



AGROSYM

BOOK OF PROCEEDINGS



*XVI International Scientific Agriculture Symposium
"Agrosym 2025"
Jahorina, October 2-5, 2025*



AGRO 2025
sym

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FOREWORD

The world is facing a range of crises that require policymakers to base their decisions on scientific data and evidence to effectively address them. Issues such as climate change, loss of biodiversity, degradation of natural resources (e.g. land and water), ongoing conflicts, persistent inequalities, and economic disruptions are progressively weakening the ability of agri-food systems to ensure food security and nutrition for all. Research plays a vital role in providing evidence and technical expertise, acting as a facilitator and policy broker in the development of agri-food strategies, investment planning, innovation policies, and other important policy processes. Additionally, research is essential for generating the knowledge, evidence, and resources required to promote responsible and inclusive innovation. It also offers support to a range of stakeholders, including farmers' organizations, businesses, and civil society groups. Integrating research with long-term policy strategies can enhance the acceptance and adoption of innovations in the agri-food sector, particularly when these innovations are promoted through inclusive platforms. To achieve a sustainable impact at scale, it is essential to improve collaboration in agri-food research and innovation. Scientific events and gatherings can be crucial in reaching this objective.

The International Agriculture Symposium AGROSYM has served as an annual forum for sixteen years, facilitating global scientific discussions on agriculture, food, rural development, the environment, and forestry. This symposium offers an excellent opportunity to share ideas, strengthen existing networks, establish new academic connections, and stimulate dialogue among academia, public institutions, the private sector, and civil society organizations. Participants engage in discussions about recent global and regional trends in the agri-food sector. The multidisciplinary findings presented at AGROSYM contribute to the dissemination of knowledge and best practices among all stakeholders in the agri-food chain, including farmers, extension agents, researchers, and policymakers. Additionally, the symposium emphasizes the importance of agriculture and food science as vital components of many national research strategies, impacting the broader community as well.

This Book of Proceedings from the 16th International Scientific Agricultural Symposium “AGROSYM 2025” encompasses articles which illustrate a wide range of research and insights across the comprehensive spectrum of agricultural disciplines. These articles address the following themes: 1) Plant production, 2) Plant protection and food safety, 3) Organic agriculture and agroecology, 4) Environmental protection and natural resources management, 5) Animal husbandry, 6) Rural development and agro-economy, and 7) Forestry and agroforestry.

We wish to express our heartfelt appreciation to all authors, reviewers, and colleagues who assisted in preparing this Book of Proceedings. Our special thanks go to co-organizers, partners, and sponsors for their unwavering support and collaboration.

We hope this multidisciplinary and international collection of research findings serves as a valuable resource for all stakeholders and encourages continuous dialogue and exchange to facilitate the transition towards sustainable, resilient, and inclusive agri-food systems.

East Sarajevo, 1 November 2025

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CONTENT

PLANT PRODUCTION	27
SEED GERMINATION OF LENTIL GENOTYPES UNDER SALINITY STRESS AND NANO-SILICON APPLICATION Naser SABAGHNIA, Mohsen JANMOHAMMADI, Fariborz SHEKARI.....	28
USING GPS AND GIS IN PRECISION AGRICULTURE OPTIMIZATION IN A HUNGAIAN FARM Ahmed EL SHAL , Péter RICZU, János TAMÁS	31
ANALYSYS AND REVIEW OF RESPONSES AGRICULTURAL PLANTS TO HUMIC SUBSTANCES Mirjana JOVOVIĆ, Zoranka MALEŠEVIĆ, Aleksandra GOVEDARICA – LUČIĆ.....	37
RESISTANCE OF TOMATO GENOTYPES TO LATE BLIGHT (<i>Phytophthora infestans</i>) UNDER CONDITIONS OF NATURAL INFECTION Milomirka MADIĆ, Nenad PAVLOVIĆ, Milan ŠEVIĆ, Vladeta STEVOVIĆ, Dalibor TOMIĆ, Branka GOVEDARICA, Dragan ĐUROVIĆ	46
ADAPTABILITY AND STABILITY OF PROMOSING BREAD WHEAT LINES USING GGE BILOT ANALYSIS Damla BALABAN GÖÇMEN, Oğuz BİLGİN, Alpay BALKAN, İsmet BAŞER.....	52
RELATIONSHIPS BETWEEN YIELD AND YIELD TRAITS IN WHEAT UNDER DIFFERENT DROUGHT APPLICATIONS İsmet BAŞER, Alpay BALKAN, Oğuz BİLGİN, Damla BALABAN GÖÇMEN, Kamil ÖZCAN.....	60
THE INFLUENCE OF SOIL TYPE ON THE QUALITY TRAITS OF POTATO Tanja JAKIŠIĆ, Milan JUGOVIĆ, Branka GOVEDARICA, Igor ĐURĐIĆ, Nevena RISTIČEVIĆ, Selena KOVAČEVIĆ	66
COMPARATIVE ANALYSIS OF ESSENTIAL OIL OF <i>HELICHRYSUM ITALICUM</i> L. FROM PLANTATION AND RECLAIMED SOILS Zoranka MALEŠEVIĆ, Jelena LAZAREVIĆ, Mirjana JOVOVIĆ, Selena KOVAČEVIĆ, Ivana BOŠKOVIĆ	72
THE EFFECT OF ZEOLITE TYPE AND DOSAGE ON PEA SEED GERMINATION AND EARLY GROWTH TRAITS Nevena RISTIČEVIĆ, Branka GOVEDARICA, Igor ĐURĐIĆ, Vesna MILIĆ, Tanja JAKIŠIĆ, Selena KOVAČEVIĆ, Aleksandar GAVRILOVIĆ	78
NDVI-BASED ASSESSMENT OF PHYSIOLOGICAL STATUS IN PROKUPAC VINEYARDS UNDER DIFFERENT CROP PROTECTION STRATEGIES Marija GAVRILOVIĆ, Vedran TOMIĆ, Biljana VELJKOVIĆ, Danijela ŽIVOJINOVIĆ, Anđelija OBRADOVIĆ	84
EFFECTS OF ABIOTIC STRESS CONDITIONS ON GENE EXPRESSION IN <i>SOLANACEAE</i> SPECIES Akife DALDA-SEKERCI, Hande Seda ÖZDAL	92

RESPONSE OF WINTER WHEAT TO REDUCED TILLAGE AND FERTILIZATION

Željko DOLIJANOVIĆ, Dušan KOVAČEVIĆ, Milena SIMIĆ, Snežana OLJAČA, Zoran JOVOVIĆ, Milena BILJIĆ 101

ANALYSIS OF THE FERTILITY POTENTIAL OF RED WINE VARIETIES GROWN IN THE TREBINJE AREA (BOSNIA AND HERZEGOVINA)

Tijana BANJANIN, Milica GLIŠIĆ, Kristina MILIŠIĆ, Zorica RANKOVIĆ VASIĆ 108

RESEARCH OF AGRICULTURE LAND FOR IRON (Fe) CONTENT IN THE AREA OF THE CITY OF SOMBOR IN SERBIA

Vladimir SABADOŠ, Danijela ŽUNIĆ 115

IN VITRO PROPAGATION OF EUROPEAN VARIETIES OF ARONIA MELANOCARPA (MICHX.) ELLIOTT 'NERO' AND 'ALEXANDRINA'

Ioana-Cătălina NICOLAE, Tatiana CALALB, Nina CHIORCHINĂ, Maria TABĂRA, Natalia ONICA, Iulia BOZBEI 122

BOTANICAL COMPOSITION OF PERMANENT GRASSLAND AND FORAGE QUALITY IN THE MUNICIPALITY OF LUČANI IN REPUBLIC OF SERBIA

Vladimir ZORNIĆ, Nedeljko RACIĆ, Đorđe LAZAREVIĆ, Zoran LUGIĆ, Dalibor TOMIĆ, Nenad PAVLOVIĆ, Mirjana PETROVIĆ..... 129

EFFECT OF NITROGEN FERTILIZERS WITH UREASE INHIBITORS ON THE QUALITY CHARACTERISTICS OF WINTER CEREALS

Dimitrios BARTZIALIS, Stefania PASCHALI-PAPANASTASIOU, Dimitrios-Marios LEKKAS, Ippolitos GINTSIODIS, Kyriakos D. GIANNOULIS, Nikolaos G. DANALATOS 135

EFFECT OF BENZYLADENINE (BA) ON GROWTH AND FLOWER QUALITY OF PURPLE - PINK PICO (*Chrysanthemum* sp.)

