UNIVERSITETI I PRISHTINËS "HASAN PRISHTINA"
FAKULTETI I SHKENCAVE MATEMATIKE NATYRORE
Rr. Xhorxh Bush, 10000 Prishtinë, Republika e Kosovës
Tel: +381-38-249-873 • E-mail: fshmn@uni-pr.edu • vvvvvv.uni-pr.edu

KËRKESË

Për: Departamentin e Kimisë
Këshillin e Studimeve të Doktoratës
Këshillin e Fakultetit të Shkencave Matematike Natyrore

Lënda: Formimi i Komisionit për Vlerësimin e Punimit të Doktoratës

Duke u bazuar në Rregulloren: Nr. 937, dt. 26.04.2023 për studimet e doktoratës, kërkoj nga organet e lartcekura të FShMN-së, që të formojnë komisionin për vlerësimin e dorëshkrimit të punimit të doktoratës, me titull: **"ANALIZË KIMIKE E MBETJEVE TË NGURTA INDUSTRIALE, KLASIFIKIMI DHE PËRDORIMI I TYRE NË EKONOMITË QARKORE"**.

Kërkesës ja bashkangjes:

- Punimin shkencor
- Dëshmitë e pjesëmarrjes në konferenca shkencore
- Chapterr, (kapitul libri në gjuhen angleze)
- Monografi shkencore
- Kopjen e dorëshkrimit
- Pëlqimin nga mentori
- Formularin F6

Kandidati:
Msc. Islam ZUZAKU

Prishtinë: 12/05/2025

UNIVERSITETI I PRISHTINËS "HASAN PRISHTINA"
FAKULTETI I SHKENCAVE MATEMATIKE-NATYRORE
PRISHTINË

Pranuar me: 12/05/2025			
Nj. org.	Numër	Sasia	Vlera
01	1422	3	—

UNIVERSITETI I PRISHTINËS "HASAN PRISHTINA"
FAKULTETI I SHKENCAVE MATEMATIKE NATYRORE
Rr. Xhorxh Bush, 10000 Prishtinë, Republika e Kosovës
Tel: +381-38-249-873 • E-mail: fshmn@uni-pr.edu

Nr. 1423 Prishtinë, dt. 12/05/2025

Për: Departamentin e Kimisë
Këshillin e Studimeve të Doktoratës
Këshillin e Fakultetit të Shkencave Matematike Natyrore

Lënda: Pëlqim nga Mentori, për dorëzimin e dorëshkrimit të punimit të doktoratës, me titull: **"ANALIZË KIMIKE E MBETJEVE TË NGURTA INDUSTRIALE, KLASIFIKIMI DHE PËRDORIMI I TYRE NË EKONOMITË QARKORE"** të kandidatit, **Msc. Islam Zuzaku.**

Mendim:

Kandidati **Msc. Islam Zuzaku**, ka ofruar të dhëna të reja, për ndikimin e ndotjes industriale, në tri lokalitetet e Kosovës (Mitrovicë, Obiliq dhe Gllogoc), me metale të rënda, si: Pb, Zn, Fe, Ni, Co, Cr, Mn, As, Cd dhe Cu, që janë analizuar në mostra të mbetjeve depozite, të: skorie-sterilit, hirit, si dhe mostra të tokës, në zonat e hulumtuara (*zona: A, B dhe C*), nëpërmjet teknikave analitike, si: ICP-OES dhe SAA.
Në këtë hulumtim shkencor, kandidati ka mbledhur gjithsej 24 mostra për analizë kimike, në tri lokacione të ndara hulumtuese, për dy periudha kohore testuese. Analizat kimike (*përpunimet statistikore*), kanë treguar vlera të larta të koncentrimit të metaleve të rënda, në mostrat e analizuara, përkatësisht zonat e hulumtuara.

- Prandaj, vlerësojmë se kandidati ka arritur *objektivat kryesore* të këtij hulumtimi shkencor, të cilat kanë qenë:

i) Studimi i burimit të metaleve të rënda *(Pb, Zn, Fe, Ni, Co, Cr, Mn, As, Cd dhe Cu),* në: zonat industriale, urbane dhe rurale *(mbetjet: skorie-steril dhe hiri),* në qytetet e lartcekura.

ii) Vlerësimi i shkallës së ndotjes (*me metale të rënda*), në tokat rreth zonave hulumtuese, si dhe investigimi i korrelimit gjithpërfshirës, midis deponive ekzistuese dhe tokave bujqësore.

iii) Studimi i reaksionit zinxhirorë, vlerësimi i shpërndarjes së ndotësve potencial në mjediset e analizuara, *(mbetje industriale, tokë bujqësore dhe ujërat e lumenjve).*

iv) Klasifikimi i mbetjeve industriale, në bazë të origjinës, karakteristikave dhe të përqëndrimit të materieve toksike në mbetjet industriale, të cilat janë të vendosura në deponi të hapura tokësore, përkatësisht ndarjen e tyre në klasa, si, p.sh: ***a.***) mbetje të ricikluveshme (*MR*), dhe ***b.***) mbetje industriale speciale, *(MIS).*

v) Mundësit *(alternativa të përshtatshme)* që këto mbetje industriale, pas procesit të trajtimit adekuat, nëpërmjet metodave të ndryshme, siç janë: *metodat e riciklimit, metodat fiziko-kimike dhe biologjike, dhe metoda me depozitim fiks, (në vend qëndrim),* të inkorporohen si primesa (*shtesë*) në lëndë të parë (*materiali amë*), dhe kësisoj të rifitohen materiale të ndryshme *(të ricikluveshme)* ripërdoruese, në ekonominë qarkore industriale-komerciale.

