti u UTT od 0,78 mg/(m^{2}d) do 1,48 mg/(m^{2}d) za kloride, od 2,53 mg/(m^{2}d) do 4,41 mg/(m^{2}d) za nitrate i od 2,59 mg/(m^{2}d) do 6,16 mg/(m^{2}d) za sulfate, dok su se na postaji (Z) te vrijednosti kretale od 86 mg/(m^{2}d) do 147mg/(m^{2}d) za UTT, od 1,13 mg/(m^{2}d) do 2,57mg/(m^{2}d) za kloride, od 2,92 mg/(m^{2}d) do 4,36mg/(m^{2}d) za nitrate i od 2,50 mg/(m^{2}d) do 6,98mg/(m^{2}d) za sulfate.

Razine UTT i kiselih komponenti klorida, nitrata i sulfata u ukupnoj taložnoj tvari (UTT) u zraku Zagreba pokazuju padajući trend za sve mjerene onečišćujuće tvari na obje mjerne postaje, osim za kloride na mjernoj postaji (Z), gdje vrijednosti pokazuju trend rasta. Statistički značajni trend utvrđen je samo za nitrate u UTT na obje mjerne postaje, dok za ostale onečišćujuće tvari trend nije statistički značajan.

Uredba o razinama onečišćujućih tvari u zraku (NN 117/2012) propisuje graničnu vrijednost (GV) razina ukupne taložne tvari, dok za razine mjerenih iona u UTT granične vrijednosti nisu propisane, stoga ocjenu kvalitete zraka s obzirom na količinu kiselih komponenti u UTT nije moguće dati.

Za promatrano razdoblje mjerenja razine ukupne taložne tvari u gradu Zagrebu nisu prelazile propisanu graničnu vrijednost te je zrak bio na razini I kategorije kvalitete.

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LEVELS OF CHLORIDE, NITRATE AND SULPHATE IN TOTAL DEPOSITED MATTER AT TWO SAMPLING SITES IN ZAGREB FOR THE PERIOD 2014 – 2018

Key-words: *TDM, trend, acidic components*

Total deposited matter (TDM) is the total mass of pollutants present in air settle on the ground and contaminate soil, plants and materials, but do not affect people and animals directly. It is usually quoted as mg/(m^2 per day). Atmospheric total deposition (bulk deposition) is an important mechanism controlling the fate of toxic airborne pollutants and their removed from the atmosphere which takes place by wet and dry processes.

This investigation focuses on the levels of major acidic species chlorides, nitrates and sulphates in total deposited matter (TDM) in Zagreb air for the period 2014 – 2018. Monthly samples (30 ± 2 days) of total deposited matter were taken continuously at two sampling sites: site (C) - city centre with high traffic density and individual heating and site (Z) - residential-industrial area in western part of the town with high traffic density. Samples of total deposited matter were collected using the Bergerhoff sampler. Total deposited matter was determined gravimetrically. Acidic anions were analysed using ion chromatography.

The annual average levels of measured pollutants at site (C) ranged from 50 mg/(m^{2}d) to 111 mg/(m^{2}d) for TDM, from 0.78 mg/(m^{2}d) to 1.48 mg/(m^{2}d) for chlorides, from 2.53 mg/(m^{2}d) to 4.41 mg/(m^{2}d) for nitrates, and from 2.59 mg/(m^{2}d) to 6.16 (mg/(m^{2}d) for sulphates, respectively, the same parameters at site (Z) ranged from 86 mg/(m^{2}d) to 147mg/(m^{2}d) for TDM, from 1,13 mg/(m^{2}d) to 2,57 mg/(m^{2}d) for chlorides, from 2,92 mg/(m^{2}d) to 4,36mg/(m^{2}d) for nitrates and from 2,50 mg/(m^{2}d) to 6,98mg/(m^{2}d) for sulphates, respectively.

At both measuring sites the levels of all measured pollutants show decreasing trend, except at site (Z) chlorides trend was slightly increasing. The trend of nitrate levels was significant, while the levels of other pollutants show not significant trend.

The national regulations the Air Protection Act (OG No.130/11, 47/14), and the Regulation on Levels of Pollutants in Air (OG No. 117/12), defined limit values for TDM, while the limit values for acidic components in TDM were not defined.

Regarding to the regulations the Air quality in Zagreb with respect to TDM was the first category of quality.

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HRVATSKA U OKVIRU MONET PROJEKTA U RAZDOBLJU 2009. - 2013.

Ključne riječi: *onečišćenje atmosfere, PCB, OCP, PAH*

Stockholmska konvencija stupila je na snagu 2004. godine, a glavni cilj konvencije je zaštita ljudi i okoliša od postojanih organskih zagađivala (engl. Persistent Organic Pollutants, POPs) tako da se njihov unos u okoliš smanji ili u potpunosti spriječi. Od članica Stokholmske konvencije (i Hrvatska je članica) zatraženo je da implementiraju obaveze konvencije, a zaključeno je da su neophodni usporedivi podaci sustavnog praćenja razina POPs. Zbog toga regionalni centri imaju važnu ulogu u koordiniranju, razvoju i provođenju programa praćenja razina POPs u okolišu. MONET projekt (engl. MOnitoring NEtwork for determination of POPs in ambient air using the polyurethane foam passive sampler) vodi se pod pokroviteljstvom regionalnog centra RECETOX (engl. Research Centre for Environmental Chemistry and Toxicology, Masaryk University, Brno, Czech Republic), te u okviru projekta sudjeluje Institut za medicinska istraživanja i medicinu rada. Ciljevi projekta su: 1) Primjena poliuretanske spužve kao pasivnog sakupljača POPs iz zraka kako bi se utvrdio učinak mjera međunarodnih konvencija o POPs; POPs u okviru Stockholmske konvencije i Konvencije o transportu na velike udaljenosti; 2) Upotpunjavanje informacija o razinama POPs u zraku u zemljama centralne i istočne Europe; 3) Evaluacija promjena razina POPs u zraku tijekom vremena kao i između različitih mjesta uzorkovanja zraka; 4) Uspostava praćenja razina POPs u zraku tijekom dužeg razdoblja; 5) Širenje znanja o novo razvijenim tehnikama za uzorkovanje, kemijsku analizu i procjenu rizika.

Broj država sudionica je proširen i izvan zemalja centralne, južne i istočne Europe. Spojevi koji se analiziraju su policiklički aromatski ugljikovodici, organoklorovi pesticidi, poliklorirani bifenili.

U razdoblju od travnja 2009. godine do travnja 2011. godine, sakupljeno je u Zagrebu pomoću pasivnih sakupljača 26 uzoraka zraka. Prosječni protok zraka kroz pasivni sakupljač je oko 3,5 m^3 dnevno. Općenito, na mjestima uzorkovanja u centralnoj Europi (Češka, Poljska, i Mađarska) izmjerene su niže vrijednosti koncentracija polikloriranih bifenila (20 – 50%) nego u južnoj i istočnoj Europi. Uzorci zraka u industrijskim mjestima Rumunjske i Rusije pokazali su vrlo visoke koncentracije α-, β- i γ- izomera HCH. Razine heksaklorbenzena u zraku podjednake su u svim zemljama sudionicama, s izuzetkom visokih razina u Rusiji. Na mjestima onečišćenja u Češkoj izmjerene su vrlo visoke koncentracije heksaklorbenzena. Visoke razine policikličkih aromatskih ugljikovodika izmjerene su Rumunjskoj, Crnoj Gori, Rusiji i Bosni i Hercegovini u zraku industrijskih mjesta.

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CROATIA WITHIN THE MONET PROJECT FOR THE PERIOD 2009 - 2013

Keywords: *atmospheric pollution, PCB, OCP, PAH*

The Stockholm Convention entered into force in 2004, and the Convention's main objective is to protect people and the environment from persistent organic pollutants by reducing or preventing their intake into the environment. Members of the Stockholm Convention (among others, Croatia) were asked to implement its obligations, and it was concluded that there was a need for comparable data of systematic monitoring of persistent organic pollutant levels. For this reason, regional centres play an important role in coordinating, developing and implementing a program for monitoring persistent organic pollutants (POPs) in the environment. The MONET project (the MOnitoring NEtwork for the determination of POPs in ambient air using the polyurethane foam passive sampler) is led under the auspices of the RECETOX Regional Center (Research Centre for Environmental Chemistry and Toxicology, Masaryk University, Brno, Czech Republic), and the Institute for Medical Research and Occupational Health is a participant in the project. The objectives of the project are: 1) application of polyurethane foam as a passive sampler for POPs from the air to determine the effect of measures from the Stockholm Convention and Convention on Long-range transboundary air pollution; 2) fill gaps in information on levels of POPs in the air of central and eastern Europe; 3) evaluate time and spatial trends of POPs in the air; 4) establish monitoring of POP levels in the air over a long period; 5) disseminate knowledge on newly developed techniques for sampling, chemical analysis and risk assessment.

The number of participating countries has expanded beyond the countries of central, southern and eastern Europe. Compounds that are analysed are polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls.