Pham THI PHUONG THAO, Le THANH TOAN, Le THI HOANG YEN, Le THI MONG CAM 141

INFLUENCE OF INTERCROPPING MAIZE WITH CLIMBING BEAN ON FORAGE YIELD AND QUALITY

Darko UHER, Dubravko MACESIĆ, Goran KIŠ, Dario JAREŠ, Ivan HORVATIĆ.... 148

CLASSIFICATION OF COMBINED STRESSES IN AUBERGINE (*SOLANUM MELONGENA* L.) USING MACHINE LEARNING AND HYPERSPECTRAL IMAGING

Maria BEMPI, Aris KYPARISSIS 154

USE OF META-TOPOLIN AS AN ALTERNATIVE CYTOKININ FOR *IN VITRO* MULTIPLICATION OF *ACTINIDIA KOLOMIKTA*

Ioana-Cătălina NICOLAE, Maria TABĂRA, Melania GHEREG, Natalia ONICA, Oana VENAT, Liliana BĂDULESCU, Nina CHIORCHINĂ..... 161

THE INFLUENCE OF DIFFERENT METHODS OF CALCIUM FERTILIZATION IN THE SOIL ON THE YIELD AND THE BLOSSOM-END ROT (BER) IN PEPPER FRUIT

Aleksandra GOVEDARICA-LUČIĆ, Mirjana JOVOVIĆ, Alma MEMIĆ, Dragica GAGOVIĆ 167

SELECTED BREEDING LINES OF SUNFLOWER SEEDS IN REDUCING DROUGHT STRESS ON MORPHOLOGICAL CHARACTERISTICS DURING THE GERMINATION PHASE

Tanja MIJATOVIĆ, Branka GOVEDARICA, Igor ĐURĐIĆ, Nevena RISTIČEVIĆ, Vesna MILIĆ 172

ORCHIDACEAE IN THE FLORA OF THE TREBEVIĆ NATURE PARK (BOSNIA AND HERZEGOVINA)

Natasa MARIC, Sladjana PETRONIC 180

CONSERVATION STATUS OF THE MACROPHYTES OF THE TIŠINA PROTECTED HABITAT (BOSNIA AND HERZEGOVINA)

Natasa MARIC, Sladjana PETRONIC, Zoran MATIC..... 187

THE EFFECTS OF FERTILIZATION METHODS ON THE MECHANICAL COMPOSITION OF GRAPES OF THE VINE VARIETY VRANAC

Nedim MARIĆ, Semira SEFO 193

ASSESSMENT OF DROUGHT IMPACT ON TRITICALE (X TRITICOSECALE WITTMAK) YIELD ACROSS VARIOUS ENVIRONMENTS

Zakaria AL AJLOUNI..... 199

BIOSTIMULANTS EFFECT ON LAVENDER (*LAVANDULA ANGUSTIFOLIA*) CULTIVATION IN THE SECOND GROWING YEAR

Maria DALAKOURA, Kyriakos D. GIANNOULIS, Dimitrios BARTZIALIS, Ippolitos GINTSIODIS, Nikolaos G. DANALATOS 204

EFFECT ON THE YIELD OF THREE VARIETIES OF CHAMOMILE (*MATRICARIA CHAMOMILLA* L.) USING DIFFERENT BIOSTIMULANTS

Anastasia-Charikleia KYRIAZAKI, Kyriakos D. GIANNOULIS, Dimitrios BARTZIALIS, Ippolitos GINTSIODIS, Nikolaos G. DANALATOS..... 210

PROPAGATION OF *CORNUS ALBA* 'SIBIRICA' BY SOFTWOOD HEEL CUTTINGS

Marija MARKOVIĆ, Mihailo GRBIĆ, Dragana SKOČAJIĆ, Danijela ĐUNISIJEVIĆ-BOJOVIĆ, Marijana MILUTINOVIĆ 216

MULTIVARIATE ANALYSIS OF BREAD WHEAT ROOT AND SHOOT TRAITS AT THE SEEDLING STAGE AND AT THE BOOTING STAGE FOR DROUGHT-TOLERANCE

Milica BLAŽIĆ, Gordana BRANKOVIĆ, Dejan DODIG, Vesna KANDIĆ, Tomislav ŽIVANOVIĆ 220

COMPUTATIONAL INTELLIGENCE FOR INVESTIGATION ON GENETIC DIVERSITY AMONG GENOTYPES OF SAFFLOWER FOR YIELD PERFORMANCE

Naser SABAGHNIA, Fariborz SHEKARI, Mohsen JANMOHAMMADI..... 228

RESPONSE OF DRAGONHEAD TO SOWING DENSITY REGARDING ESSENTIAL OIL YIELD AND SOME BIOCHEMICAL TRAITS

Naser SABAGHNIA, Mohsen JANMOHAMMADI, Fariborz SHEKARI..... 233

FUNGAL COMMUNITY ASSOCIATED WITH SWEET POTATO ROOTS DURING STORAGE	
Beatrice Michaela IACOMI, Elena DOBRIN, Lenuța CHIRA, Adrian CHIRA, Elena Maria DRAGHICI	237
THE EFFECT OF ABIOTIC STRESS ON THE FLOWERING AND PRODUCTIVITY OF ZUCCHINI	
Zdenka GIREK, Suzana PAVLOVIĆ, Milan UGRINOVIĆ, Jelena DAMNJANOVIĆ, Dejan CVIKIĆ, Nenad PAVLOVIĆ	243
VARIATIONS OF MAIZE YIELD IN LONG-TERM CROP ROTATION	
Milena SIMIĆ, Miodrag TOLIMIR, Vesna DRAGIČEVIĆ, Željko DOLIJANOVIĆ, Natalija PAVLOVIĆ, Milan BRANKOV	249
EFFECTS OF THE DIFFERENT TERM GRAPE THINNING ON THE YIELD AND GRAPE QUALITY OF CABERNET SAUVIGNON CV. GRAPES	
Milica GLIŠIĆ, Aleksandra MARKOVIĆ, Danijela ŽIVOJINOVIĆ, Andreja PREKOVIĆ, Zoran PRŽIĆ, Saša MATIJAŠEVIĆ	255
PHYSICAL AND CHEMICAL CHARACTERIZATION OF PLUM CULTIVARS (<i>PRUNUS DOMESTICA</i> L.)	
Mirjana RADOVIC, Mihajlo LIZDEK, Mirko KULINA, Slavisa MILOVANOVIC, Dejan ZEJAK	261
QUALITY PROPERTIES OF WHEAT BREAD	
Desimir KNEŽEVIĆ, Vesna DJUROVIĆ, Mirela MATKOVIĆ STOJŠIN, Dragan GRČAK, Milosav GRČAK, Dušan UROŠEVIĆ, Sarina REZAEI SHOJAEI, Simin HAGH-NAZARI	270
VARIABILITY OF MASS OF SPIKE AMONG WHEAT VARIETIES	
Dušan UROŠEVIĆ, Desimir KNEŽEVIĆ, Mirela MATKOVIĆ STOJŠIN, Artiona LAZE, Gordana BRANKOVIĆ, Jelena STOJILJKOVIĆ, Veselinka ZEČEVIĆ	277
PHENOTYPIC VARIABILITY AND SIMILARITY OF NUMBER OF SPIKELETS IN PRIMARY SPIKE IN WHEAT VARIETIES (<i>Triticum aestivum</i> L.)	
Dušan UROŠEVIĆ, Desimir KNEŽEVIĆ, Mirela MATKOVIĆ STOJŠIN, Jelica ŽIVIĆ, Danica MIĆANOVIĆ, Adriana RADOSAVAC, Vesna KANDIĆ	285
EFFECT OF OAT INTERCROPPING ON <i>ERYSIPHE PISI</i> DISEASE INDEX IN WINTER PEA	
Milosav GRČAK, Dragan GRČAK, Desimir KNEŽEVIĆ, Radivoje JEVTIĆ, Vesna ŽUPANSKI, Branka ORBOVIĆ, Vera RAJIČIĆ	293
DETERMINATION OF YIELD AND YIELD COMPONENTS OF SOME SALSOLA AND SUAEDA SPECIES ACCORDING TO PHENOLOGICAL PERIODS	
Bilal KESKİN, Süleyman TEMEL, Ali İhsan ATALAY, Faruk TOHUMCU, Seda AKBAY TOHUMCU	301
MECHANICALLY-AIDED HARVESTING OF TABLE GRAPES WITH AN ELECTRICALLY PROPELLED PROTOTYPE	
Roberto TOMASONE, Mauro PAGANO, Carla CEDROLA	308
PLANT PROTECTION AND FOOD SAFETY	314