- Faktikisht, këto *objektiva përbëjnë thelbin kryesor*, të *qëllimit* të këtij hulumtimi shkencor, sepse kandidati ka vlerësuar (konstatuar), se:

*Ndotja e tokës nga aktivitetet antropogjenë, është një çështje e rëndësishme mjedisore, veçanërisht në qytetet e industrializuara, prandaj mu për këtë, është vlerësuar impakti mjedisor i industrive prodhuese, si: "Trepça", TC "Kosova'' dhe "Ferronikeli", përkatësisht impakti i mbetjeve toksike (*skorie-steril dhe hiri*), në mjedisin natyrorë.

*Është përforcuar fakti shkencor dhe është vë në pah, potenciali dhe ndikimet kryesore në mjedis, që shkaktohen nga *"hot-spotet"* e ngurta mjedisore (*deponit industriale*), në zonat e studiuara.

*Këto deponi, kanë impakt mjedisor të madh, në: *atmosferë, hidrosferë dhe litosferë*, prandaj duke marrë parasysh që deponitë ekzistuese rreth zonave industriale, janë të pa përshtatshme për mbrojtje të mjedisit, dhe kësisoj kontaminojnë gjithë ekosistemin, andaj është nevojë imediate që në lokacionet ku gjinden këto deponi, urgjentisht të bëhet studimi gjeneral i fizibilitetit, pastaj në mënyrë kontinuele këto deponi industriale, të kontrollohen dhe menaxhohen në mënyrë strikte, nga dikasteret ministrore, përkatësisht, institucionet kompetente shtetërore.

Në këtë drejtim, kandidati ka vlerësuar (*konstatuar*), se ndotja shumëvjeçare e mjedisit nga "Industritë Prodhuese në Kosovë", sidomos nga: kompleksi "New Co Ferronikeli", kompleksi "Trepça" dhe TC "Kosova A & B", kanë shkaktuar ç`rregullime në ekosistem, sepse këto industri prodhuese, duke filluar nga eksploatimi i materialit fillestarë, deri tek bartja dhe prodhimi i produktit përfundimtarë, në masë të konsiderueshme kanë ndikim në ndotjen e mjedisit.

Prandaj, kjo dukuri paraqet shqetësim të madh tek banorët rezident dhe më gjer, sepse mundësia e depërtimit të këtyre elementeve kimike, në forma të ndryshme në mjediset: *ajër, ujë* dhe *tokë*, dhe përmes tyre deri në zinxhirin ushqimor, është më se evidente dhe tejet shqetësuese. Veqënarisht (sidomos), kur kemi parasysh se koha e qëndrimit të metaleve të rënda në tokë, është mjaft e gjatë, atëherë edhe kontaminimi i tokës, ujërave sipërfaqësore dhe nëntokësore, me metale të rënda, paraqet rrezik permanent në përgjithësi për mjedisin natyrorë dhe në veçanti për speciet e gjalla.

Kandidat, **Msc. Islam Zuzaku**, gjatë kësaj periudhe kohore të hulumtimit shkencor, një pjesë të rezultateve eksperimentale të punimit të doktoratës i ka publikuar (*punim shkencor*) në revistën, **"Environment Protection Engineering"** revistë kjo e cila është e indeksuar në platformat: ***Web of Science (SCIE)*** dhe ***SCOPUS***, po ashtu, ka publikuar një kapitull libri në gjuhën angleze, **(Chapters)**, në: **Research Advances in Environment, Geography and Earth Science**. Vol.10. Universiti Sains Malaysia, Malaysia. ISBN 978-93-48119-93-3, DOI: https: //doi.org/ 10.9734/ bpi/ raeges/ v10, gjithashtu ka marr pjesë në tri **Konferenca shkencore** me karakter ndërkombëtar, dhe ka të publikuar edhe një **Monografi shkencore**, me: ISBN 978-9951-28-469-1.

- **Punimet shkencore:**

  I. ZUZAKU, J. DHIMITRI, M. SADIKU, J. HALILI, B. ISMAJLI, S. DEMAKU

- THE ECOLOGICAL RISK OF CONTAMINATION WITH TOXIC METALS IN THE SOILS AROUND THE TREPÇA COMPLEX, THE KOSOVO THERMAL POWER PLANTS, AND A NEW FERRONICKEL COMPLEX. Vol. 49. 2023. No. 2 DOI: 10.37190/ epe230201.

- **Konferencat shkencore**:

- International Ankara Multidisciplinary Studies Congress, Ankara– Turkey. https:// www.izdas. Org/ multidicsiplinaryankara.
- IRDCP (International Research and Development Center for Publication). https:// irdcp.org/ conferences.
- 1st International Future Engineering Conference held on December 25-26, 2023/, Sirnak University, Turkey, https://dergipark.org.tr/en/download/journal-file/29617.