In the period from April 2009 to April 2011, 26 air samples were collected in Zagreb by passive samplers. The average air flow through the passive collector was about 3.5 m^3 per day. In general, sampling sites in central Europe (Czech Republic, Poland, and Hungary) showed lower concentrations of polychlorinated biphenyls (20-50%) than in southern and eastern Europe. Air samples at industrial sites in Romania and Russia showed very high concentrations of α-, β- and γ- isomers HCH. Hexachlorobenzene levels in the air were uniform in all participating countries with the exception of high levels in Russia. Pollution sites in the Czech Republic had very high concentrations of hexachlorobenzene. High levels of polycyclic aromatic hydrocarbons were measured in Romania, Montenegro, Russia and Bosnia and Herzegovina in the air of industrial sites.

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UKUPNA BETA AKTIVNOST ZRAKA U ZADRU

Ključne riječi: *onečišćenje zraka, radioaktivne tvari, ukupna beta aktivnost zraka*

Sastavni dio atmosfere su i radioaktivne tvari. Podrijetlo radioaktivnih tvari u atmosferi je kozmogeno ili terestrijalno, a od sredine dvadesetoga stoljeća u atmosferi su prisutne i radioaktivne tvari proizvedene i oslobođene u atmosferu djelovanjem ljudi. Praćenje i određivanje radioaktivnih tvari u zraku započelo je u Hrvatskoj 1961. godine i provodi se neprekidno do danas. Prisutnost radioaktivnih tvari u zraku ispituje se mjerenjem ukupne beta aktivnosti kao početni podatak. Za određivanje pojedinih radionuklida prisutnih u uzorku provode se i posebne radiokemijske analize pojedinih radionuklida, alfa, beta i gamaspektrometrijskim metodama. Cilj ovoga istraživanja je prodiskutirati pojavnost radioaktivnih tvari u zraku u gradu Zadru.

U Zadru na lokaciji sakupljača, vanjskoga suradnika Instituta za medicinska istraživanja i medicinu rada (IMI) neprekidno se i svakodnevno na visini jedan metar iznad tla prosisava zrak kroz filter papir Schneider-Poelman plavi. U sakupljenom uzorku zraka najmanje 120 sati nakon uzorkovanja mjeri se ukupna beta aktivnost u beta brojaču niskih aktivnosti (Low-level beta GM multicounter system; model RISØ GM-25-5). Kalibracija učinkovitosti efikasnosti provedena je standardima Češkog metrološkog instituta.

U ovom su radu prikazani rezultati određivanja ukupne beta aktivnosti zraka na uzorcima sakupljenima od 2013. do 2018. godine. Prosječna vrijednost ukupne beta aktivnosti zraka u promatranom razdoblju iznosi 1,046 $mBqm^{-3}$, uz nešto nižu vrijednost medijana koji iznosi 0,865 $mBqm^{-3}$. Dnevne vrijednosti kretale su se od 0,11 $mBqm^{-3}$ do 41 $mBqm^{-3}$. Rezultati su međusobno uspoređeni s vrijednostima ukupne beta aktivnosti zraka izmjerenima u Zagrebu na lokaciji IMI. U Zagrebu su se vrijednosti kretale u rasponu od 0,05 $mBqm^{-3}$ do 118 $mBqm^{-3}$ uz prosjek 1,155 $mBqm^{-3}$ i medijan 0,927 $mBqm^{-3}$. Maksimalne izmjerene vrijednost ukupne beta aktivnosti izmjerene su na obje lokacije početkom listopada 2017. godine kada se nad Europom tijekom nekoliko dana nadvio oblak rutenija (^{106}Ru), antropogenog beta emitera. Na sreću, zbog niskih koncentracija nije bilo potrebe za zaštitnim akcijskim djelovanjima.

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TOTAL BETA ACTIVITY IN THE AIR IN ZADAR

Keywords: *air pollution, radioactive matter, total beta activity in the air*

Radiation and radioactive substances are natural and permanent features of the atmosphere. The origin of radioactive substances in the atmosphere is cosmogenic or terrestrial. Additionally, since the 1950s radioactive substances have been produced and released in the atmosphere by humans. Long-term investigations of radioactive matter in air in Croatia started in 1961 as a significant part of an extended and still ongoing monitoring programme of radioactive contamination of human environment in Croatia. The presence of radioactive substances in the air is tested by measuring total beta activity as initial data; to find out which radionuclide is present in the sample, special radiochemical analyses of particular radionuclides, by alpha, beta and gammaspectrometric methods. The aim of this study was to discuss the occurrence of radioactive substances in the air in the city of Zadar.

At a sampling place in the city of Zadar, air was passed through a filter medium (Schneider-Poelman filter paper - blue) one meter above ground. In the collected sample, at least 120 hours after sampling, total beta activity was measured in a beta counter (low-level beta GM multicounter system; model RISØ GM-25-5). Efficiency calibration was carried out using the standards of the Czech Metrology Institute.

This paper presents the results of the determination of total beta activity in samples collected from 2013-2018. The average value of the total air activity beta in the observed period was 1.046 $mBqm^{-3}$, with a slightly lower median value of 0.865 $mBqm^{-3}$. The daily values ranged from 0.11 $mBqm^{-3}$ to 41 $mBqm^{-3}$. The results were compared with the values of the total beta activity of the air measured in Zagreb at one site. In Zagreb, the values ranged from 0.05 $mBqm^{-3}$ to 118 $mBqm^{-3}$ with an average of 1.15 $mBqm^{-3}$ and a median of 0.927 $mBqm^{-3}$. The maximum values of the total beta activity were measured at both sites at the beginning of October 2017 when a cloud of ruthenium (^{106}Ru), an anthropogenic beta-emitter, hovered over Europe for a few days. Fortunately, due to low concentrations, there was no need for any protective action.

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ANALIZA KONCENTRACIJE TROPOSFERSKOG OZONA U SJEVERNOM DIJELU ZAGREBA OD 2003. DO 2016.

Ključne riječi: *ozon, onečišćenje, analiza dugotrajnih podataka, analiza trenda*

Kao i stratosferski ozon, tako je iznimno značajan i troposferski ozon s obzirom da je najjednostavniji indikator atmosferskog onečišćenja. Fotokemijsko onečišćenje karakterizira negativni utjecaj ozona kako na biljke tako i na životinje. Povišene vrijednosti koncentracije ozona štete vegetaciji te, istovremeno mogu uzrokovati dišne probleme u životinja i ljudi. Kako bi se takav negativan utjecaj spriječio, potreban je kontinuirani nadzor razine ozona u troposferi, a također i analiza prikupljenih podataka.

Mjerenja ozona izvedena su automatskim analizatorima ozona stacioniranima na Institutu za medicinska istraživanja i medicinu rada (45° 50' 04" N; 15° 58' 41 E). Ta je postaja dio lokalne mreže Zagreba za praćenje kvalitete zraka. Meteorološki podaci s obližnje stanice Maksimir Državnog hidrometeorološkog zavoda korišteni su radi bolje procjene. Za račun je korišten softver Statistica (Fourierove transformacije) i Excel (svi ostali proračuni).

Srednja vrijednost godišnjih volumnih udjela ozona, razmjernih koncentracijama, analizirana Mann-Kendallovim statističkim testom pokazuje linearnu ovisnost podataka s nagibom od 0,23 ppb god^{-1}, dok sezonski ljetni podaci (od travnja do rujna) imaju nagib od 0,32 ppb god^{-1}. Vrijednosti 95.-percentila imaju nagib od 0,009 ppb god^{-1} (podaci za cijelu godinu), odnosno –0,072 ppb god^{-1} (podaci za ljetnu sezonu). Fourierova transformacija korištena je za analizu periodičnosti u volumnim udjelima ozona. Dokazan je dnevni i tjedni hod što je za ozon vrlo karakteristično.

Po završetku procjene svih podataka u periodu od 2003. do 2016. godine, može se zaključiti da su razine onečišćenja u sjevernom dijelu Zagreba relativno male uz iznimku nekoliko epizoda visokih volumnih udjela. Mann-Kendallov test ne pokazuje značajan pozitivan trend za porast koncentracije ozona. Nastavi li se ovako i ne bude li značajnih novih izvora prekursora, Zagreb će još neko vrijeme ostati pošteđen dugotrajnih ekstremno visokih razina ozona. Ipak, kontinuirani nadzor je nužan te će se nastaviti u okviru stalnog praćenja koncentracije ozona u ovom području.

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ASSESSMENT OF TROPOSPHERIC OZONE CONCENTRATION DATA FROM THE NORTHERN ZAGREB AREA FOR THE PERIOD FROM 2003 TO 2016

Keywords: *ozone, pollution, long-term analysis, trend analysis*

Apart from stratospheric ozone, tropospheric ozone is an important and the simplest indicator of photochemical pollution. Photochemical pollution is characterised by its negative influence on both animals and plants. Elevated ozone levels may easily damage leaves and, at the same time, cause respiratory problems for animals and humans. To prevent such a negative influence, continuous monitoring and analysis of acquired data are important.

Measurements were conducted by automatic ozone analysers located at the Institute for Medical Research and Occupational Health (45° 50' 04" N; 15° 58' 41 E). This monitoring station is part of the Zagreb local network for air quality monitoring. Meteorological data from the nearby Croatian Meteorological and Hydrological Service station (Maksimir; 45° 49' 25" N; 16° 2' 9" E) were used in this assessment. Calculations were carried out using Statistica (for FT analysis) and Excel (for all other calculations).