STUDY OF THE INFLUENCE OF STORAGE PERIOD ON THE ACCUMULATION OF HYDROXYMETHYLFURFURAL IN CANNED PRODUCTS BASED ON CARROT

Zinaida YEGOROVA, Anastasia NAVROTSKAYA, Angelina BUTKO, Tatiana SHACHEK 315

THE HARMFULNESS OF LEAFMINER *NAPOMYZA GYMNOSTOMA* Loew (Diptera, Agromyzidae) IN BIJELJINA AREA (BOSNIA AND HERZEGOVINA)

Dejana STANIĆ, Jovana OBRADOVIĆ 324

INFLUENCE OF GROWING LOCATION ON BIOACTIVE COMPOUNDS AND ANTIOXIDATIVE ACTIVITY OF 'CLERY' STRAWBERRY FRUITS IN HERZEGOVINA

Maja KAZAZIC, Emina MEHIC, Amna OMANOVIC 331

ASSESSMENT OF NATURAL RADIOACTIVITY LEVELS IN AGRICULTURAL SOIL AND TRANSFER IN RICE IN THE KOCHANI REGION, NORTH MACEDONIA

Aleksandra ANGELESKA, Radmila CRCEVA NIKOLOVSKA, Elizabeta DIMITRIESKA STOJKOVIKJ, Ljupco ANGELOVSKI, Igor ESMEROV, Risto UZUNOV 337

ASSESSMENT OF RADIOACTIVITY AND RADIOLOGICAL HAZARD FROM NATURAL RADIONUCLIDES CONTAINED IN RICE FROM NORTH MACEDONIA

Aleksandra ANGELESKA, Radmila CRCEVA NIKOLOVSKA, Elizabeta DIMITRIESKA STOJKOVIKJ, Igor ESMEROV, Stefan JOVANOVIĆ, Ljupco ANGELOVSKI, Risto UZUNOV 344

SCIENTIFIC AND REGULATORY PERSPECTIVES ON IRRADIATED FOOD: DETECTION STANDARDS AND SAFETY EVALUATION

Ljupco ANGELOVSKI, Elizabeta DIMITRIESKA STOJKOVIKJ, Radmila CRCEVA NIKOLOVSKA, Igor ESMEROV, Risto UZUNOV, Sandra MOJSOVA, Aleksandra ANGELESKA 351

THE ROLE OF RURAL TOURISM IN ADVANCING SUSTAINABLE DEVELOPMENT IN NORTH MACEDONIA

Ljupco ANGELOVSKI, Aleksandra ANGELESKA, Radmila CRCEVA NIKOLOVSKA, Snezana DIMITROVSKA, Sandra MOJSOVA, Igor ESMEROV, Elizabeta DIMITRIESKA STOJKOVIKJ 359

LIST OF SOME INVASIVE INSECTS ESTABLISHED IN NORTH MACEDONIA

Stanislava LAZAREVSKA, Sterja NACHESKI, Miroljub GOLUBOVSKI, Blagoj SURBEVSKI 368

***MORINGA OLEIFERA* OVERDOSE: ALLELOPATHIC EFFECTS OF HIGH-CONCENTRATION EXTRACT ON BAMBARA GROUNDNUT**

Abdel Kader NAINO JIKA 374

VIALE BIOTECHNOLOGICAL WAYS FOR LEGUMICULTURE: INTEGRATION OF COMPOST AND BIOACTIVE SYSTEMS BASED ON BYOPOLIMERS

Valentina-Elena GORGAN, Petronela NECHITA, Gabriela Elena BAHIRIM 380

BEE DIVERSITY IN SEMI-NATURAL HABITATS IN AGRICULTURAL LANDSCAPES IN VOJVODINA PROVINCE, SERBIA	
Ivana KAVGIĆ, Zlata MARKOV RISTIĆ, Sonja MUDRI-STOJNIC	386
EXPLORING THE POTENTIAL OF AUTOCHTHONOUS PROBIOTIC STARTER CULTURES STRAINS IN FRESH CHEESE PRODUCTION	
Dušan BASTA, Ksenija ČOBANOVIĆ, Nataša GOLIĆ, Katarina VELJOVIĆ, Nikola POPOVIĆ, Snežana GLAMOČIĆ	392
THE INFLUENCE OF SUBSTRATE ACIDITY ON PRODUCTION OF MUSHROOM <i>LENTINULA EDODES</i> (BERK.) PEGLER	
Miroslava MARKOVIĆ, Renata GAGIĆ-SERDAR, Goran ČEŠLJAR	398
EDIBLE MUSHROOMS AS NEW FOOD AND NEW ADDITIVES	
Višnja SIKIMIĆ, Slavica ČABRILO, Nada JELIĆ	404
EXTRACTION METHODS USED IN OBTAINING PHYTOMELATONIN-RICH EXTRACTS FROM CITRUS SPECIES	
Özgül GERÇEKER, Sevcan ÜNLÜTÜRK, Tolga AKCAN, Şelale Öncü GALUE	413
USE OF HALOCHROMIC SYSTEMS IN INTELLIGENT FOOD PACKAGING	
Ozlem Kizilirmak ESMER, Sevgi CAY	422
EFFECT OF RHIZOSPHERIC BACTERIA IN CONTROLLING <i>FUSARIUM OXYSPORUM</i>	
Redouan QESSAOUI, Safouane BENJAAA, Salahddine CHAFIKI, Abdelmalk MAHROUG, Soumaya EL ASSRI, Abdelhadi AJERRAR, Hasna ELHJOUJI, Mohamed ALOUANI, Rachid BOUHARROUD	427
ORGANIC AGRICULTURE AND AGROECOLOGY	435
CHEMICAL COMPOSITION OF LEAVES FROM FIVE <i>Vitis vinifera</i> L. CULTIVARS	
Ladislav VASILIŠIN, Goran VUČIĆ, Srđan LJUBOJEVIĆ, Nataša LAKIĆ-KARALIĆ, Staniša LATINOVIĆ	436
INCREASING THE PRODUCTIVITY POTENTIAL OF THE CHERNOZEM IN THE REPUBLIC OF MOLDOVA IN CONDITIONS OF CLIMATE RESILIENCE	
Tatiana DAVID, Leonid POPOV, Valerian CERBARI	444
MULTIVARIATE VISUALIZATION UNLOCKS OPTIMAL SEED PRIMING STRATEGIES FOR SAHELIAN FARMERS: A MORINGA-BAMBARA GROUNDNUT CASE STUDY	
Abdel Kader NAINO JIKA	450
CHALLENGES, CONCEPTS AND INTERNATIONAL VIEWS ON ORGANIC WINE CERTIFICATION AND CONSUMPTION	
Cosmina - Ionela VASILACHE, Adrian Gheorghe ZUGRAVU	456
SUSTAINABLE MANAGEMENT OF THE PROTECTION OF VEGETABLE CROPS IN THE ORGANIC FARMING SYSTEM	
Divna SIMIĆ, Snežana JANKOVIĆ, Željko DOLIJANOVIĆ, Vera POPOVIĆ, Vojin CVIJANOVIĆ, Jelena MARKOVIĆ, Vladan PEŠIĆ	463

CITIZEN SCIENCE INSIGHTS INTO DECOMPOSITION ACROSS FARMS USING TEA BAGS AND COTTON FABRIC

Dušanka VUJANOVIĆ, Andrijana ANDRIĆ, Jelena JOVIĆ, Kristina KALKAN, Nataša LJUBIČIĆ, Ljiljana ŠAŠIĆ ZORIĆ, Aleksandar IVEZIĆ, Tijana BAROŠEVIĆ 469