- **Chapter:**

- Chapters, publication in: "Research Advances in Environment, Geography and Earth Science". Vol.10. Universiti Sains Malaysia, Malaysia. ISBN 978-93-48119-93-3 (Print), ISBN 978-93-48119-93-4 (e Book). "The Impact of Deposit Materials on Environment Pollution Around Industrial Areas in Kosovo". DOI: https: //doi.org/ 10.9734/ bpi/ raeges/ v10.

- **Monografi shkencore:**

- "Udhëzues Teorik dhe Praktik për Marrjen dhe Përgaditjen e Mostrave". Prishtinë, 2025, ISBN 978-9951-28-469-1.

Andaj, nga ajo që u tha si më lartë, vlerësojmë se kandidati, **Msc. Islam Zuzaku**, ka përmbushur të gjitha kushtet/ kriteret, për dorëzimin e Temës së Doktoratës.

Prof. Asoc. Skender DEMAKU

PARAQITJA E PUNIMIT TË DOKTORATËS[1]	
TË DHËNAT E PËRGJITHSHME	
Doktoranti:	**Msc. Islam Zuzaku**
Adresa:	Gjilan
Tel./ fax:	+383 49 102 233
E-mail:	islam.zuzaku@student.uni-pr.edu; alkoslab@gmail.com;
Emërtimi i studimit:	Programi i doktoratës - Kimi
Udhëheqësi i studimit:	FSHMN- UNIVERSITETI I PRISHTINËS
TË DHËNAT PËR PUNIMIN E DOKTORATËS	
Titulli në gjuhën shqipe	ANALIZË KIMIKE E MBETJEVE TË NGURTA INDUSTRIALE, KLASIFIKIMI DHE PËRDORIMI I TYRE NË EKONOMITË QARKORE
Titulli në gjuhën angleze	CHEMICAL ANALYSIS OF SOLID INDUSTRIAL WASTE - THEIR CLASSIFICATION AND USE IN CIRCULAR ECONOMIES
Fusha e hulumtimit	KIMI E MJEDISIT
DEKLARATA E MENTORIT/BASHKËMENTORIT	

Kandidati **Msc. Islam Zuzaku**, ka ofruar të dhëna të reja, për ndikimin e ndotjes industriale, në tri lokalitetet e Kosovës (qytetet: Mitrovicë, Obiliq dhe Gllogoc), me metale të rënda, si: Pb, Zn, Fe, Ni, Co, Cr, Mn, As, Cd dhe Cu, që janë analizuar në mostra të mbetjeve depozite të: skorie-sterilit, hirit, si dhe mostra të tokës, në zonat e hulumtuara (*zona: A, B dhe C*), nëpërmjet teknikave analitike, si: ICP-OES dhe SAA.

Në këtë hulumtim shkencor, kandidati ka mbledhur gjithsej 24 mostra për analizë kimike, në tri lokacione të ndara hulumtuese, për dy periudha kohore testuese. Analizat kimike (*përpunimet statistikore*), kanë treguar vlera të larta të koncentrimit të metaleve të rënda, në mostrat e analizuara, përkatësisht zonat e hulumtuara.

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[1] Lutei që ta plotësoni formularin dhe ta dërgoni të nënshkruar me postë elektronike.

ii) Vlerësimi i shkallës së ndotjes (*me metale të rënda*), në tokat rreth zonave hulumtuese, si dhe investigimi i korrelimit gjithëpërfshirës, midis deponive ekzistuese dhe tokave bujqësore.

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*Këto deponi, kanë impakt mjedisor të madh, në: *atmosferë, hidrosferë dhe litosferë*, prandaj duhet marrë parasysh, që deponitë ekzistuese rreth zonave industriale, janë të pa përshtatshme për mbrojtje të mjedisit, dhe kësisoj kontaminojnë gjithë ekosistemin, andaj është nevojë imediate që në lokacionet ku gjinden këto deponi, urgjentisht të bëhet studimi gjeneral i fizibilitetit, pastaj në mënyrë kontinuele këto deponi industriale, të kontrollohen dhe menaxhohen në mënyrë strikte, nga dikasteret ministrore, përkatësisht institucionet kompetente shtetërore.

Në këtë drejtim, kandidati ka vlerësuar se, ndotja shumëvjeçare e mjedisit nga "Industritë Prodhuese në Kosovë", sidomos nga: kompleksi "New Co Ferronikeli", kompleksi "Trepça" dhe TC "Kosova A & B", kanë shkaktuar ç`rregullime në ekosistem, sepse këto industri prodhuese, duke filluar nga eksploatimi i materialit fillestarë, deri të bartja dhe prodhimi i produktit përfundimtarë, në masë të konsiderueshme kanë ndikim në ndotjen e mjedisit.

Prandaj, kjo dukuri paraqet shqetësim të madh tek banorët rezident dhe më gjer, sepse mundësia e depërtimit të këtyre elementëve kimike, në forma të ndryshme në mjediset: ajër, ujë dhe tokë, dhe përmes tyre deri në zinxhirin ushqimor, është më se evidente dhe tejet shqetësuese. Veqënarisht, kur kemi parasysh se koha e qëndrimit të metaleve të rënda në tokë, është mjaft e gjatë, atëherë edhe kontaminimi i tokës, ujërave sipërfaqësore dhe nëntokësore me metale të rënda, paraqet rrezik permanent në përgjithësi për mjedisin natyrorë, dhe në veçanti për speciet e gjalla.