The mean value of the annual ozone volume fractions, calculated by Mann-Kendall's statistical test, showed a linear dependence with a slope of 0.23 ppb yr^{-1}, while the seasonal (April-to-September) mean values had a slope of 0.32 ppb yr^{-1}. The 95-percentile values had slopes of 0.009 ppb yr^{-1} (annual data) and –0.072 ppb yr^{-1} (seasonal data), respectively. Fourier transformation was used to analyse the data for periodic behaviour, which revealed the existence of diurnal and weekly modulations which are very usual for ozone.

After assessing all of the ozone data in the observed period of time (2003-2016), it can be concluded that pollution levels in northern Zagreb are rather low, with the exception of a few episodes. Mann-Kendall's test did not show a high positive trend for ozone. If this trend continues, and there are no new pollution sources that would increase the trend, it is rather safe to say that extremely high long-term ozone levels will not occur in Zagreb in the near future. Nevertheless, constant monitoring is important and will continue in the future as part of the continuous monitoring of ozone levels in the area.Tablica 1. Raspon TEQ-ova

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OPERATIVNI MODEL ZA SLANJE SMS OBAVIJESTI PRILIKOM PREKORAČENJA KONCENTRACIJA SO_2, NO_2 I O_3 U VANJSKOM ZRAKU

Ključne riječi: *koncentracije SO_2, NO_2 i O_3 u vanjskom zraku, prekoračenje praga obavješćivanja i praga upozorenja, Državna mreža za trajno praćenje kvalitete zraka*

Mjerenja koncentracija sumporova dioksida (SO_2), dušikova dioksida (NO_2) i ozona (O_3) u vanjskom zraku se provode pomoću mjernih uređaja na mjernim postajama za mjerenje kvalitete zraka u Državnoj mreži za trajno praćenje kvalitete zraka. Podaci mjerenja kvalitete zraka se kontinuirano prenose sa pojedine mjerne postaje za mjerenje kvalitete zraka u bazu podataka mjerenja kvalitete zraka DHMZ-a. Tijekom ljeta 2018. godine je razvijen operativni model za slanje SMS (eng. Short Message Service) poruke kontakt osobama radi informiranja korisnika o prekoračenju pragova upozoranje (Uredba o razinama onečišćujućih tvari u zraku; NN 117/2012 i NN 84/2017) za koncentracije SO_2 i NO_2 u vanjskom zraku (500 μgm^{-3} i 400 μgm^{-3}; satne koncentracije mjerenja u vanjskom zraku na pojedinoj mjernoj postaji moraju biti veće od navednih pragova tijekom svakog sata u protekla tri sata). U slučaju koncentracija ozona, operativni model provodi slanje SMS poruka kontakt osobama prilikom prekoračenja praga obavješćivanja (180 μgm^{-3}) ili prilikom prekoračenja praga upozorenja (240 μgm^{-3}).

U ovom radu će biti predstavljeni glavni elementi operativnog sustava za slanje SMS poruka. Glavna komponenta sustava je Node-RED modul u kojem se svakih sat vremena definiraju scenariji povezani sa vrijednostima koncentracija SO_2, NO_2 i O_3 u vanjskom zraku. Ovisno o rezultatima mjerenja, Node-RED modul može pokrenuti proces slanja SMS poruke prema korisnicima. Node-RED je alat za vizualno programiranje razvijen od strane IBM (eng. International Business Machines Corporation) pomoću kojega je moguće povezivati (eng. flows) različite fizičke uređaje, API (eng. Application programming interface) i online servise. Programiranje u Node-RED se provodi u web pregledniku pomoću raznih elemenata (veliki izbor osnovnih elemenata) i funkcija (JavaScript funkcije se mogu definirati unutar pojedinog elementa). Dodatni elementi operativnog sustava su proces prijenosa podataka mjerenja iz baze podataka DHMZ-a na server (lokalna datoteka sa mjerenjima) i aplikacija za analizu podataka mjerenja koncentracija SO_2, NO_2 i O_3 u proteklih 3 sata na pojedinoj mjernoj postaji za mjerenje kvalitete zraka.

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OPERATIONAL MODEL FOR SENDING SMS MESSAGES DURING HIGH CONCENTRATIONS OF SO_2, NO_2 AND O_3 IN AMBIENT AIR

Keywords: *concentrations of SO_2, NO_2 and O_3 in ambient air, exceedance of alert and information thresholds, State Air Quality Measurement Network*

Concentrations of sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and ozone (O_3) are continuously measured by air quality analysers at air quality stations within the State Air Quality Network. Air quality data are continuously transferred from the air quality stations to the database at the Croatian Meteorological and Hydrological Service (DHMZ). During the summer of 2018, an operational model was developed for sending SMS messagesto responsible contact persons in order to inform users about ambient air concentrations exceeding the alert threshold (Ordinance on Pollutant Levels in Air; OG 117/2012 and 84/2017) for SO_2 and NO_2 in ambient air (500 μgm^{-3} and 400 μgm^{-3}; hourly concentrations in ambient air in every hour have to be larger than the alert threshold's for SO_2 and NO_2 during the previous 3 hours). In case of ozone, the operational model sends an SMS to contacts when the hourly concentration value of ozone is higher than the information threshold (180 μgm_{-3}) or alert threshold (240 μgm_{-3}).

This work will present the main components of the operational system for sending SMS messages. The main component of the system is a Node-RED module that analyses different events according to the air quality measurement concentrations of SO_2, NO_2 and O_3 in ambient air every hour. Depending on the results, the Node-RED module can activate the process of sending an SMS message to the users. Node-RED is a tool for graphic programming developed by IBM that can be used to connect different physical devices, APIs and online services. Programming in Node-RED is done in a web browser editor using different nodes (great range of basic components) and functions (JavaScript functions can be defined in the node). An additional element of the operational system is the process of data transfer from the database with air quality measurements to a local computer with a Node-RED server and an executable application for analysis of air quality measurements during the last 3 hours on air quality stations.

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ISPITIVANJE DULJINE RAZDOBLJA ZAMJENE FILTARA ZA ODSTRANJIVANJE ČESTICA NA MJERNIM UREĐAJIMA ZA MJERENJE ANORGANSKIH SPOJEVA (SO_2, NO_X, CO I O_3) I HLAPLJIVIH ORGANSKIH SPOJEVA U VANJSKOM ZRAKU

Ključne riječi: *kvaliteta zraka, ispitivanje, filtar čestica, razdoblje zamjene, državna mreža za mjerenje kvalitete zraka*

Normirane ispitne metode za mjerenje koncentracija anorganskih spojeva (sumporova dioksida (SO_2), dušikovih oksida (NO_x), ugljikova monoksida (CO) i ozona (O_3)) i hlapljivih organskih spojeva BTEX (benzen, toluen, etilbenzen i ksileni) u vanjskom zraku (HRN EN 14662-3, HRN EN 14212, HRN EN 14211, HRN EN 14626 i HRN EN 14625) određuju aktivnosti i postupke za osiguranje kvalitete mjerenja mjernih uređaja tijekom rada na mjernoj postaji za mjerenje kvalitete zraka. Jedan od postupaka za ocjenu prikladnosti mjernog uređaja na lokaciji mjerne postaje je ispitivanje duljine vremenskog razdoblja zamjene filtra za odstranjivanje čestica. Ispitivanje se provodi na način da se određuje razlika mjerenja koncentracija plina na uređaju sa onečišćenim filtrom i bez filtra za odstranjivanje čestica. Mjerenje se provodi pomoću referentnog materijala (plin iz boce; SO_2, CO, NO, benzen) ili pomoću plina ozona (O_3) generiranog pomoću UV lampe u mjernom uređaju. Ispitivanje filtra se provodi u različitim razdobljima nakon postavljanja u liniju za uzorkovanje, a trajanje razdoblja se povećava dok se ne dosegne zadani kriterij. Rezultati ispitivanja se koriste u svrhu određivanja kritičnog razdoblja za zamjenu filtra (razlika u mjerenju sa i bez filtra za odstranjivanje čestica >3% u odnosu na koncentraciju bez filtra).

Tijekom razdoblja od 2014. do 2019. godine provedena su ispitivanja intervala zamjene filtra za odstranjivanje čestica na mjernim postajama Desinić, Plitvička jezera, Slavonski Brod-1, Varaždin-1 i Karlovac-1 i to na mjernoj opremi za mjerenje koncentracija SO_2, NO, CO, O_3 i BTEX. U ovom radu je prikazana metodologija provedbe terenskog ispitivanja razdoblja zamjene filtara za odstranjivanje čestica, rezultati razlika izmjerenih vrijednosti koncentracija plinova po mjerenim razdobljima i utvrđena razdoblja zamjene filtra na pojedinom uređaju po pojedinoj postaji.