MORINGA PODS: AN ORGANIC WASTE SOLUTION FOR *TETRANYCHUS URTICAE* CONTROL

Redouan QESSAOUI, Darbali Fatima ZAHRA, Salahddine CHAFIKI, Abdelmalk MAHROUG, Soumaya EL ASSRI, Bahoch SAID, Abdelhadi AJERRAR, Hasna ELHJOUJI, Ait Aabd NAIMA, Tahiri ABDEGHANI, Rachid BOUHARROUD 477

IMPACT OF SUCCESSIONAL AGROFORESTRY SYSTEMS ON SOIL BIOLOGY IN THE MEDITERRANEAN

Pedro R. SOARES, Carla S. S. FERREIRA, Lyudmyla SYMOCHKO, Patrícia SANTOS, Coen RITSEMA, Luuk FLESKENS 484

ENVIRONMENT PROTECTION AND NATURAL RESOURCES

MANAGEMENT 491

VALORIZATION OF ORGANIC WASTE, THE CASE OF DATE STONES, IN WATER TREATMENT

Mimouna YAKOUBI, Nasser BELBOUKHARI, Khaled SEKKOUM 492

IMPERVIOUSNESS DENSITY OF LAND IN BOSNIA AND HERZEGOVINA

Branislav DRAŠKOVIĆ, Ljiljana TANASIĆ, Milan GLIŠIĆ 499

A DAMAGE ASSESSMENT OF THE BEECH-FIR ECOSYSTEM AFTER EXPLOITATION

Fatima MUHAMEDAGIĆ, Zemira DELALIĆ, Nihad GERZIĆ, Merjem HUSKIĆ 505

INVASIVE ALIEN PLANT SPECIES OF THE MUNICIPALITY OF GRUDE (BOSNIA AND HERZEGOVINA)

Mate BOBAN, Helena BREKALO, Safija BOŠKAILO, Toni GALIĆ, Aldin BOŠKAILO, Danijela PETROVIĆ 511

DIVERSITY OF ENDEMIC PLANTS AT SPRING OF BUNICA AND BUNA CHANNELS, BOSNIA AND HERZEGOVINA

Lejla RIĐANOVIĆ, Robert KEPIĆ, Emina ADEMOVIĆ, Sanel RIĐANOVIĆ 518

ETHNOBOTANICAL ANALYSIS OF THE TRADITIONAL USE OF WILD PLANTS AND MUSHROOMS IN THE AREA OF BUSOVAČA (BOSNIA AND HERZEGOVINA)

Iva RELOTA, Sandra MEDIĆ, Antonela MUSA, Safija BOŠKAILO, Aldin BOŠKAILO, Danijela PETROVIĆ 524

GERMPLASM COLLECTIONS OF NEGLECTED AND UNDERUTILIZED SPECIES AS RESEARCH AND CONSERVATION PLATFORMS FOR THEIR VALORIZATION

Zakaria KIEBRE, Mariam KIEBRE, Romaric Kiswendsida NANEMA, Fanta Sheirita Reine TIETIAMBOU, Veli-Matti ROKKA, Hamid EL BILALI, Filippo ACASTO, Jacques NANEMA 531

WATER RETENTION CHARACTERISTICS OF TERRA ROSSA IN RELATION TO HUMUS CONTENT

Aleksandra BENZA, Mirjam NIKOLIĆ, Danijela JUNGIC, Nikolina JURKOVIĆ BALOG..... 539

SPATIAL AND TEMPORAL HISTORICAL LANDSCAPE CHANGE IN A MICRO BIODIVERSITY HOTSPOT OF GREECE

Asimina SKOUTERI, Vassilios P. PAPANASTASIS..... 545

INTEGRATED STATISTICAL APPROACHES TO SUSTAINABLE AQUACULTURE DEVELOPMENT: INSIGHTS FROM THE BALTIC SEA REGION FOR ENVIRONMENT PROTECTION AND NATURAL RESOURCE MANAGEMENT

Inese SKAPSTE..... 551

FLOWERING AND FRUITING BIOLOGY OF *PYRUS ELAEAGNIFOLIA* PALL. IN THE CONDITIONS OF THE REPUBLIC OF MOLDOVA

Irina SFECLĂ, Elena TOFAN-DOROFEEV..... 557

***EPIPACTIS MUELLERI* GODFERY (ORCHIDACEAE) – A NEW SPECIES FOR THE FLORA OF THE REPUBLIC OF MOLDOVA**

Olga IONITA..... 568

NITRATE NITROGEN AND NITRATE REDUCTASE ACTIVITY REGIME IN SOILS OF AGROCENOSSES OF THE DONETSK PEOPLE'S REPUBLIC

Andrey BEREZOVSKIY, Dmitry SYSHCHYKOV, Irina AGUROVA..... 574

ASSESSMENT OF ERODIBILITY INDICES AND THE DEGREE OF SOIL AGGREGATION DEPENDING ON THE TYPE OF LAND USE (EASTERN SERBIA)

Boško GAJIĆ, Milan ĐORĐEVIĆ, Miloš MANIĆ, Mrđan ĐOKIĆ, Ranko DRAGOVIĆ, Aleksandar ČUPIĆ, Mihajlo JOVIĆ, Ivana SMIČIKLAS, Snežana DRAGOVIĆ..... 579

LIGNOCELLULOSIC ARCHITECTURE AND BIOCONVERSION POTENTIAL OF *ARUNDO DONAX* AND *ZEA MAYS*: A FLUORESCENCE APPROACH

Daniela ĐIKANOVIĆ, Dragana BARTOLIĆ, Mira STANKOVIĆ, Gabor STENBACH, Miloš PROKOPIJEVIĆ, Aleksandar KALAUZI, Ksenija RADOTIĆ..... 585

INFLUENCE OF DRYING TREATMENT ON ANTIOXIDANT ACTIVITY IN FOUR DIFFERENTLY PIGMENTED MAIZE (*ZEA MAYS* L.) SEED CULTIVARS

Daniela ĐIKANOVIĆ, Miloš PROKOPIJEVIĆ, Mira STANKOVIĆ, Olivera PRODANOVIĆ, Branka ŽIVANOVIĆ, Ksenija RADOTIĆ, Dragana BARTOLIĆ.... 591

THE IMPACT OF HARVEST TIME ON THE CONTENT OF POLYPHENOLIC COMPOUNDS AND ANTIOXIDANT CAPACITY OF FRUITS OF *Chaenomeles japonica* (Thunb.) Lindl. ex Spach

Mirjana OCOKOLJIĆ, Jelena ČUKANOVIĆ, Radenka KOLAROV, Djurdja PETROV, Nevenka GALEČIĆ, Dejan SKOČAJIĆ, Isidora SIMOVIĆ..... 595

THE IMPACT OF LOCAL ADAPTATION ON THE PHENOLOGICAL PATTERNS OF FLOWERING IN *Buddleja davidii* 'PINK DELIGHT' IN KARADORDEV PARK, BELGRADE (SERBIA)