Kandidat, **MSc. Islam Zuzaku**, gjatë kësaj periudhe kohore të hulumtimit shkencorë, një pjesë të rezultateve eksperimentale të punimit të doktoratës i ka publikuar (*punim shkencor*) në revistën, "**Environment Protection Engineering**", revistë kjo e cila është e indeksuar në platformat: ***Web of Science (SCIE)*** dhe ***SCOPUS***, po ashtu, ka publikuar një **Chapters**, në: **Research Advances in Environment, Geography and Earth Science**. Vol.10. Universiti Sains Malaysia, Malaysia. ISBN 978-93-48119-93-4 (**e Book**), DOI: https: //doi.org/ 10.9734/ bpi/ raeges/ v10, gjithashtu ka marr pjesë në tri **Konferenca shkencore** me karakter ndërkombëtar, dhe ka të publikuar edhe një **Monografi shkencore**, me; ISBN 978-9951-28-469-1.

- **Punimi shkencor:**

I. ZUZAKU, J. DHIMITRI, M. SADIKU, J. HALILI, B. ISMAJLI, S. DEMAKU

- THE ECOLOGICAL RISK OF CONTAMINATION WITH TOXIC METALS IN THE SOILS AROUND THE TREPÇA COMPLEX, THE KOSOVO THERMAL POWER PLANTS, AND A NEW FERRONICKEL COMPLEX. Vol. 49. 2023. No. 2 DOI: 10.37190/ epe230201.

- **Konferencat shkencore**:
  - International Ankara Multidisciplinary Studies Congress, Ankara–Turkiye. https:// www.izdas. Org/ multidisciplinary Ankara.
  - IRDCP (International Research and Development Center for Publication). Https: //irdcp.org/ conferences.
  - 1st International Future Engineering Conference held on December 25-26, 2023/, Sirnak University, Turkey, https://dergipark.org.tr/en/download/journal-file/29617.

- **Chapters:**
  - Publikuar në: Research Advances in Environment, Geography and Earth Science. Vol.10. Universiti Sains Malaysia, Malaysia. ISBN 978-93-48119-93-3 (Print), ISBN 978-93-48119-93-4 (e Book), DOI: https: //doi.org/ 10.9734/ bpi/ raeges/ v10.

- **Monografi shkencore:**
  - "Udhëzues teorik dhe praktik për marrjen dhe përgaditjen e mostrave". Prishtinë, 2025, ISBN 978-9951-28-469-1.

Andaj, nga ajo që u tha si më lartë, vlerësojmë se kandidati, **MSc. Islam Zuzaku**, ka përmbushur të gjitha kushtet/ kriteret, për dorëzimin e Temës së Doktoratës.

Vendi, data dhe nënshkrimi
Në Prishtinë, 12.05.2025 — **Prof. Asoc. Skender DEMAKU** (*Emri e mbiemri i mentorit*) Nënshkrimi ________ V.V.

UNIVERSITETI I PRISHTINËS "HASAN PRISHTINA"
FAKULTETI I SHKENCAVE MATEMATIKE-NATYRORE
DEPARTAMENTI I KIMISË

ISLAM ZUZAKU

ANALIZË KIMIKE E MBETJEVE TË NGURTA INDUSTRIALE, KLASIFIKIMI DHE PËRDORIMI I TYRE NË EKONOMITË QARKORE

PUNIMI I DOKTORATËS

Mentori: Prof. Asoc. Skender DEMAKU

Prishtinë, 2025

UNIVERSITY OF PRISHTINA "HASAN PRISHTINA"
FACULTY OF MATHEMATICS AND NATURAL SCIENCES - DEPARTMENT OF CHEMISTRY

ISLAM ZUZAKU

CHEMICAL ANALYSIS OF SOLID INDUSTRIAL WASTE THEIR CLASSIFICATION AND USE IN CIRCULAR ECONOMIES

DOCTORAL THESIS
Prishtina, 2025

UNIVERSITETI I PRISHTINËS "HASAN PRISHTINA"
FAKULTETI I SHKENCAVE MATEMATIKE-NATYRORE
DEPARTAMENTI I KIMISË

ISLAM ZUZAKU

ANALIZË KIMIKE E MBETJEVE TË NGURTA INDUSTRIALE, KLASIFIKIMI DHE PËRDORIMI I TYRE NË EKONOMITË QARKORE

PUNIMI I DOKTORATËS
Prishtinë, 2025

REZYMEJA

Evolucioni njerëzorë së bashku me revolucionin industrialë, kanë shkaktuar ndryshime të mëdha në cilësinë e mjediseve natyrore, në të cilat njeriu jeton dhe ushtron veprimtarinë e tij. Toka luan një rol të rëndësishëm në këtë proces, pasi shërben si "depozitë" për akumulimin e ndotësve kimikë. Metalet e rënda, në dallim nga ndotësit organikë, nuk janë të biodegradueshëm. Prania e këtyre ndotësve në mjedis, lidhet me aktivitetet industriale, me emetimin gjatë proceseve të djegies së lëndëve fosile, me ekonomit familjare dhe me trafikun.
Po ashtu, edhe ndotësit organikë të qëndrueshëm (POP-et), mbeten në qendër të vëmendjes shkencore, për shkak të shpejtësisë së ulët të degradimit, natyrës lipofilike, toksicitetit, aftësisë për t'u transportuar në distanca të mëdha, dhe për tu bioakumuluar në organizmat e gjallë.
Rreth 70 viteve më herët, në Kosovë janë ndërtuar industri të ndryshme prodhuese, kryesisht si industri të metalurgjisë së zezë dhe nxjerrjes së thëngjillit, për prodhim të energjisë elektrike, të cilat industri prodhuese, pothuajse funksionojnë edhe në ditët e sotme, anipse disa nga to, jo me kapacitetin e plotë prodhues, siç kanë qenë para dy dekadave.