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TESTING THE LIFETIME OF PARTICLE FILTERS ON MEASURING DEVICES FOR THE MEASUREMENT OF INORGANIC COMPOUNDS (SO_2, NO_X, CO AND O_3) AND VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

Keywords: *air quality, measurement, particle filter, replacement interval, state network for air quality measurement*

Standard test methods for measurement of inorganic compounds (sulphur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO) and ozone (O_3)) and Volatile Organic Compounds BTEX (benzene, toluene, ethylbenzene and xylenes) in ambient air (HRN EN 14662-3, HRN EN 14212, HRN EN 14211, HRN EN 14626 and HRN EN 14625) define the activities and procedures to ensure the measurement quality of measuring devices during the operation of an air quality measurement station. One of the procedures for the suitability rating of the measuring device at the measuring station is its response to span gas passing the particle filter. The lifetime of a particle filter on a particular measuring device is determined so as to measure the difference between the concentrations of gas measured on the device with a contaminated (previously used) filter and without one. The measurement is carried out using reference materials (gas from a cylinder, SO_2, CO, NO, benzene) or ozone gas (O_3), generated by an UV lamp in the measuring device. Particle filter testing is performed at different time scales after installing it in the sample line and the time period is gradually increased until a predetermined condition is reached. The test results are used to determine the critical time interval for filter replacement (difference in measurement with the particle filter and without the filter > 3% of the concentration of measurement without the filter).

During the period between 2014 and 2019, the particle filter duration test was performed at the measuring stations Desinić, Plitvička jezera, Slavonski Brod-1, Varaždin-1 and Karlovac-1 on measuring equipment for concentration measurement of SO_2, NO, CO, O_3 and BTEX. In this paper the field testing methodology and the results of differences of measured gas concentrations in relation to time intervals are presented as well as results of determined time intervals for filter replacement on particular air quality measurement instruments at certain air quality stations.

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ISPITIVANJE KVALITETE ZRAKA NA PODRUČJU GRADA SPLITA

Ključne riječi: *onečišćenje zraka, uredba, PM_{10}, metali, kvaliteta zraka*

Na području grada Splita tijekom 2018. godine provedeno je ispitivanje kvalitete zraka na dvije mjerne postaje (središte grada i Karepovac). Analizirane su masene koncentracije PM_{10} frakcije lebdećih čestica, masene koncentracije metala (As, Cd, Ni i Pb) u PM_{10}, te koncentracije plinova (SO_2 i NO_x). Dobiveni rezultati uspoređeni su s propisanim vrijednostima iz Uredbe o razinama onečišćujućih tvari u zraku (NN 117/12; NN 84/17). Srednje godišnje masene koncentracije lebdećih čestica PM_{10} izmjerene na obje mjerne postaje bile su niže od granične vrijednosti GV (PM_{10} 40 µg/m^3). Prema Uredbi broj dopuštenih prekoračenja dnevne GV (PM_{10} 50 µg/m^3) je 35 puta. Na mjernoj postaji Karepovac zabilježeno ih je sedam tijekom 2018. god., pri čemu su najviše vrijednosti izmjerene u travnju 181,58 µg/m^3 za vrijeme intenzivnih radova na sanaciji odlagališta. Na mjernoj postaji u središtu grada zabilježeno ih je pet, a najviša vrijednost bila je također u travnju (163,02 µg/m^3). Srednje godišnje masene koncentracije metala u PM_{10} na obje mjerne postaje bile su niže od propisanih graničnih i ciljnih vrijednosti. Usporedba mjernih postaja ukazuje da su uz odlagalište Karepovac zabilježene više srednje godišnje vrijednosti lebdećih čestica PM_{10} i metala (As i Cd) u odnosu na centar grada, dok se srednje godišnje vrijednosti Pb i Ni nisu značajnije razlikovale. Obrada satnih i dnevnih rezultata mjerenja plinova ukazuje na više vrijednosti NO_x u središtu grada kao posljedicu intenzivnog cestovnog prometa. Izmjerena srednja satna vrijednost NO_2 iznosila je 22,40 µg/m^3 u središtu grada, dok je na Karepovcu bila 13,55 µg/m^3. Usporedba provedenih mjerenja s rezultatima iz 2017. god. (prije sanacije odlagališta) ukazuje da je došlo do laganog rasta sadržaja pojedinih metala. U odnosu na prošlu godinu, na mjernoj postaji Karepovac u 2018. god. zabilježene su nešto više vrijednosti As, Cd i Ni, dok su u središtu grada u 2018. godini zabilježene više vrijednosti As, Ni i Pb. Prema provedenim rezultatima ispitivanja za 2018. god. zrak je na mjernim postajama na području grada Splita bio neznatno onečišćen, odnosno I. kategorije kvalitete.

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MEASUREMENTS OF AIR QUALITY IN THE AREA OF THE CITY SPLIT

Keywords: *air pollution, regulations , PM_{10}, metals, air quality*

Air quality testing was conducted using two measuring stations (city centre and Karepovac) in the city of Split during 2018. We analysed mass concentrations of PM_{10} particle fraction in the air, metal composition in particulate matter, and gas concentrations (SO_2 and NO_x). The final results have been compared with the prescribed values of Regulations regarding the levels of pollutants in ambient air (OG 117/12; 84/17). The average annual values of PM_{10} measured at the two measuring stations were lower than the limit value (PM_{10} 40 $\mu g/m^3$). According to regulations, the acceptable number of exceedances allowed for PM_{10} (50 $\mu g/m^3$) is 35 times The seven over-values were recorded on the Karepovac measuring station during 2018., when the highest values were measured in April (181.58 $\mu g/m^3$) during intensive works on the remediation of waste landfills. The highest values were also measured in April (163.02 $\mu g/m^3$) at the measuring station in the city centre, when the five exceedances were recorded. The mean measured annual mass concentrations of metal in PM_{10} at two measuring stations were lower than the values prescribed. By comparing the results of two measurament sites we can conclude that Karepovac had higher mean annual values of mass concentrations of PM_{10} particle fraction and metals (As and Cd) than the measurement station city centre, however the mean annual values of metals Pb and Ni were not significantly different. Analysis of the hourly and daily results of gases indicates increased NO_x values in the centre of the city due to increased road traffic. The mean hourly value of NO_x measured in the centre of the city was 22.40 $\mu g/m^3$, while at Karepovac 13.55 $\mu g/m^3$. The comparison of measurements last year (before landfill remediation) with the measurements results from 2018 year indicate a slight increase in the content of certain metals. The measurement results of As, Cd and Ni at Karepovac were higher in 2018 as were results of As, Ni and Pb measured in the centre of the city. Due to the results of air quality examinations in 2018 we can conclude that the air of Split was slightly contaminated and therefore rated as being of 1st category.

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PROBLEMI KOD TERENSKOG MJERENJA RADIOAKTIVNOSTI U ZRAKU

Ključne riječi: *gamaspektrometrija, osnovno zračenje, terenska mjerenja*

Nadzor radioaktivnosti okoliša u Republici Hrvatskoj uglavnom se provodi kroz sakupljanje uzoraka na terenu i mjerenja istih u laboratorijskim uvjetima. Takav mjerni postupak je spor, ali vodi do visoke točnosti (u engleskom je napisano ispravno) rezultata, Terenska mjerenja su u pravilu manje točna no odlikuju ih velika mobilnost i brzina dobivanja rezultata, što omogućava da se u vrlo kratkom roku dobije radiološka slika određenog područja na osnovi velikog broja mjerenja s različitih lokacija. Posebni problemi se javljaju pri terenskim mjerenjima radioaktivnosti u zraku. U prosincu 2018. provedena su terenska mjerenja radioaktivnosti u Hrvatskoj na 4 lokacije u blizini nuklearne elektrane Krško (Slovenija) i na 4 lokacije u blizini nuklearne elektrane u Paksu (Mađarska).

Terenska mjerenja uključivala su visokorezolucijska gamaspektrometrijska mjerenja uređajima ORTEC Detective-EX i Canberra HPGe "P"-TYPE. Mjerenja su provođena na visini od 1m detektorom okrenutim prema tlu bez kolimatora. Uzorci zraka uzorkovani su na mjestu mjerenja prijenosnom pumpom za uzorkovanje zraka RADECO H-810. Uzorci su sakupljeni na filterima od staklenih vlakana, promjera 4,7 cm. Sakupljeni uzorci zraka, odnosno filteri, su analizirani u laboratoriju visokorezolucijskom gamaspektrometrijom koristeći GAMMA-X HPGe detektor ORTEC rezolucije 2,2 keV te relativne efikasnosti od 74%, sve na 1,33 MeV ^{60}Co, povezan s elektroničkim sustavom i osobnim računalom. Kalibracija energije i efikasnosti gamaspektrometara učinjena je uz pomoć kalibracijskih izvora Češkog metrološkog instituta (ERX), koji pokrivaju energiju između 40 i 2000 keV.

Prilikom mjerenja uočeni su brojni praktični problemi. Gotovo nemoguće je izmjeriti koncentraciju aktivnosti radionuklida u filterima zraka na terenu iz dva razloga. Prvo, mjerenja su pokazala da je doprinos radioaktivnosti zraka ukupnoj radioaktivnosti zanemariv u odnosu na doprinos tla. Drugo, pumpa predviđena za uzorkovanje zraka na terenu ima premali protok odnosno konačni prosisani volumen zraka (a time i veličina uzoraka) je nedostatna za precizna kvalitativna mjerenja te su sve vrijednosti koncentracija aktivnosti bile ispod granice detekcije mjerne metode. Također, ne postoji adekvatni štit na terenu koji bi štitio od osnovnog zračenja te je uzorke stoga opet potrebno mjeriti u laboratoriju.

Zaključak jest, da je komercijalna oprema (pumpa i odsustvo štita) nedostatna kako bi se, odmah na terenu, mogla kvalitativno odrediti koncentracija aktivnosti radionuklida u zraku.