Mirjana OCOKOLJIĆ, Nevenka GALEČIĆ, Dejan SKOČAJIĆ, Jelena ČUKANOVIĆ, Radenka KOLAROV, Dragan VUJIČIĆ, Djurdja PETROV	602
A STUDY ON THE FLOWERING CHARACTERISTICS OF CHAENOMELES × SUPERBA 'PINK LADY'	
Mirjana OCOKOLJIĆ, Djurdja PETROV, Nevenka GALEČIĆ, Dejan SKOČAJIĆ, Sara ĐORĐEVIĆ, Radenka KOLAROV, Jelena ČUKANOVIĆ	609
SPATIAL USE AND THE NEEDS OF VISITORS OF THE BOJČIN FOREST NATURE MONUMENT (BELGRADE, SERBIA)	
Jovana PETROVIĆ, Nenad STAVRETOVIĆ, Dušan JOKANOVIĆ, Vesna NIKOLIĆ JOKANOVIĆ	615
INVASIVE AND ALLERGENIC PLANT SPECIES ON RUNNING TRAILS OF ADA CIGANLIJA (BELGRADE, SERBIA)	
Jovana PETROVIĆ, Nenad STAVRETOVIĆ, Dušan JOKANOVIĆ, Vesna NIKOLIĆ JOKANOVIĆ	621
STRENGTHENING ORGANIZATIONAL QUALITY THROUGH ISO 9001 AND ISO 10005 INTEGRATION	
Marija PEROVIĆ, Marija TODORVIĆ, Tatjana MITROVIĆ	628
ENVIRONMENTAL BEHAVIOR AND TRACER POTENTIAL OF FLUORIDE IN GROUNDWATER	
Marija PEROVIĆ, Tatjana MITROVIĆ	634
BEE-ING IN THE NEWS: ANALYZING SERBIAN NEWSPAPER COVERAGE OF BEES	
Snežana POPOV, Zlata MARKOV RISTIĆ, Dušanka VUJANOVIĆ	639
TOXICOLOGICAL RISKS PEDICTION OF THE METOLACHLOR HERBICIDE AS ENVIRONMENTAL CONTAMINANT	
Tatjana MITROVIĆ, Darija OBRADOVIĆ, Saša LAZOVIĆ, Marija PEROVIĆ	644
ECOLOGICAL STATUS EVALUATION OF SERBIAN SURFACE WATERS BASED ON PHOSPHORUS CONCENTRATIONS	
Tatjana MITROVIĆ, Marija PEROVIĆ, Tijana MILICEVIĆ	649
APPLYING SWOT ANALYSIS TO THE VALUATION OF POLLINATION ECOSYSTEM SERVICES	
Zlata MARKOV RISTIĆ, Sonja MUDRI-STOJNIĆ	655
CULTIVATION OF HOVERFLIES ON FARMS: BIOLOGICAL, PRACTICAL AND ECONOMIC PERSPECTIVES	
Zlata MARKOV RISTIĆ, Snežana POPOV	661
IMPACTS OF AGRICULTURAL WATER USE AND SEASONAL DROUGHT ON WATER RESOURCES: A CASE STUDY OF KESKIN DAM, TURKIYE	
Eray HARMAN	667
HISTORICAL SHARK EXPLOITATION AND CONTEMPORARY CONSERVATION EFFORTS IN THE TURKISH SEAS	
Ertan TASKAVAK, Halit FILIZ	674

GEOGRAPHICALLY WEIGHTED REGRESSION BASED APPROACHES FOR ENHANCING PRECIPITATION ESTIMATION IN AGROECOSYSTEMS	
Filiz DADASER-CELİK, Mete CELİK, Ali Ümran KÖMÜŞCÜ.....	680
MODELLING HYDROLOGICAL PROCESSES AT BURDUR LAKE BASIN (TURKEY) WITH SWAT	
Mehmet SOYLU, Meltem KACIKOC, Filiz DADASER-CELİK.....	685
PRELIMINARY ASSESSMENT OF WATER QUALITY IN EĞİRDİR LAKE BASED ON FIELD MONITORING	
Meltem KACIKOC, Eda BOYACIOGLU, Filiz DADASER-CELİK.....	691
A SOLUTION TO CLIMATE CHANGE AND WATER SCARCITY: STUDIES ON RAINWATER HARVESTING IN TURKEY	
Yoldaş EKTİREN.....	700
IMPROVING WATER EFFICIENCY IN AGRICULTURE: A DEFICIT IRRIGATION APPROACH FOR TURKEY	
Yoldaş EKTİREN.....	705
CULTURAL LANDSCAPES OF THE BIOSPHERE RESERVE “OS ANCARES LUCENSES E MONTES DE CERVANTES, NAVIA E BECERREÁ”	
Ignacio J. DIAZ-MAROTO.....	710
HOW DO CULTURAL ECOSYSTEM SERVICES IN MOUNTAIN AREAS CONTRIBUTE TO THE WELL-BEING OF LOCAL COMMUNITIES?	
Ignacio J. DIAZ-MAROTO.....	717
THE ROLE OF SUSTAINABLE FOREST RESOURCE MANAGEMENT IN THE SOCIOECONOMIC GROWTH OF THE EASTERN MOUNTAINS OF GALICIA IN SPAIN	
Ignacio J. DIAZ-MAROTO.....	723
POTENTIAL ROLES OF MELATONIN AND ITS METABOLITES IN REDUCING HEAVY METAL TOXICITY IN VEGETABLES	
Aygül KARACA	729
AN ANALYSIS OF THE SOCIO-ECONOMIC CHARACTERISTICS OF PADDY FARMS IN TURKEY	
Sema Ezgi YÜCEER, Sibel TAN.....	736
THE USE OF SEAWEED EXTRACTS TO MITIGATE ABIOTIC STRESSES IN VEGETABLES	
Aygül KARACA, Nusret ÖZBAY	743
ANIMAL HUSBANDRY	749
RAW MILK QUALITY AS A BASIS FOR CHEESE PRODUCTION	
Drazenko BUDIMIR, Milijana ŠKRBIĆ	750
BACTERIA AND LOWER RESPIRATORY TRACT DISEASES IN HORSES	
Mariyana NIKOLOVA, Sasho SABEV	755

CLINICAL STUDIES OVER EQUINE GASTROULCERATIVE SYNDROME IN HORSES (EGUS)

Sasho SABEV, Mariyana NIKOLOVA 763

PRODUCTIVITY AND EGG QUALITY OF LAYING HENS FED WITH BLACK SOLDIER FLY (*HERMETIA ILLUCENS*) LARVAE MEAL

Aiga NOLBERGA-TRŪPA, Niklāvs KLEINS, Kārlis SAMS 770

THE INFLUENCE OF THE LEPTIN GENE ON MILK PRODUCTION IN THREE CONSECUTIVE LACTATIONS IN HOLSTEIN FRIESIAN CATTLE

Igor ESMEROV, Radmila CRCEVA NIKOLOVSKA, Nikolay MARKOV, Risto UZUNOV, Ljupco ANGELOVSKI, Aleksandra ANGELESKA, Ljupco MICKOV ... 778

PORTUGUESE CONSUMERS' PREFERENCE REGARDING THE PRESENTATION OF PROTECTED DESIGNATION OF ORIGIN TRANSMONTANO GOAT CHEESE

António José FERNANDES, Fernando SOUSA, Dina AVEIRO, Maria Isabel RIBEIRO 784

PORK MEAT CONSUMPTION: A COMPARATIVE ANALYSIS BETWEEN BRAZILIAN AND PORTUGUESE CONSUMERS

António José FERNANDES, Juan de Oliveira MORAIS, Maria Isabel RIBEIRO 791

PORTUGUESE CONSUMERS' PREFERENCE REGARDING THREE PROTECTED DESIGNATION OF ORIGIN TRANSMONTANO GOATLING BUTCHER PIECES

António José FERNANDES, Fernando SOUSA, Dina AVEIRO, Maria Isabel RIBEIRO 798

PHARMACEUTICAL CONTAMINANTS IN AQUATIC ENVIRONMENTS: IMPACT ON EDIBLE FISH AND SUSTAINABLE MANAGEMENT PERSPECTIVES

Daniela-Nicoleta ROPOTAN, Lorena DEDIU 804

EFFECT OF GLYCEROL SUPPLEMENTATION ON BLOOD CONCENTRATIONS OF INSULIN AND BIOCHEMICAL PARAMETERS IN PERIPARTUM DAIRY COWS

Julijana TRIFKOVIĆ, Dušan BOŠNJAKOVIĆ, Slavica DRAŽIĆ, Ljubomir JOVANOVIĆ, Milica STOJKOVIĆ, Danijela KIROVSKI, Željko SLADOJEVIĆ 810

THE POSSIBILITY OF USING ESSENTIAL OILS OF *ORIGANUM VULGARE* L., *MENTHA X PIPERITA* L. AND *SATUREJA MONTANA* L. AGAINST GASTROINTESTINAL NEMATODES IN SHEEP

Filip ŠTRBAC, Radomir RATAJAC, Nataša TOLIMIR, Divna SIMIĆ, Slađan STANKOVIĆ, Antonio BOSCO, Laura RINALDI, Nataša SIMIN, Dejan ORČIĆ, Slobodan KRNJAJIĆ, Dragica STOJANOVIĆ 817

THE INFLUENCE OF WEATHER ON THE QUALITY OF HONEY IN RASINA REGION FOR THE PERIOD OF 2019-2024

Goran JEVIĆ, Snežana BABIĆ, Snežana ANDELKOVIĆ, Đorđe LAZAREVIĆ, Mirjana PETROVIĆ, Vladimir ZORNIĆ, Kazimir MATOVIĆ 826