Meqë industria metalurgjike, njihet si një burim i rëndësishëm i emetimit të substancave të ndryshme kimike në mjedis, si dhe duke marrë shkak nga denoncimet e vazhdueshme të medias së shkruar dhe visive, mbi nivelin e lartë të ndotjes së prodhuar, nga industritë që operojnë brenda territorit të Republikës së Kosovës-së, në këtë punim, është realizuar vlerësimi i ndotjes aktuale, nga metalet e rënda, si: Pb, Zn, Fe, Ni, Co, Cr, Mn, As, Cd dhe Cu, në mostra të materive toksike depozite (skorie-steril), si dhe mostra toke, në zonat e hulumtuara (*zona: A, B dhe C*), nëpërmjet teknikave analitike, si: ICP-OES dhe SAA.
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RESUME

Human evolucion, together with the industrial revolucion, has caused great changes in the quality of the natural environments, in which man lives and exercises his activity. The soil plays an important role in this process, as it serves as a "repository" for the accumulation of chemical pollutants. Heavy metals, unlike organic pollutants, are not biodegradable. The presence of these pollutants in the environment is related to industrial activities, emission during the burning of fossil materials, family economy and traffic.

Also, persistent organic pollutants (POPs) remain in the center of scientific attention, due to their low degradation rate, lipophilic nature, toxicity, ability to be transported over long distances, and to bioaccumulate. in living organisms.

About 70 years ago, various manufacturing industries were built in Kosovo, mainly as ferrous metallurgy and coal extraction industries, for the production of electricity, which manufacturing industries are almost still functioning today, although some of them, not with full production capacity, as they were two decades ago.

Since the metallurgical industry is known as an important source of emission of various chemical substances in the environment, as well as due to the constant denunciations of the written and visual media, on the high level of pollution produced, by the industries operating within territory of the Republic of Kosovo, in this work, the evaluation of the current pollution, from heavy metals, such as: Pb, Zn, Fe, Ni, Co, Cr, Mn, As, Cd and Cu, in samples of materials was carried out toxic deposits (scorie-sterily), as well as soil samples, in the researched areas (areas: A, B and C), through analytical techniques, such as: ICP-OES and SAA.

Therefore, this scientific research presents the assessment of environmental pollution in industrial, urban and rural areas in the cities: Mitrovica, Kastriot and Drenas, recognizing these areas as among the largest centers of heavy manufacturing industry in our country.

Key words: *Manufacturing industry, environmental impacts, soil pollution, water pollution, deposit materials, research areas, heavy metals, analytical methods; ICP-OES and SAA, laboratory instruments, contamination of areas, industrial, urban and rural areas, chemical reagents, environmental protection, polluting substances, environmental hot-spots, rivers of Kosovo, agricultural lands, air pollution, animal world, world plant, food chain, etc.*

REZYMEJA

Evolucioni njerëzorë së bashku me revolucionin industrialë, kanë shkaktuar ndryshime të mëdha në cilësinë e mjediseve natyrore, në të cilat njeriu jeton dhe ushtron veprimtarinë e tij. Toka luan një rol të rëndësishëm në këtë proces, pasi shërben si "depozitë" për akumulimin e ndotësve kimikë. Metalet e rënda, në dallim nga ndotësit organikë, nuk janë të biodegradueshëm. Prania e këtyre ndotësve në mjedis, lidhet me aktivitetet industriale, me emetimin gjatë proceseve të djegies së lëndëve fosile, me ekonomit familjare dhe me trafikun.

Po ashtu, edhe ndotësit organikë të qëndrueshëm (POP-et), mbeten në qendër të vëmendjes shkencore, për shkak të shpejtësisë së ulët të degradimit, natyrës lipofilike, toksicitetit, aftësisë për t'u transportuar në distanca të mëdha, dhe për tu bioakumuluar në organizmat e gjallë.

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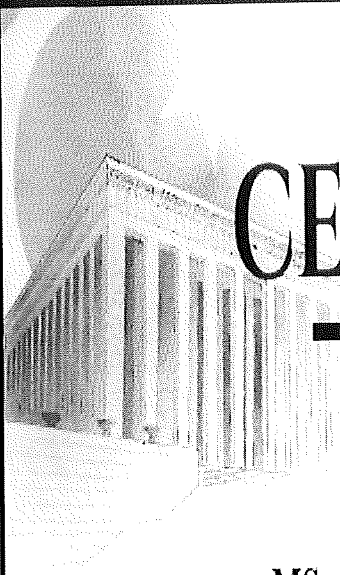

CERTIFICATE

OF PARTICIPATION

This certificate is proudly presented to

MSc. Islam ZUZAKU. PhD. Cand.