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PROBLEM IN FIELD MEASUREMENTS OF RADIOACTIVITY IN AIR

Keywords: *gamma-ray spectrometry, background radiation; on-site measurements.*

Environmental radioactivity monitoring in the Republic of Croatia is mainly carried out by field sampling and measurements of collected samples in laboratory conditions. This procedure leads to a high accuracy but is slow. On-site measurements are less accurate but they are characterised by high mobility and reduced time required to obtain results, which enables to scan the radiological condition of a given area rather quickly, on the basis of a large number of measurements on different locations. There is, however, a problem with measurements of radioactivity in air. In December 2018, we performed on-site measurements in Croatia on 4 locations that were close to the nuclear power plant Krško (Slovenia), as well as on 4 locations close to the nuclear power plant in Paks (Hungary).

For the on-site measurements, we used high-resolution gamma-ray spectrometers ORTEC Detective-EX and Canberra HPGe P-TYPE without collimators, measuring radionuclide activity at 1 m above the ground and with the detectors directed towards the ground. Air was sampled on the measurements locations by using a RADECO H-810 portable pump. We used fiberglass filters of the 4.7 cm diameter. Collected air samples, i.e., filters, were subjected to a laboratory high-resolution gamma-ray spectrometry based on an ORTEC GAMMA-X HPGe detector with a 2.2 keV resolution and a relative efficiency of 74%, all at 1.33 MeV ^{60}Co, connected to a computerised electronic system.

During the measurements, we identified numerous practical problems. It was virtually impossible to detect radionuclide activity in air, for two reasons. First, the contribution of airborne radioactivity was negligible in comparison with that of soil. Second, the pump used to sample air had an insufficient flow, that is, the pumped air volume was too small for accurate quantitative measurements, which led to activity concentrations being below detection limit. There was also no adequate shield which could provide protection from background radiation, so that the collected samples had to eventually be measured under laboratory conditions.

We conclude that the commercial equipment (the pump and the absence of a shield) were inadequate for a quantitative determination of airborne radionuclide activity concentrations by means of on-site measurements.

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SEZONSKA OVISNOST RASPODJELE POLICIKLIČKIH AROMATSKIH UGLJIKOVODIKA U PM_{10} I $PM_{2,5}$ FRAKCIJI U ZAGREBU

Ključne riječi*: PAU, HPLC-FLD, linearna regresija*

Policiklički aromatski ugljikovodici (PAU) zbog svoje kemijske stabilnosti i inertnosti čine skupinu široko rasprostranjenih organskih spojeva u okolišu. Istraživanja su pokazala da su PAU u zraku uglavnom vezani na lebdeće čestice manjeg aerodinamičkog promjera ($PM_{2,5}$ i PM_1), te da se svi PAU nalaze u respirabilnoj frakciji bez obzira na godišnje doba. Cilj ovog rada bio je istražiti utjecaj sezonskih promjena na sastav i raspodjelu PAU te odrediti moguće izvore PAU vezanih na PM_{10} i $PM_{2,5}$ frakcije lebdećih čestica na mjernoj postaji u stambenom dijelu grada Zagreba. U tu svrhu provedeno je paralelno sakupljanje 24-satnih uzoraka PM_{10} i $PM_{2,5}$ frakcije na filtre od kvarcnih vlakana u hladnijem dijelu godine (od 01. do 31. siječnja 2017.), te u toplijem dijelu godine (od 01. – 31. srpnja 2017.). Ekstrakcija PAU spojeva s filtra provedena je korištenjem smjese toluena i cikloheksana u ultrazvučnoj kupelji, nakon čega su uzorci upareni u blagoj struji dušika do suha i otopljeni u acetonitrilu. Analiza PAU je provedena na tekućinskom kromatografu visoke djelotvornosti s fluorescentnim detektorom promjenjivih valnih duljina ekscitacije i emisije (HPLC-FLD). Raspon srednjih vrijednosti masenih koncentracija deset mjerenih PAU u PM_{10} frakciji kretao se od 1,018 ng m^{-3} do 8,596 ng m^{-3} u hladnijem dijelu godine, odnosno u toplijem je bio u rasponu 0,021 – 0,116 ng m^{-3}. U $PM_{2,5}$ frakciji utvrđena je ista sezonska ovisnost s nižim koncentracijama u ljetnom periodu (0,011 – 0,073 ng m^{-3}), te višim koncentracijama (0,770 – 7,617 ng m^{-3}) u zimskom periodu godine. Udio PAU većih molekulskih masa (benzo(a)antracen (BaA), krizen (Kri), benzo(b)fluoranten (BbF), benzo(k)fluoranten (BkF), benzo(a)piren (BaP), dibenzo(ah)antracen (DahA), benzo(ghi) perilen (BghiP) i indeno(1,2,3-cd)piren (IP)) u sumi PAU bio je statistički značajno veći (> 77 %) u odnosu na PAU srednjih molekulskih masa (fluoranten (Flu) i piren (Pir)) u obje frakcije tijekom cijelog razdoblja mjerenja. Također, uočeno je povećanje udjela PAU sa šest benzenskih prstena (DahA, BghiP i IP) u ljetnom periodu mjerenja u obje frakcije (> 34 % u $PM_{2,5}$ i > 29 % u PM_{10} frakciji) u odnosu na zimsko razdoblje (> 25 % u $PM_{2,5}$ i > 22 % u PM_{10}). Metodom linearne regresije potvrđeno je da su PAU uglavnom vezani na manje čestice ($PM_{2,5}$), što je bilo najizraženije tijekom zimskog razdoblja mjerenja. Tijekom zime udio PAU u $PM_{2,5}$ frakciji u odnosu na PM_{10} frakciju bio je više od 95 % (osim za Flu i Pir), dok je u ljetnom razdoblju iste godine više od 48 % svih PAU (osim Flu i Pir) bilo vezano na $PM_{2,5}$ frakciju lebdećih čestica. Rezultati ovog istraživanja su pokazali da su ispušni plinovi automobila dominantan izvor PAU tijekom ljetnog perioda, dok u zimskom periodu potencijalni izvor PAU čine kućna ložišta.

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SEASONAL DEPENDENCE OF POLYCYCLIC AROMATIC HYDROCARBONS' DISTRIBUTION IN PM_{10} AND $PM_{2.5}$ FRACTIONS IN ZAGREB

Keywords: *PAHs, HPLC-FLD, linear regression*

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic compounds in the environment, due to their chemical stability and inertness. Studies have shown that the PAHs in the air are mostly bound on airborne particles with a smaller aerodynamic diameter ($PM_{2.5}$ and PM_1), and can be found in the respirable fraction, regardless of the season. The aim of this contribution was to investigate the influence of seasonal variations on PAHs composition and distribution and also to determine possible PAHs sources related to PM_{10} and $PM_{2.5}$ at the urban background site in the residential part of Zagreb. For this purpose, 24-hour samples of PM_{10} and $PM_{2.5}$ particle fractions were collected on quartz fiber filters in winter season (from 1st till 31st January 2017), and in the summer season (from 1st till 31st July 2017). Filters were extracted with a solvent mixture of toluene and cyclohexane in an ultrasonic bath, after which the samples were evaporated in a mild stream of nitrogen to dryness and re-dissolved in acetonitrile. The analysis was performed using liquid chromatography with a fluorescence detector and programmed changes in excitation and emission wavelengths (HPLC-FLD). The mean concentrations of ten measured PAHs in the PM_{10} fraction ranged from 1.018 ng m^{-3} to 8.596 ng m^{-3} in the winter season, and in summer season from 0.021 to 0.116 ng m^{-3}. In the $PM_{2.5}$ fraction were observed the same seasonal variations with lower concentrations in the summer period (0.011 – 0.073 ng m^{-3}) and higher concentrations (0.770 – 7.617 ng m^{-3}) during the winter part of the year. The proportion of high molecular weight PAHs (benzo(a)anthracene (BaA), chrysene (Kri), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(ah)anthracene (DahA), benzo(ghi)perylene (BghiP) and indeno(1,2,3-cd)pyrene (IP)) of the total PAHs was significantly higher (> 77 %) compared to the medium molecular weight PAHs (fluoranthene (Flu) and pyrene (Pir)) in both fractions throughout the measurement period. There was also an increase in PAHs with six benzene rings (DahA, BghiP and IP) in the summer measurement period in both fractions (> 34 %)in the PM2.5 and > 29 % in the PM_{10} fraction) over the winter period (> 25 % in $PM_{2.5}$ and > 22 % in PM_{10}). The linear regression method confirmed adsorption of PAHs on smaller particles ($PM_{2.5}$), which was most pronounced during the winter season. During the winter, more than 95 % of all measured PAHs (except for Flu and Pir), were present in the $PM_{2.5}$, while in the summer season more than 48 % of all PAHs (except for Flu and Pir) were related to $PM_{2.5}$ particle fraction. The results of this research indicated vehicle emissions as the dominant source of PAHs during the summer period, while in the winter period the potential source of the PAHs is wood combustion.

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PRAĆENJE KONCENTRACIJA MERKAPTANA I SUMPOROVODIKA U ZRAKU NA PLINSKOM POLJU MOLVE U RAZDOBLJU 2012.-2016.