PORCINE REPRODUCTIVE RESPIRATORY SYNDROME AS A HEALTH PROBLEM IN SWINE PRODUCTION

Jovan BOJKOVSKI, Sreten NEDIĆ, Sveta ARSIĆ, Radiša PRODANOVIĆ, Aleksandra MITROVIĆ, Branko ANGELOVSKI, Milan NINKOVIĆ 832

CONSTRUCTIVE ALIGNMENT OF LEARNING OUTCOMES, TEACHING METHODS AND ASSESSMENT STRATEGIES IN THE FARM ANIMAL BIOSECURITY COURSE

Slavca HRISTOV, Branislav STANKOVIC, Dimitar NAKOV, Milica RADJENOVIC 837

CHARACTERISTICS OF KAJMAK PRODUCED IN THE VALJEVO AREA IN SERBIA

Tanja VUČIĆ, Snežana JOVANOVIĆ, Kristina SOFRONIĆ 845

EFFECT OF PROTEASE AND SEX ON CARCASS QUALITY AND ABDOMINAL FAT OF SLOW-GROWING HYBRID OF CHICKEN

Vladimir DOSKOVIĆ, Snežana BOGOSAVLJEVIĆ-BOŠKOVIĆ, Zdenka ŠKRBIĆ, Miloš LUKIĆ, Bojan STOJANOVIĆ, Simeon RAKONJAC, Veselin PETRIČEVIĆ.. 851

RISK ASSESSMENT OF ANIMAL WASTE FOR OCCUPATIONAL HEALTH AND SAFETY IN LIVESTOCK SECTOR

Turgut AYGÜN 857

SOME ENVIRONMENTAL EFFECTS ON BODY WEIGHT AT WEANING AND SHEARING AND GREASY WOOL YIELD IN MORKARAMAN EWES

Turgut AYGÜN 863

RAISING SYSTEMS IN SMALL RUMINANT HUSBANDRY IN EASTERN ANATOLIA OF TÜRKİYE

Turgut AYGÜN 869

SUPPLEMENTATION WITH GARLIC POLYSULFIDES EFFECTIVELY REDUCES ENTERIC METHANE EMISSIONS IN DAIRY COWS

Julijana TRIFKOVIĆ, Dušan BOŠNJAKOVIĆ, Sreten NEDIĆ, Ljubomir JOVANOVIĆ, Ivan VUJANAC, Željko SLADOJEVIĆ, Danijela KIROVSKI 875

FISH FEED: AN ANALYSIS OF OLD AND NEW TECHNOLOGIES

Albana UKA 883

DEVELOPMENT OF COMPETENCES OF VETERINARIANS AND ANIMAL HUSBANDRY ENGINEERS FOR BIOSECURITY MEASURES IMPLEMENTATION ON ANIMAL FARMS

Branislav STANKOVIC, Slavča HRISTOV, Dimitar NAKOV, Sonja OBRENOVIC, Milica RADJENOVIC, Ivana MILOSEVIC-STANKOVIC 888

EVALUATION OF EGGSHELL HYGIENE AND QUALITY OF TABLE EGGS FOLLOWING SURFACE DISINFECTION WITH LIQUID CHLORINE DIOXIDE

Ajla ALIŠAH, Nedim BEGIĆ, Julijana TRIFKOVIĆ, Miroslav LALOVIĆ, Abdulah GAGIĆ 895

ANALYSIS OF THE USE AND PRESENCE RESIDUES OF ANTIBIOTICS IN TABLE EGGS IN MODERN LAYING HEN FARMS IN THE DAKAR REGION AND SURROUNDING AREA (SENEGAL)	
Khalifa Serigne Babacar SYLLA, Arame THIOUNE, Sadibou BA, Rianatou BADA-ALAMBEDJI.....	900
RURAL DEVELOPMENT AND AGROECONOMY	909
PUBLIC POLICIES, PRIVATE INITIATIVES AND RURAL DEVELOPMENT FOR CLIMATE-RESILIENT AGRICULTURE IN BOSNIA AND HERZEGOVINA	
Branka TOPIĆ-PAVKOVIĆ	910
BUYING BEHAVIOUR IN CONSUMERS OF FRESH VEGETABLES	
Elma SEFO, Zrinka KNEZOVIĆ, Anamarija ŠEVO.....	920
FISH CONSUMPTION PREFERENCES AND CONSUMER CHARACTERISTICS IN HERZEGOVINA-NERETVA CANTON, BOSNIA AND HERZEGOVINA	
Predrag IVANKOVIĆ, Marija LASIĆ, Luka DRAGIĆEVIĆ	927
ANALYSIS OF THE ECONOMIC PROFITABILITY OF DIFFERENT BELL PEPPER PRODUCTION METHODS	
Radomir BODIROGA, Milica STOJANOVIĆ, Uroš GALINAC, Ljubiša ŠEVKUŠIĆ, Koštana VINČIĆ	933
SUPPLY CHAIN FINANCE AS A FUNDING OPPORTUNITY FOR FARMERS	
Zorica GOLIĆ, Saša LALIĆ.....	939
INCLUSIVE GREEN FINANCE: IMPORTANCE FOR STRENGTHENING THE AGRICULTURAL RESILIENCE TO CLIMATE CHANGE	
Zorica GOLIĆ.....	948
AGRICULTURAL BIOGAS PLANTS IN EUROPEAN RURAL DEVELOPMENT AND THE ENERGY TRANSITION	
Krzysztof PILARSKI, Agnieszka A. PILARSKA	957
HEALTH AND SAFETY OF FARMERS IN POLAND	
Władysław MIGDAŁ, Joanna MAKULSKA, Barbara TOMBARKIEWICZ, Michał CUPIAŁ.....	966
DEMOGRAPHIC TRENDS AND THEIR IMPLICATIONS FOR SUSTAINABLE RURAL DEVELOPMENT: A CASE STUDY OF THE BUFTEA AREA, ILFOV COUNTY, ROMANIA	
Andreea Roxana FIRĂȚOIU, Elena SOARE, Aurelia-Ioana CHEREJI, Irina-Adriana CHIURCIU, Liviu MĂRCUȚĂ	973
RURAL LABOR: AN ANALYSIS OF THE PROSPECTS FOR EMPLOYMENT OF YOUTH IN THE AGRICULTURAL SECTOR	
Irina CHEKHOVSKIKH	982
THE ROLE OF KNOWLEDGE TRANSFER TRAININGS IN FIELD CROP AND VEGETABLE PRODUCTION: AN ANALYSIS OF A TEN-YEAR PERIOD	
Divna SIMIĆ, Snežana JANKOVIĆ, Vojin CVIJANOVIĆ, Vedran TOMIĆ, Marijana MASLOVARIĆ, Ivana STANIMIROVIĆ, Nataša TOLMIR	989