University of Pristina "HASAN PRISHTINA" Faculty of Mathematical and Natural Sciences- Department of Chemistry, Kosovo

attended the V. International Ankara Multidisciplinary Studies Congress held on January 27-29, 2023 / Ankara, Türkiye, organised by IKSAD Institute with an oral presentation entitled

THE ECOLOGICAL RISK OF CONTAMINATION WITH TOXIC METALS, IN THE SOILS AROUND THE "TREPÇA" COMPLEX, THE "KOSOVO" THERMAL POWER PLANTS AND THE NEW FERRONICKEL COMPLEX

Dr. Ethem İlhan ŞAHİN
Organizing Committee Member

CERTIFICATE

OF PARTICIPATION

THIS IS TO CERTIFY THAT

Islam Zuzaku

attended the 1st International Future Engineering Conference
held on December 25-26, 2023 / Şırnak, Türkiye
organised by Şırnak University & IKSAD Institute
with an oral presentation entitled

The Ecological Risk Of Contamination With Toxic Metals In The Soils, Waste And Ash, Around The "Trepça" Complex, The "Kosovo" Thermal Power Plants And The New Ferronickel Complex

Assoc. Prof. Dr. Mahmut DIRIK
Conference Co-Head

Assoc. Prof. Dr. Asaf Tolga ULGEN
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This is to certify that **MSc. ISLAM ZUZAKU**, **University of Pristina "HASAN PRISHTINA" Faculty of Mathematical-Natural Sciences, Department of Chemistry- Pristina- Kosovo** has orally presented a paper entitled **The ecological risk of contamination with toxic metals, in the soils around the "Trepça" complex, the "Kosovo" thermal power plants and the new Ferronickel complex** in ICEAWRD-2023 held during February 11-12, 2023, organized by International Research and Development Center for Publication (IRDCP).

Convener, ICEAWRD-2023
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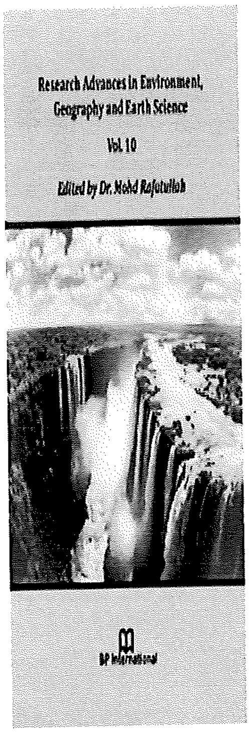

The Impact of Deposit Materials on Environment Pollution Around Industrial Areas in Kosovo

Skender DEMAKU ; Islam ZUZAKU ; Donika SYLLEJMANI ; Arbnora ALIU

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Abstract

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ABSTRACT

Human evolution, together with the industrial revolution, has caused great changes in the quality of the natural environments, in which man lives and exercises his activity. The soil plays an important role in this process, as it serves as a "repository" for the accumulation of chemical pollutants. Heavy metals, unlike organic pollutants, are not biodegradable. The presence of these pollutants in the environment is related to industrial activities, emissions during the burning of fossil materials, family economy and traffic. Also, persistent organic pollutants (POPs) remain at the center of scientific attention, due to their low degradation rate, lipophilic nature, toxicity, ability to be transported over long distances, and to bioaccumulate in living organisms. Around 70 years ago, various manufacturing industries were established in Kosovo, primarily focusing on ferrous metallurgy and coal extraction for electricity production. Many of these manufacturing industries are still operational today, though some no longer function at their full production capacity as they did two decades ago.

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1. INTRODUCTION

Human evolution, together with the industrial revolution, has caused great changes in the quality of the natural environments, in which man lives and

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Effective measures are currently in place in the majority of countries to prevent copper poisoning and to reduce the amount of copper used in food production, as well as in plants and animals. However, water pipes and copper vessels pose a risk of contamination, and humans can tolerate up to 200 mg/g of Cu in food, which is 20 times higher than the normal human concentration, [6-8]. Although copper is a rare element in natural waters, it can enter contaminated waters through a variety of channels. It has been demonstrated that copper is harmful to fish and other aquatic life at quantities that do not constitute any risk to humans, and it has also been demonstrated experimentally that the copper ion (II) is the primary toxic form; this is because the concentration of the Cu (II) ion falls with increasing pH, alkalinity, and organic matter content, which in turn reduces copper toxicity, [6-8]. Additionally, copper chloride is employed as a disinfectant, food additive, wood preservative (fixer) in fabric dyeing and printing, pigment for glass and ceramics, and catalyst in a variety of organic reactions, including the chlorination of hydrocarbons [21-24].

Lastly, we recognize that the theoretical part has been adequately and recently covered in the literature, and we are confident that the basic literature mentioned will help us understand, compare, and assess the practical part as well as the various experimental and laboratory results.

3. CONCLUSIONS

The geoaccumulation index (Igeo) study of soil samples from three different industrial zones in Kosovo offers a comprehensive view of the environmental contamination by various toxic metals. Zone A (Gllogoc-New Co Ferronickel) demonstrates extreme pollution across all measured metals, with CR and Ni showing particularly high I.ego values of 17.61 and 16.00 respectively. This indicates severe environmental degradation due to industrial activities in this area.

Zone B (Mitrovica-Trepça), although also affected by industrial activities, exhibits a broader range of contamination levels. While Cd (5.66) and AS (5.60) indicate extreme pollution, metals like Pb (1.20), Ni (1.76), and Cr (1.43) range from uncontaminated to moderately polluted, suggesting variable sources and intensities of pollution within this zone.