Ključne riječi*: R-SH, H_2S, kvaliteta življenja, spektrofotometrija, granična vrijednost*

Merkaptani (R-SH) i sumporovodik (H_2S) spadaju u grupu spojeva neugodna i nadražujuća mirisa čija prisutnost u zraku u većim koncentracija značajno narušava kvalitetu življenja. Izvor R-SH i H_2S uglavnom je raspad ugljikovodika u anaerobnim uvjetima. U zrak mogu dospjeti i kao jedni od nusprodukata tijekom eksploatacije i prerade prirodnog plina. Uredbom o razinama onečišćujućih tvari u zraku (NN 117/2012, NN 84/17) propisane su granične vrijednosti (GV) koncentracija s obzirom na kvalitetu življenja (dodijavanje mirisom) na temelju 24-satnih prosjeka (GV (R-SH) = 3 μg/m^3, GV (H2S) = 5 μg/m^3) kao i učestalost dozvoljenih prekoračenja tijekom kalendarske godine (prekoračenje GV ≤ 7 puta).

Na lokalitetu plinskog polja Molve u Podravini od početka eksploatacije prirodnog plina osamdesetih godina prošlog stoljeća započelo se i sa sustavnim mjerenjima onečišćenja zraka, vode, tla, vegetacije i radioaktivnosti. Mjerenja se provode u okviru Programa utvrđivanja stanja okoliša u zoni utjecaja Centralne plinske stanice (CPS) Molve kao mogućeg izvora onečišćenja. Koncentracije R-SH i H_2S u zraku praćene su na 5 mjernih postaja smještenih na CPS Molve i okolnim bušotinama. Prikazani su rezultati mjerenja R-SH i H_2S u razdoblju od 2012. do 2016. godine. Mjerenja su se provodila 24-satnim uzorkovanjem tijekom trideset dana u toplijem i trideset dana u hladnijem dijelu godine. Uzorci R-SH i H_2S prikupljani su prosisavanjem zraka kroz impregnirane filtar papire, a masene koncentracije u zraku određene su spektrofotometrijski, pri čemu se koncentracija merkaptana odnosi na ukupne merkaptane, R-SH. Dobiveni rezultati obrađeni su statistički te interpretirani prema navedenoj Uredbi.

Rezultati pokazuju da su se srednje mjesečne koncentracije merkaptana na plinskom polju Molve u toplijem dijelu godine kretale u rasponu od 0,27 μg/m^3 (2014.) do 1,11 μg/m^3 (2015.), dok su u hladnijem dijelu godine bile nešto veće, od 0,34 μg/m^3 (2013.) do 2,93 μg/m^3 (2015.). U promatranom razdoblju od pet godina, samo je tijekom zimskog razdoblja 2015. godine došlo do prekoračenja GV više od 7 puta, koliko je dozvoljeno Uredbom, na dvije mjerne postaje (9 i 10 puta). Za H^2S se srednja mjesečna koncentracija u toplijem dijelu godine kretala od 0,66 μg/m^3 (2012.) do 3,88 μg/m^3 (2014.), a u zimskom periodu vrijednosti su bile nešto niže i kretale su se u rasponu od 0,28 do 2,05 μg/m^3 (2012.). U petogodišnjem razdoblju praćenja dolazilo je povremeno do prekoračenja GV za H_2S no učestalost dozvoljenih prekoračenja tijekom kalendarske godine nikad nije bila veća od propisanih 7 puta.

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MERCAPTANS AND HYDROGEN SULPHIDE CONCENTRATION MONITORING IN THE AIR OF MOLVE GAS FIELD DURING 2012-2016

Keywords: *R-SH, H_2S, quality of life, spectrophotometry, limit values*

Mercaptans (R-SH) and hydrogen sulphide (H_2S) belong to the group of foul-smelling compounds whose higher concentrations in the air significantly impact quality of life. The source of R-SH and H_2S is mainly hydrocarbon degradation under anaerobic conditions. They may also appear in the air as byproducts during the exploitation and processing of natural gas. The Regulation on Air Pollutant Levels (OG 117/2012, OG 84/17) provides limit values (LV) for concentrations based on the quality of life (scent) for 24-hour averages (LV (R-SH) = 3 μg/m^3, LV (H2S) = 5 μg/m^3) as well as the frequency of permissible overdrafts during a calendar year (overdraft ≤ 7 times).

At the site of the Molve gas field in Podravina, Croatia, systematic measurements of air, water, soil, vegetation and radioactivity pollution have been carried out since the beginning of the exploitation of natural gas, in the 1980s. Measurements were carried out within the Environmental Impact Assessment Program in the zone of Molve Central Gas Station (CPS) as a potential source of contamination. Mass concentrations of R-SH and H_2S in the air were monitored at 5 measuring stations located at CPS Molve and surrounding wells. R-SH and H_2S concentrations are given for a five-year period (2012–2016). The measurements were performed with 24-hour sampling for thirty days in each, the warmer and the colder part of the year. Samples of R-SH and H_2S were collected by forcing the air through impregnated filter paper and mass concentrations in the air were determined spectrophotometrically where the concentration of mercaptans is referred to total mercaptans, R-SH. The obtained results were processed statistically and interpreted according to the mentioned Regulation.

The results show that the average monthly mercaptans concentrations at the Molve gas field during warmer part of the year ranged from 0.27 μg/m^3 (2014) to 1.11 μg/m^3 (2015), while slightly higher values were obtained in the colder part of the year, from 0.34 μg/m^3 (2013) to 2.93 μg/m^3 (2015). In the observed period, LV exceeded the allowed levels more than 7 times only during the winter period of 2015 at two local stations (9 and 10 times). For H_2S, the average monthly concentration in the warmer part of the year ranged from 0.66 μg/m^3 (2012) to 3.88 μg/m^3 (2014), and in the winter the values were slightly lower, ranging from 0.28 to 2.05 μg/m^3 (2012). During the five-year period of monitoring, the LV for H_2S was occasionally exceeded, but the frequency of permissible overdrafts during the calendar years was never greater than the allowed 7 times.

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ORGANSKI I ELEMENTNI UGLJIK U FRAKCIJAMA LEBDEĆIH ČESTICA $PM_{2,5}$ I $PM_{1,0}$ U ZRAKU ZAGREBA

Ključne riječi*: EC, OC, omjer OC/EC, sezonska raspodjela, SOC*

Cilj istraživanja bio je ispitati razlike u razinama masenih koncentracija elementnog (EC) i organskog (OC) ugljika u frakcijama lebdećih čestica aerodinamičkog promjera manjeg od 2,5 μm ($PM_{2,5}$) i 1 μm ($PM_{1,0}$) u zraku grada Zagreba. Mjerenja su provedena tijekom siječnja i srpnja 2018. godine u sjevernom dijelu grada. 24-satni uzorci frakcija lebdećih čestica $PM_{2,5}$ i $PM_{1,0}$ sakupljani su iz približno 55 m^3 zraka na filtre od kvarcnih vlakana (Pallflex Tissuequartz 2500 QAT–UP, Pall Life Science), prethodno žarene na 850 °C tijekom 3 sata. Sakupljanje frakcija lebdećih čestica $PM_{2,5}$ kao i određivanje njihovih masenih koncentracija provedeno je sukladno normi HRN EN 12341:2014. Sakupljanje i određivanje masenih koncentracija $PM_{1,0}$ frakcije lebdećih čestica provedeno je na isti način. Sadržaj OC i EC u frakcijama lebdećih čestica $PM_{2,5}$ i $PM_{1,0}$ u zraku određen je metodom termičko-optičke transmisije (TOT) na analizatoru ugljika (Sunset Laboratory) s plameno ionizacijskim detektorom korištenjem EUSAAR_2 temperaturnog protokola na način opisan u normi HRN EN 16909:2017. Podaci su statistički obrađeni u računalnom programu STATISTICA 13.

Masene koncentracije frakcije lebdećih čestica $PM_{2,5}$ kretale su se u rasponu od 4,1 μg m^{-3} do 53,4 μg m^{-3}, dok su za frakciju lebdećih čestica $PM_{1,0}$ iznosile od 2,2 μg m^{-3} do 34,7 μg m^{-3}. Rezultati pokazuju statistički značajne razlike masenih koncentracija ugljika u $PM_{2,5}$ i $PM_{1,0}$ frakcijama lebdećih čestica s višim vrijednostima zabilježenim u hladnijem u odnosu na topliji period mjerenja. Doprinos ukupnog ugljika ukupnoj masi frakcija lebdećih čestica viši je za frakciju $PM_{1,0}$ nego za frakciju $PM_{2,5}$ neovisno o periodu mjerenja što se vjerojatno može objasniti činjenicom da je veći dio ugljika sadržan u sitnijim česticama. Vrijednosti omjera masenih koncentracija OC/EC bili su viši od 3 što ukazuje na veći udio SOC (sekundarni organski ugljik) u OC u obje frakcije lebdećih čestica u zraku grada Zagreba za provedeno razdoblje mjerenja.