SMART AGRICULTURE AND CRYPTOECONOMICS: CHALLENGES AND OPPORTUNITIES FOR THE WESTERN BALKANS	
Vedran TOMIĆ, Robert RADIŠIĆ, Marija GAVRILOVIĆ, Stevan ČANAK, Nikola LJILJANIĆ	998
IMPORTANCE OF THE TEMPERATURE-HUMIDITY INDEX IN ENSURING OPTIMAL SHELTER CONDITIONS FOR ANIMAL PRODUCTION IN TURKEY	
Merve Nur EKTIREN, Yoldaş EKTIREN	1004
ASSESSING GENDER SENSITIVITY OF THE SMALL-SCALE MECHANIZED RAISED BED TECHNOLOGY (MRB) IN EGYPT	
Gehan A.G. ELMENOFI, Aman ELGARHY, Bezaiet DESSALEGN, Biju GEORGE	1009
AGRICULTURAL TRENDS AND CHALLENGES IN SLOVAKIA IN COMPARISON WITH BOSNIA AND HERZEGOVINA	
Branislav DUDIC, Velibor SPALEVIC	1019
EVALUATION OF THE ECONOMIC EFFICIENCY OF FRUIT ORCHARD PRODUCTION WITH RISK CONSIDERATION	
Jozef REPISKÝ, Nándor NAGY	1025
FORECASTING APRICOT PRODUCTION IN TÜRKİYE USING THE ARIMA (BOX-JENKINS) MODEL	
Ashl DALGIC.....	1032
FORESTRY AND AGRO-FORESTRY	1040
ANALYSIS OF CHAINSAW OPERATORS’ EXPERIENCE IN FORESTRY	
Dane MARČETA, Miodrag ŠTRBAC, Vladimir PETKOVIĆ, Danijela PETROVIĆ, Milan SUKUR	1041
BRANDING CHALLENGES AND PERSPECTIVES OF NON-TIMBER FOREST PRODUCTS IN SARAJEVO-ROMANIJA REGION IN BOSNIA AND HERZEGOVINA	
Nedeljka ELEZ	1049
CHEMICAL COMPOSITION OF <i>Morchella costata</i> (Vent.) Pers AND FOUR OTHER EDIBLE MUSHROOMS FROM BOSNIA AND HERZEGOVINA	
Srđan LJUBOJEVIĆ, Ladislav VASILIŠIN, Goran VUČIĆ, Nataša LAKIĆ-KARALIĆ, Staniša LATINOVIĆ	1054
GERMINATION OF <i>Fagus sylvatica</i> L. SEEDS DEPENDING ON X-RAY DOSE	
Dina ELISOVETCAIA, Raisa IVANOVA, Jan BRINDZA	1064
MORPHOLOGICAL DIVERGENCE AMONG SIX SAHELIAN TREE SPECIES: IMPLICATIONS FOR FUNCTIONAL AGROFORESTRY DESIGN	
Abdel Kader NAINO JIKA	1072
RESEARCH ON THE POSSIBILITY OF IMPLEMENTING FOREST CLIMATE PROJECTS IN THE FOREST FUND OF THE RUSSIAN FEDERATION	
Svetlana MORKOVINA, Denis KUZNETSOV, Andrey TOPCHEEV	1078

MONITORING LAND USE CHANGE IN VOJVODINA USING THE COLLECT EARTH TOOL	
Dragan BOROTA, Damjan PANTIĆ, Brano VAMOVIĆ, Aleksandar GOLUBOVIĆ	1085
HYDROLOGICAL REGIME OF HIGROPHILOUS FORESTS ON THE ISLANDS ALONG THE DANUBE RIVER	
Dušan JOKANOVIĆ, Vesna NIKOLIĆ JOKANOVIĆ	1094
MORPHOLOGICAL LEAF TRAITS VARIATION WITHIN AND AMONG FIVE PEDUNCULATE OAK (<i>Quercus robur</i> L.) POPULATIONS IN REPUBLIC OF SRPSKA (BOSNIA AND HERZEGOVINA)	
Milena STANKOVIĆ NEĐIĆ, Srđan STOJNIĆ, Marko GUTALJ, Boban MILETIĆ, Branislav FILIPIĆ, Branislav KOVAČEVIĆ, Lazar KESIĆ, Miloš BAČIĆ Saša ORLOVIĆ.....	1101
REHABILITATION OF DAMAGED FORESTS AS A RESULT OF CLIMATE CHANGE IN THE FUNCTION OF ENVIRONMENTAL PROTECTION	
Zvonimir BAKOVIĆ, Vladimir VASIĆ, Bratislav KISIN	1108
AUTHOR INDEX.....	1117

ENVIRONMENTAL BEHAVIOR AND TRACER POTENTIAL OF FLUORIDE IN GROUNDWATER

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Abstract

Understanding tracer behavior in groundwater is crucial for accurately interpreting flow dynamics, residence times, and hydrogeochemical processes, thereby supporting effective aquifer recharge and potential pollution sources. Fluoride (F⁻) in groundwater is a significant geochemical constituent whose mobility and distribution are governed by a range of hydrogeochemical factors. This paper reviews the behavior of fluoride in groundwater and evaluates its potential as an environmental tracer. Although fluoride in groundwater predominantly occurs because of natural geochemical processes, mainly the dissolution of F-bearing minerals such as fluorite and apatite, it can also originate from anthropogenic sources. These include industrial emissions, phosphate fertilizer application, and mining or processing of phosphate and fluorite ores, particularly in oxic shallow aquifers near contaminated sites. It is generally not redox-sensitive, remaining as fluoride across a range of redox conditions. Key controls on fluoride concentrations include pH, alkalinity, calcium availability, mineralogy, and the presence of competitive anions like bicarbonate and phosphate. Owing to its conservative behavior under many conditions, fluoride has been used as a natural tracer to infer groundwater origin. The conducted literature review concludes that fluoride, though usually considered as a contaminant of health concern, can serve as an informative geochemical tracer in hydrogeology when its controlling factors are known and examined.

Keywords: *fluoride, groundwater.*

Introduction

Fluoride in groundwater represents both a valuable resource and a potential contaminant, depending on its concentration and hydrogeochemical context. As an anion (F⁻), fluoride is primarily introduced into groundwater through the weathering and dissolution of fluorine-bearing minerals, usually fluorite (CaF₂), fluorapatite (Ca₅(PO₄)₃F), and certain silicate minerals such as biotite and hornblende (Nordstrom & Jenne, 1977; Edmunds & Smedley, 2013). The release of fluoride is enhanced by extended water–rock interaction, elevated temperatures, and geochemical conditions that increase mineral solubility. Globally, fluoride concentrations in groundwater typically range from just a few micrograms to several milligrams per liter. In some regions with specific geological settings and climatic conditions, concentrations can exceed 10 mg/L (WHO, 2017). Elevated levels are particularly common in arid and semi-arid regions, where low recharge rates, prolonged groundwater residence time, and evaporative concentration favor fluoride enrichment (WHO, 2006). The global median fluoride concentration in groundwater is about 0.3 mg/L, but roughly 10% of tested sources exceed the World Health Organization (WHO) guideline value of 1.5 mg/L for safe drinking water (WHO, 2017). Chronic exposure to such concentrations has been linked to dental and skeletal fluorosis, making fluoride both a geochemical concern and a public health issue. While the health impacts of fluoride contamination have been widely studied, less attention has been paid to its geochemical behavior as a tracer of groundwater processes. Unlike redox-sensitive elements,

fluoride remains stable across a broad range of conditions, often behaving conservatively in aquifers. Its concentration is influenced by factors such as pH, alkalinity, calcium availability, mineralogy, and the presence of competing anions like bicarbonate and phosphate. Because of these characteristics, fluoride can provide valuable insights into groundwater origin, residence time, and flow dynamics, as well as potential anthropogenic influences from industrial emissions, fertilizer use, or mining activities. Understanding the dual role of fluoride, as both a contaminant of concern and a potential geochemical tracer, offers opportunities to better link hydrogeochemical research with groundwater management. Tracer studies are increasingly used in hydrogeology to improve aquifer characterization, assess recharge processes, and identify pollution pathways. Positioning fluoride within this framework can contribute to a more detailed understanding of groundwater systems, especially in regions where its concentrations are naturally elevated. The objective of this paper is to review the hydrogeochemical behavior of fluoride in groundwater and to evaluate its potential use as an environmental tracer. In doing so, the paper aims to bridge the gap between studies that treat fluoride solely as a contaminant and those that consider its broader geochemical significance for understanding groundwater origin, flow, and contamination pathways.

Materials and Methods

Fluoride's only stable oxidation state in aqueous environments is -1 , and it remains as the fluoride ion (F^-) under both oxic and anoxic conditions (Langmuir, 1997; Edmunds & Smedley, 2013; Smedley & Kinniburgh, 2002). Therefore, fluoride mobility in groundwater is governed by mineral solubility equilibrium and adsorption–desorption processes, rather than redox chemistry. Its behavior is particularly sensitive to pH, calcium concentration, and the presence of competing anions such as bicarbonate and phosphate (Smedley & Kinniburgh, 2002; Edmunds & Smedley, 2013; Kim & Jeong, 2005).

Fluoride solubility is controlled by equilibrium with fluorite (CaF_2), a poorly soluble mineral. In calcium-rich waters with near-neutral to slightly alkaline pH, fluoride concentrations in water may be limited by fluorite precipitation. Conversely, in sodium-bicarbonate type waters, often characterized by low calcium content, high alkalinity, and elevated pH, fluoride tends to accumulate due to reduced precipitation and enhanced desorption from mineral surfaces (Apambire et al., 1997; Edmunds & Smedley, 2013).

In this study, the key geochemical controls on fluoride mobility in groundwater are explored and its use as a tracer of subsurface processes is evaluated. Selected case studies from varied geological settings illustrate the applicability of fluoride as a tool for understanding groundwater flow, origin, and evolution.