Zone C, commonly known as the Prishtina Industrial Zone, has considerable pollution due to as (8.71) and Cr (10.86), Pb (0.86), Ni (0.89) and Cd (2.93) indicate lower pollution values, indicating a range from almost uncontaminated to moderately polluted. This fluctuation indicates that the pollutant profile in this area is influenced by a variety of industrial activities and insufficient environmental regulations. Zone B, on the other hand, despite having high levels of certain metals, shows a mixed pollution profile, pointing to possible differences in industrial practices and pollution control measures.

The results highlight the necessity of more stringent regulatory measures and focused environmental cleanup, especially in Zones A and C, to address the severe pollution. Given the high concentrations of hazardous metals found there, reducing pollution in these places is essential for safeguarding the ecosystem and the general public's health.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

This chapter is the original description of the authors, and the results data is the original scientific research of the authors participating in this chapter.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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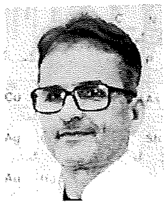
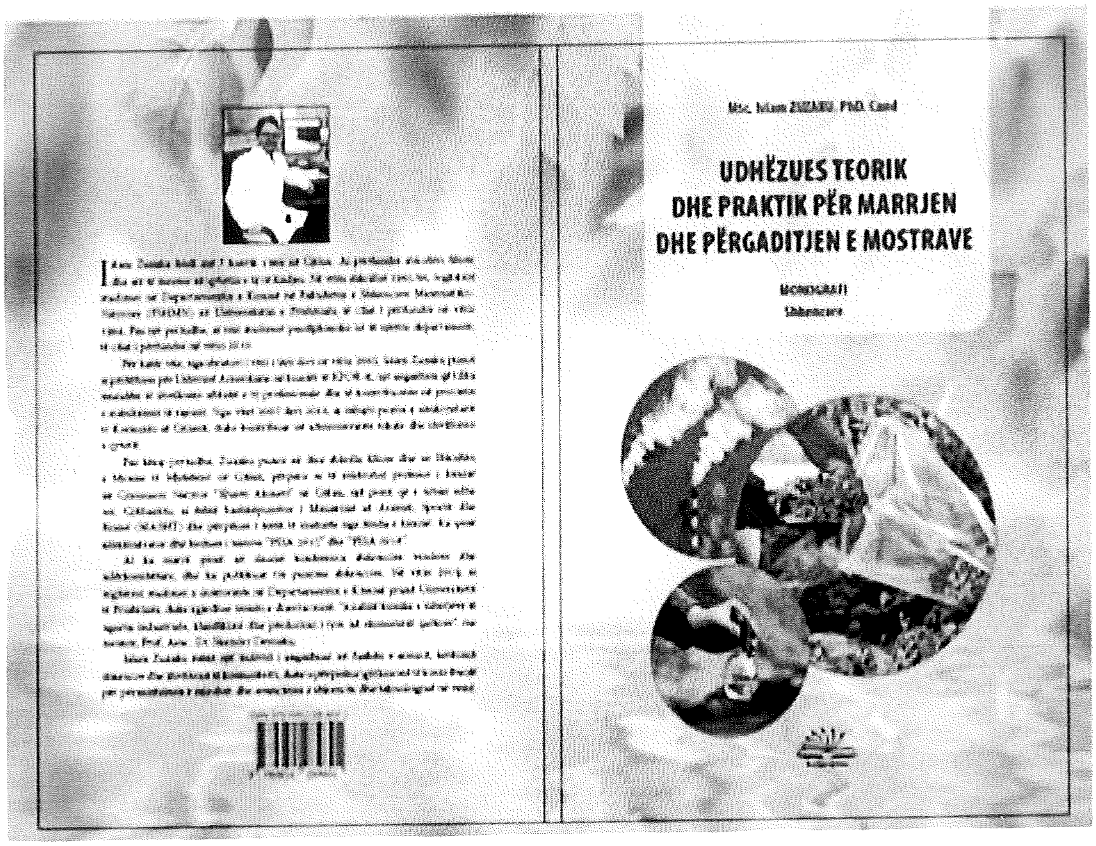
He completed his education at the University of Prishtina "Hasan Prishtina," starting with a degree in chemical engineering, followed by a master's in chemical sciences, focusing on environmental chemistry and environmental protection. In 2012, he earned his doctorate in environmental chemistry. In November 2021, he was appointed to teach several subjects, including General Chemistry, Environmental Chemistry, Environmental Protection, Polymeric Materials in Chemical Engineering, Chemistry of Synthetic Polymers, and Green Chemistry. All co-authors of his published works are experts in specialized fields related to inorganic and organic pollutants across various environments, such as air, water, soil, and toxic waste.

His areas of research mainly include environmental chemistry, environmental protection, environmental pollution, green chemistry, general chemistry, earth chemistry, atmospheric chemistry, natural water chemistry, polymeric materials, etc.



Islam ZUZAKU, MSc
Department of Chemistry, Faculty of Mathematics and Natural Science, University of Prishtina "Hasan Prishtina", George Bush Street, 10000, Pristine - Kosovo.