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ORGANIC AND ELEMENTAL CARBON IN THE $PM_{2.5}$ AND $PM_{1.0}$ PARTICLE FRACTIONS IN ZAGREB AIR

Keywords: *EC, OC, OC/EC ratio, seasonal distribution, SOC*

The aim of this study was to investigate the differences in levels of carbon mass concentrations, elemental carbon (EC) and organic carbon (OC), in $PM_{2.5}$ (particulate matters with an equivalent aerodynamic diameter less than 2.5 μm) and $PM_{1.0}$ (particulate matters with an equivalent aerodynamic diameter less than 1.0 μm) fractions in Zagreb air. Measurements were investigated during January and July of 2018 in the northern part of Zagreb. $PM_{2.5}$ and $PM_{1.0}$ samples were collected during 24-hour periods from approximately 55 m^3 of ambient air on quartz fibre filters (Pallflex Tissuequartz 2500 QAT - UP, Pall Life Science), previously pre-fired at 850 °C for 3 hours. The collection of $PM_{2.5}$ fraction as well as the determination of mass concentrations was carried according to norm HRN EN 12341:2014. The collection of $PM_{1.0}$ fraction as well as the determination of its mass concentrations was carried the same way. The content of OC and EC in $PM_{2.5}$ and $PM_{1.0}$ were measured by the thermal-optical transmittance (TOT) method using a carbon analyser (Sunset Laboratory) with a flame ionization detector using the EUSAAR_2 temperature protocol described in HRN EN 16909:2017. The data were statistically processed using STATISTICA 13.

Mass concentrations of $PM_{2.5}$ ranged from 4.1 μg m^{-3} to 53.4 μg m^{-3}, while for $PM_{1.0}$ between 2.2 μg m^{-3} and 34.7 μg m^{-3}. Results show statistically significant differences between mass concentrations of carbon in $PM_{2.5}$ and $PM_{1.0}$ fractions with higher values determined in colder compared to the warmer period of measurements. The mass contributions of total carbon to the total particulate matter mass was higher for $PM_{1.0}$ fraction than for $PM_{2.5}$ fraction regardless of the measurement period, which is likely to be explained by the fact that all of the carbon was contained in smaller particles. The values of OC/EC mass concentration ratios were higher than 3,which indicates higher contribution of the secondary organic carbon (SOC) in OC in both fractions of particulate matter observed in Zagreb air for the period of measurement.

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ATMOSFERSKO TALOŽENJE ORGANSKIH SPOJEVA: USPOREDBA RAZLIČITIH IZVEDBI UZORKIVAČA

Ključne riječi*: otvoreni uzorkivač, PAU, ukupna taložna tvar*

Atmosfersko taloženje jedno je od glavnih mehanizama uklanjanja organskih onečišćujućih tvari iz atmosfere. Policiklički aromatski ugljikovodici (PAU) uglavnom su u zraku prisutni vezani za lebdeće čestice tako da se njihovo uklanjanje prvenstveno odvija putem gravitacijskog taloženja lebdećih čestica (suho taloženje) ili oborinskim ispiranjem onečišćujućih tvari (mokro taloženje).

Cilj ovog rada bio je utvrditi utjecaj izvedbe uzorkivača na učinkovitost uzorkovanja pri određivanju PAU u uzorcima ukupne taložne tvari (što uključuje suho i mokro taloženje, engl. bulk). Ispitivano je postoji li značajna razlika u razinama PAU prikupljenih pomoću otvorenog uzorkivača u dvije različite izvedbe: staklena posuda promjera 100 mm (B) i staklena posuda s lijevkom promjera 150 mm (BL). U oba slučaja posuda se nalazila na stalku na visini 2 m od tla. Uzorkovanje se provelo u Zagrebu, na Institutu za medicinska istraživanja i medicinu rada, sakupljanjem dvotjednih uzoraka u razdoblju od veljače do svibnja 2019. godine. Uzorci su pripravljeni ekstrakcijom na čvrstoj fazi upotrebom kolona punjenih silikagelom, a za eluiranje adsorbiranih PAU s kolone koristila se smjesa diklormetana i heksana (1:1, v/v). Nakon ekstrakcije, ekstrakt je uparen u struji dušika i otopljen u heksanu. U uzorcima su određene masene koncentracije 12 PAU-a (fluoranten, piren, benzo(a)antracen, krizen, benzo(b)fluoranten, benzo(k)fluoranten, benzo(j) fluoranten, benzo(a)piren, benzo(e)piren, indeno(1,2,3-cd)piren, dibenzo(a,h)antracen i benzo(g,h,i) perilen) analizom na plinskom kromatografu s masenim spektrometrom.

U provedenom razdoblju mjerenja ukupno taloženje izraženo kao zbroj masa PAU (∑12PAU) po površini po danu iznosilo je između 71,6 ng m^{-2} d^{-1} i 507,5 ng m^{-2} d^{-1} za uzorkivač B te između 234,9 ng m^{-2} d^{-1} i 1045,2 ng m^{-2} d^{-1} za uzorkivač BL. Mase fluorantena, pirena, krizena i benzo(b) fluorantena najviše su doprinosile ukupnoj masi PAU-a neovisno o izvedbi otvorenog uzorkivača. Iz rezultata ovog rada može se zaključiti da izvedba otvorenog uzorkivača može značajno utjecati na izmjerene razine PAU. Veće razine atmosferskog taloženja PAU određene su u uzorcima sakupljenim pomoću uzorkivača s lijevkom (BL). U budućim istraživanjima ispitat će se utjecaj različitih izvedbi otvorenih uzorkivača na razine polikloriranih bifenila (PCB) u uzorcima ukupne taložne tvari.

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ATMOSPHERIC DEPOSITION OF ORGANIC COMPOUNDS: COMPARISON BETWEEN DIFFERENT PERFORMANCES OF A BULK COLLECTOR

Keywords: *bulk, PAH, total deposited matter*

Atmospheric deposition is one of the main mechanisms for removing organic pollutants from the atmosphere. Polycyclic aromatic hydrocarbons (PAHs) are largely present in the air bound on particulate matter, which is why their removal is primarily carried out by the gravitational deposition of particles (dry deposition) or washout by polluting substances (wet deposition).

The aim of this paper was to determine the effect of bulk collector performance on PAH sampling efficiency in total deposited matter, which includes dry and wet deposition. We investigated whether there was a significant difference in PAH levels in atmospheric deposition samples collected by bulk method, at two different performances: open cylindrical glass bottle with a diameter of 100 mm (B) and a glass bottle connected to a funnel with a diameter of 150 mm (BL). Sampling was performed in Zagreb at the Institute for Medical Research and Occupational Health from February to May 2019. The biweekly samples were prepared by solid phase extraction with silica cartridges and a mixture of dichloromethane and n-hexane (1:1, v/v) was used for elution. After extraction, the extract was concentrated under a nitrogen stream and dissolved in hexane. In bulk atmospheric deposition samples, 12 PAHs (fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k) fluoranthene, benzo(j)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene) were analysed by gas chromatography coupled with mass spectrometric detection (GC-MS/MS).

During the measurement period, the deposition rates (ng m^{-2} d^{-1}) of ∑12PAHs varied between 71.6 and 507.5 for B and from 234.9 to 1045.2 for BL, respectively. Fluoranthene, pyrene, chrysene and benzo(b)fluoranthene were the major compounds detected in both performances of the bulk collectors. Results show that the design of the bulk collectors can significantly affect the measured levels of PAHs. The comparison among different bulk collector performances showed that higher deposition rates of PAHs were obtained with a BL collector. Future studies will investigate the impact of different performance of bulk collectors at the levels of polychlorinated biphenyls (PCBs) in atmospheric deposition samples.

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- Ispitni laboratorij s dozvolom Ministarstva zaštite okoliša i energetike za obavljanje djelatnosti praćenja kvalitete zraka
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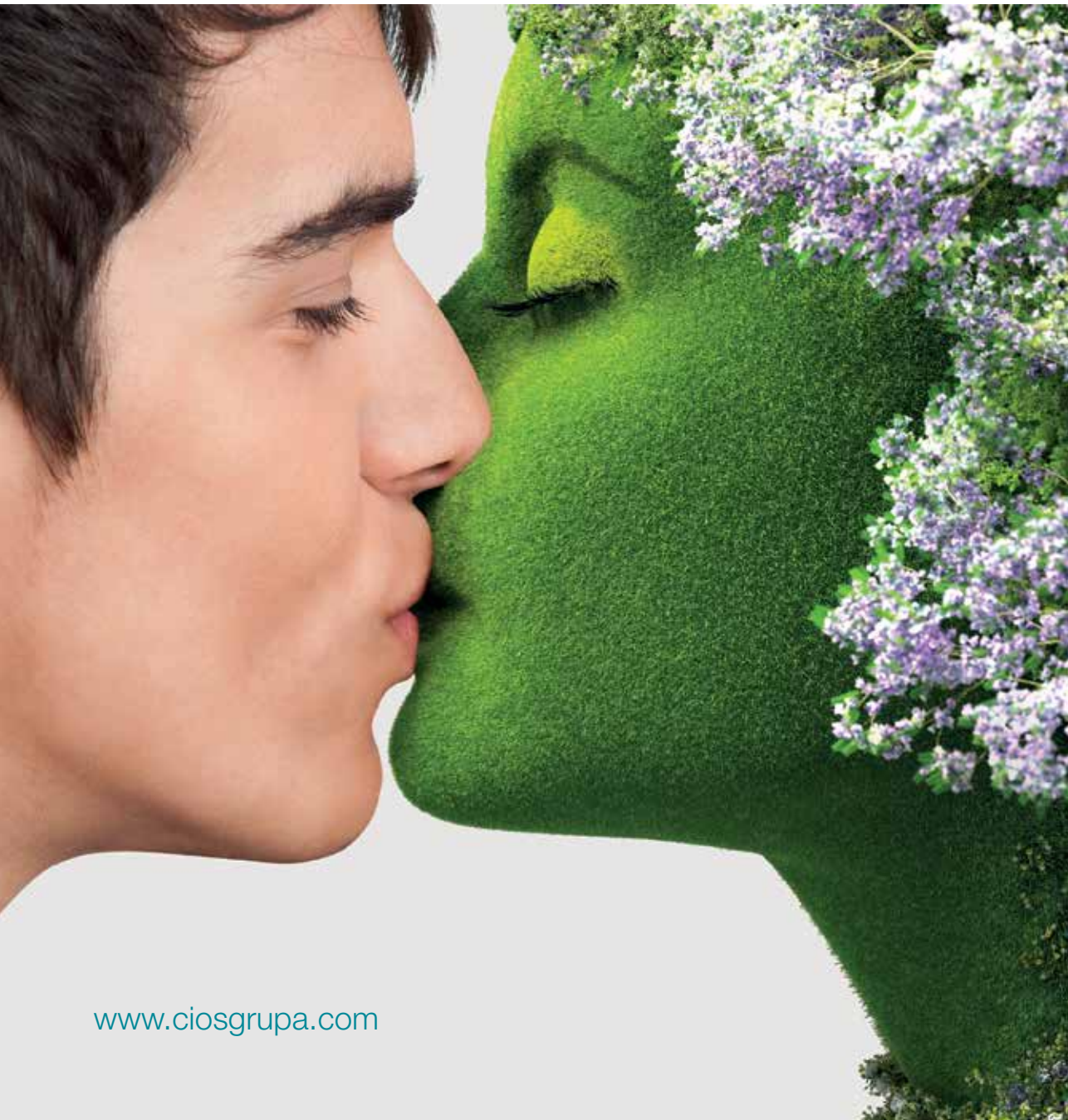