Results and Discussion

Fluoride concentrations in groundwater can be in a wide range of variability globally, with values ranging from below 0.5 mg/L in fresh recharge zones to well above 5 mg/L in arid, geothermal, or anthropogenically influenced regions (McMahon et al., 2020; Podgorski & Berg, 2022). These concentrations are governed by a complex interplay of natural geochemical factors and, to a lesser extent, anthropogenic activities.

Under oxic conditions, fluoride occurs primarily as a product of mineral weathering. Geogenic sources include fluorite, fluorapatite, and micas, particularly in igneous and metamorphic rocks (Edmunds & Smedley, 2013; Apambire et al., 1997). In such environments, groundwater with high pH and low Ca^{2+} content, commonly Na– HCO_3 type waters, exhibit enhanced fluoride mobility due to desorption and suppressed fluorite precipitation (Cao et al., 2023). These conditions are typical in arid and semi-arid zones, such as the East African Rift, North China

Plain, and parts of India and Argentina (Rango et al., 2012; Cao et al., 2023; Aullón Alcaine et al., 2020).

Anthropogenic sources also contribute to elevated fluoride in localized areas. Industrial emissions (e.g., aluminum smelting), phosphate rock mining, and the use of phosphate fertilizers can result in fluoride enrichment, particularly in oxic settings (Cronin et al., 2000; Schlesinger et al., 2020). These contributions are typically limited in spatial extent and secondary to geogenic controls. Under anoxic conditions, fluoride remains stable due to its redox-independence, but its concentrations may increase with longer residence times, mineral dissolution, and lack of adsorption capacity. Confined aquifers, particularly those with elevated bicarbonate and depleted calcium, may accumulate fluoride to levels exceeding 1.5 mg/L, as documented in parts of China’s Datong Basin (Edmunds & Smedley, 2013). Fluoride’s co-occurrence with elements such as arsenic, boron, and lithium, especially under alkaline and oxidizing conditions, further supports its use as a geochemical tracer (Aullón Alcaine et al., 2020; McMahon et al., 2020). Because it is unaffected by redox processes, does not biodegrade, and reflects cumulative geochemical interaction, fluoride is effective for tracing groundwater origin, flow paths, and evolution.

The combined evidence indicates that fluoride’s utility as both a contaminant and a tracer depend on understanding the mineralogy, water chemistry, redox status, residence time and recharge of groundwater. Fluoride quantification alongside other geochemical indicators allows identification of different aquifer zones with distinct recharge origin or lithological signatures, especially in complex hydrogeological settings. In arid and semi-arid regions, evaporation further concentrates fluoride, often alongside sodium and chloride (Edmunds & Smedley, 2013). High fluoride levels in these conditions are indicative of both evaporative concentration and geochemical maturity. In oxic aquifers, particularly in shallow and well-recharged settings, fluoride is primarily geogenic. Although fluoride is redox-independent, elevated concentrations are often found under anoxic conditions particularly in deep, stagnant, or confined aquifers with long residence times, due to extended water–rock interaction rather than redox-driven processes (Smedley & Kinniburgh, 2002). Under reducing conditions, fluoride can be released via desorption from iron and manganese oxides or through sustained dissolution of F-bearing minerals, especially when Ca^{2+} is removed through calcite precipitation (Cao et al., 2023; Edmunds & Smedley, 2013). Anthropogenic fluoride in anoxic aquifers is less frequent but can result from industrial leachates (e.g., phosphate effluents, coal ash ponds) that infiltrate into confined zones. These pollution plumes are often limited in extent and are more difficult to remediate due to slow flow and minimal dilution in confined settings. Figure 1 presents fluoride concentrations in groundwater from reviewed representative aquifer types. Volcanic settings (e.g., East African Rift) show the highest levels (around 10 mg/L), followed by sedimentary–evaporative basins (e.g., China, Texas, around 6 mg/L) and crystalline aquifers (e.g., India, Sri Lanka, around 4 mg/L). These variations reflect the influence of geology and water–rock interaction on fluoride concentration and mobilization.

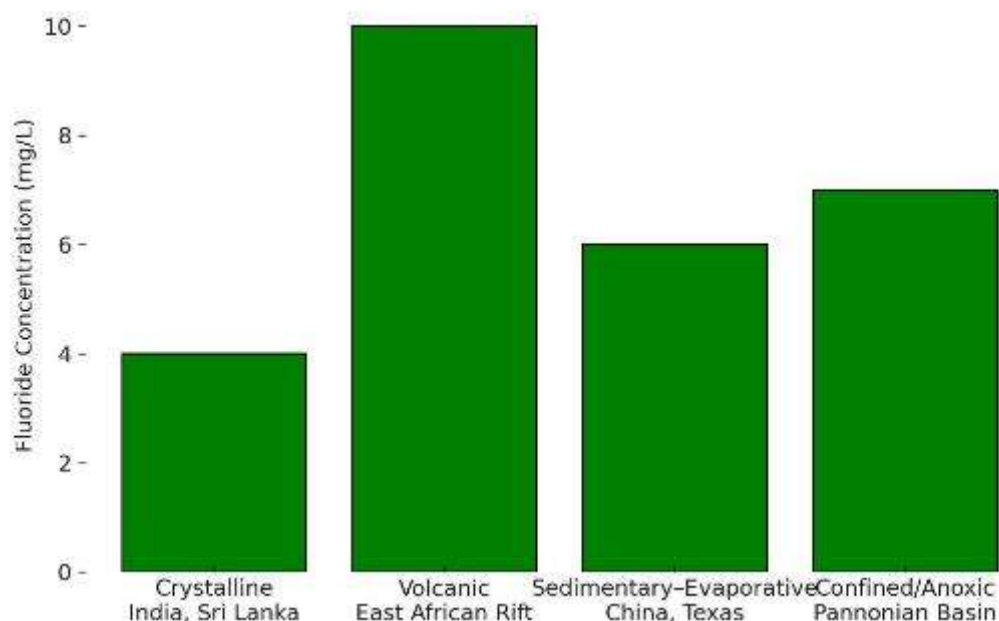


Figure 1. Typical Fluoride Concentrations in Groundwater by Aquifer Type

In the Republic of Serbia, the maximum allowable concentration of fluoride in drinking water is set at 1.2 mg/L, as stipulated in List IIIa of the Rulebook on the Hygienic Safety of Drinking Water (Official Gazette RS, No. 42/98, 44/99, 28/19), while for bottled water, the permitted limit is 1.0 mg/L. According to the Decree on Limit Values of Pollutants in Water, fluoride is also classified as a pollutant in groundwaters, listed under Annex II. Furthermore, the Decree on Emission Limit Values for Pollutants in Wastewater prescribes a maximum discharge concentration of 30 mg/L of total fluoride into surface waters from wastewater treatment processes (Annex 4a.1). In addition, the Rulebook on Permitted Quantities of Hazardous and Harmful Substances in Soil and Irrigation Water (Official Gazette RS, No. 23/94) defines the maximum fluoride content as up to 300 mg/kg in soil and 1.5 mg/L in irrigation water. In the Republic of Serbia, fluoride is not included in the official program for regular monitoring of surface and groundwater quality, although it is classified as a pollutant under national environmental legislation.

Conclusions

Fluoride's occurrence in groundwater is governed by well-defined geochemical processes, particularly its mobilization under alkaline, low-calcium conditions and its conservative behavior in the absence of redox sensitivity (Edmunds & Smedley, 2013; Jayawardana et al., 2010; Smedley & Kinniburgh, 2002). These same properties that make fluoride a contaminant also make it useful as a natural groundwater tracer. Elevated fluoride levels are frequently associated with prolonged water–rock interaction, ion exchange, evaporative concentration, and geothermal influences (Apambire et al., 1997; Podgorski & Berg, 2022). When used in conjunction with other hydrochemical parameters, fluoride can help identify sources of recharge, and reveal subsurface processes such as lithological influence or mixing of geochemically distinct waters (Rao, 1997; McMahan et al., 2020). It is important to emphasize that secondary processes (e.g., calcium influx or pH changes) may alter fluoride concentrations, its widespread measurement and sensitivity to geochemical conditions make it an accessible and powerful tracer (Belitz et al., 2022).

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