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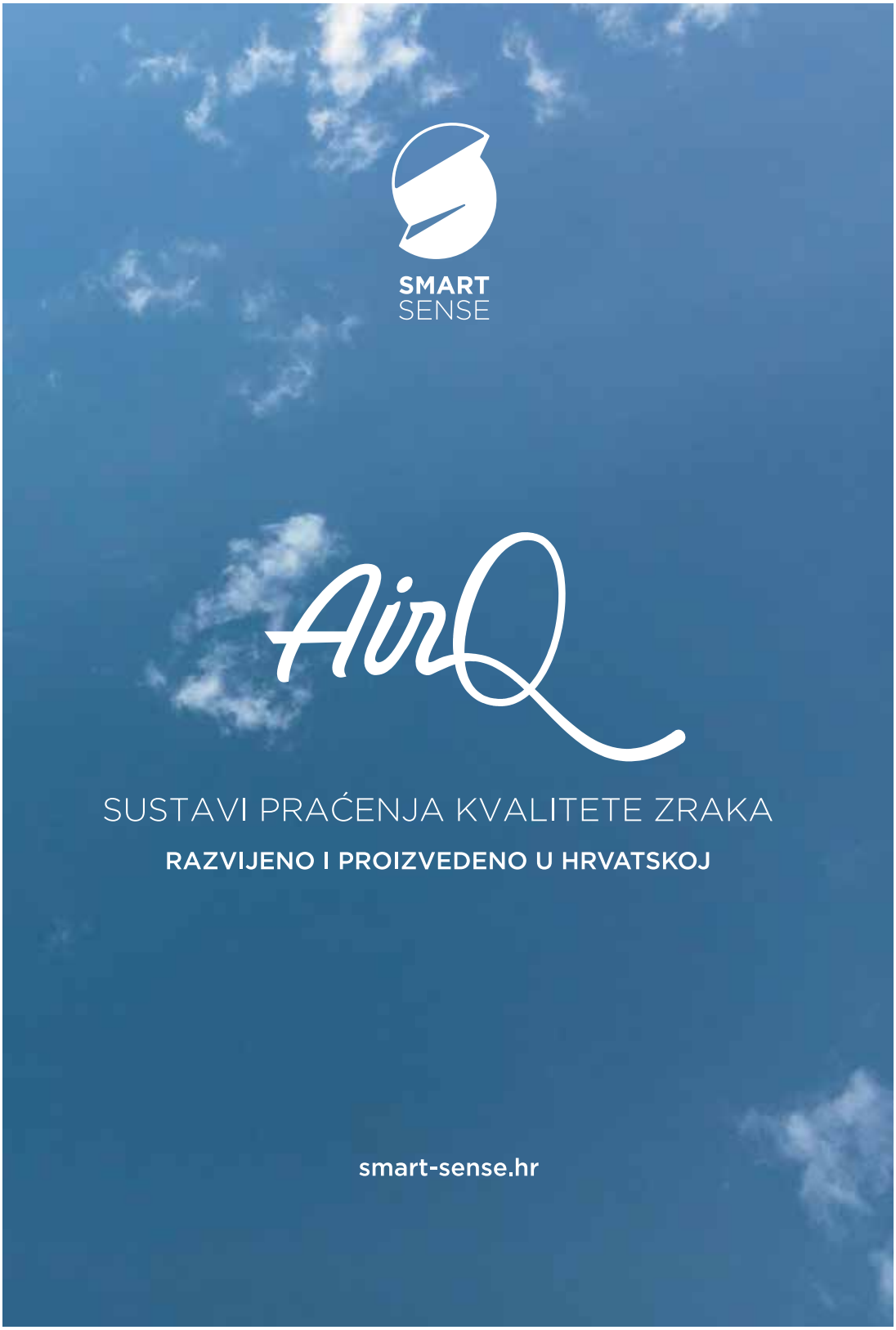
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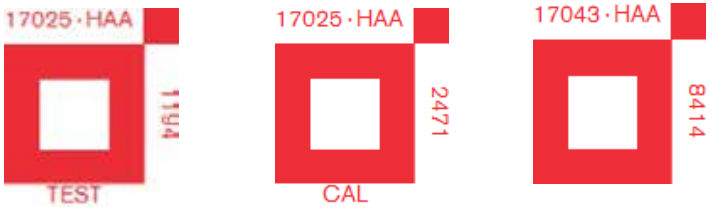

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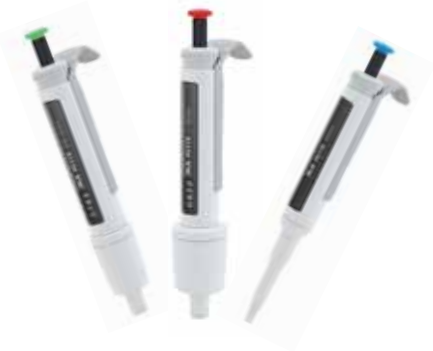




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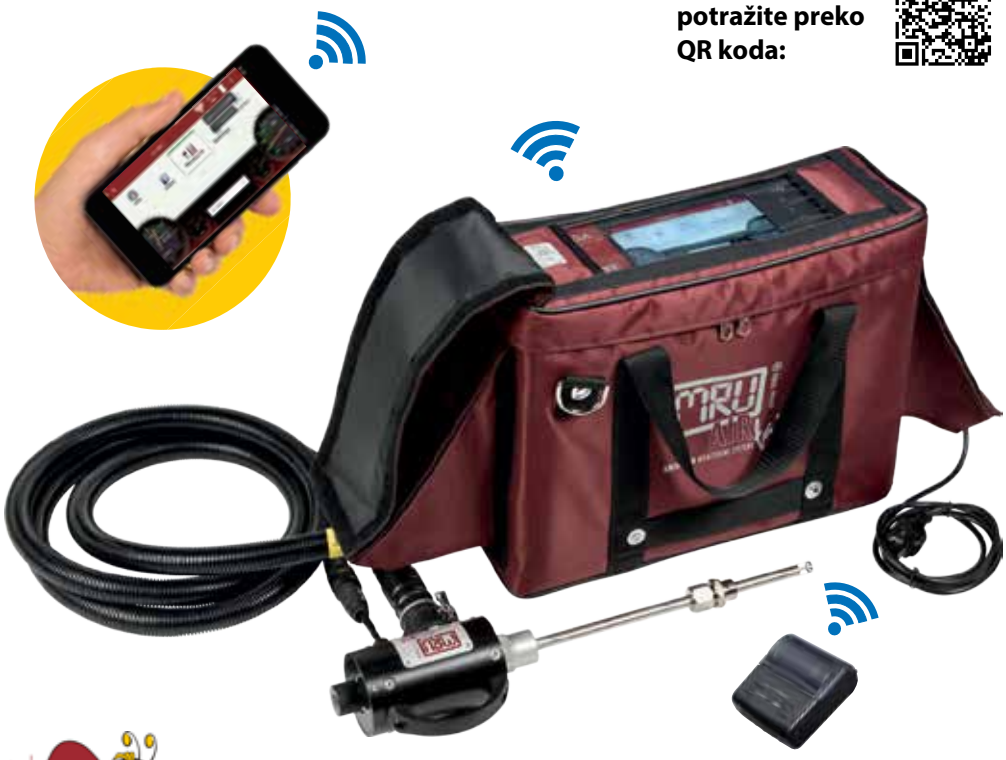

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