He was born in 1966 in Gjilan. He finished primary and secondary school in Gjilan. In the 1985/86 school year, he registered his studies at the Chemistry Department of the FSHMN in Prishtina, which he completed in 1994. He began his postgraduate studies in the Chemistry Department at the FSHMN in Prishtina in 1997 and completed them in 2010. He began his doctoral studies in the academic year 2019/20, in the Department of Chemistry at FSHMN-UP. From September 1999, for 4 years he worked as an interpreter in the American Army in KFOR. From 2007-2010, he was the deputy mayor of the Municipality of Gjilan. Then he worked in several elementary schools, then also in the high school of medicine in Gjiilan, and he currently works as a chemistry professor at the "Xhavit Ahmeti" natural high school in Gjilan.



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THE ECOLOGICAL RISK OF CONTAMINATION WITH TOXIC METALS IN SOILS AROUND THE TREPÇA COMPLEX, THE KOSOVO THERMAL POWER PLANTS, AND A NEW CO FERRONICKELI COMPLEX

Toxic waste, soil, and ash samples were collected in the landfill (solid environmental hot spots) near the Trepça complex, New Co Ferronickeli, and Kosovo thermal power plants. They were analyzed by the ICP-OES method to measure the concentration of some toxic metals. The pollutant with the highest mean concentration (in an acidic medium) was Fe (36 400.0), followed by Mn (8683.0), Cr (6575.0), As (4739.0), Pb (3364.0), Zn (2394.0), Ni (922.6), Cu (297.6), Co (46.6), and Cd (61.8) (all concentrations in mg/kg). Three pollution indices were used such as the geoaccumulation index (I_{geo}), contamination factor (CF_i), and pollution load index (*PLI*). The CF_i values determined for Fe, Mn, Cr, As, Pb, Zn, Ni, Cu, Co, and Cd indicated high contamination. In all soil samples, the *PLI* values showed the presence of soil pollution.

1. INTRODUCTION

Because of the toxic waste left over from mining, chemical fertilizers, and pesticides, heavy metal pollution of agricultural soil is a severe ecological problem [1, 2]. Heavy metal concentrations in the soil rise because of repeated use of manure and chemical fertilizers [3]. While some heavy metals are essential for plant growth, others, when absorbed and stored by plants, can be hazardous to humans if consumed [4].

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In the region of Mitrovica, Obiliq, and Gllogoc in Kosovo, soil samples from three different land uses and traffic conditions were discovered to include heavy metals such as Pb, Zn, Fe, Ni, Cr, Mn, and As [5, 6]. The waste in Kelmend, Cikatovo, and Obilic landfills contain Pb, Zn, Fe, Mn, and As [7, 8]. Fe, Zn, Ni, Pb, Mn, Cr, and As concentrations in agricultural land in rural Mitrovica, Obilic, and Gllogoc areas were found to be higher than 1.0 mg/kg [5, 6]. There is still a serious problem with toxic metal poisoning of the biosphere, which started with the industrial revolution and urbanization [2–5].

With a cumulative effect and risk to the ecosystem, environmental pollution by toxic metals has become a substantial global problem in recent decades [6, 7]. Even while there exist harmful metals in the Earth's crust naturally, anthropogenic activities have increased their amounts to toxic levels in many ecosystems [6, 7]. Industrial activity is the principal source of hazardous metals in the soil surrounding factories [6–9]. Significant sources of soil pollution include mining and thermal power facilities [1–6]. Urban areas, mining areas, and locations close to thermal power plants are high-risk sites for soil contamination [3]. Toxic metals such as Cd, Zn, As, and Pb are released during the combustion of coal in thermal power plants [3–5].

Through the diffusion or leaching of dust, leftover tailings slag, and waste rock produced by mining and transportation activities, toxic metals infiltrate the soil [1–4]. A preventative method is required since remediating toxic metal-contaminated soil is expensive and complicated [5, 6].

Studies have been done to evaluate the site's soil quality [6–9], however, there is little information available on soil contamination and ecological assessments in Kosovo's industrial zones. According to research, Kosovo's urban and industrial soil has large concentrations of harmful metals, including those found in minerals, the old metallurgical sector, the Fe-Ni manufacturing plant, and Zn-Pb concentrate [8–10]. Instead of hazardous metals, industrial zones are typically investigated for other pollutants [9, 10]. Thermal power plants and mineral ore mining in the vicinity of Mitrovica, Obiliq, and Gllogoc have an impact on the levels of hazardous metals in the soil and represent ecological problems [8–10]. Sources of pollution from the atmosphere, fertilizers, pesticides, and other pollutants have been investigated to assess the level of toxic metal contamination in soils and the ecological concerns close to the Trepça, New Co Ferronickeli and Kosovo thermal power plants. This investigation aims to offer useful data for ecological risk reduction and long-term planning in industrial areas [4, 5].

2. MATERIALS AND METHODS

Study area. Three significant industrial sites in Kosovo: the Kosovo power plant, Trepça complex, and New Co Ferronickeli complex (Fig. 1) were the focus of this study. Large volumes of trash from the New Co Ferronickeli, which contain heavy metals and other pollutants, are emitted into the atmosphere through a variety of technical procedures [4, 5]. These activities can produce dust that can spread over great areas and contain harmful materials in the air, water, and soil [8]. With its ore mining and flotation procedure, the Trepça complex, an inactive lead and zinc mine close to Mitrovica city, has a substantial negative environmental impact [8–10]. The community and ecosystem in the area are at risk from the mine's production of sterile material.

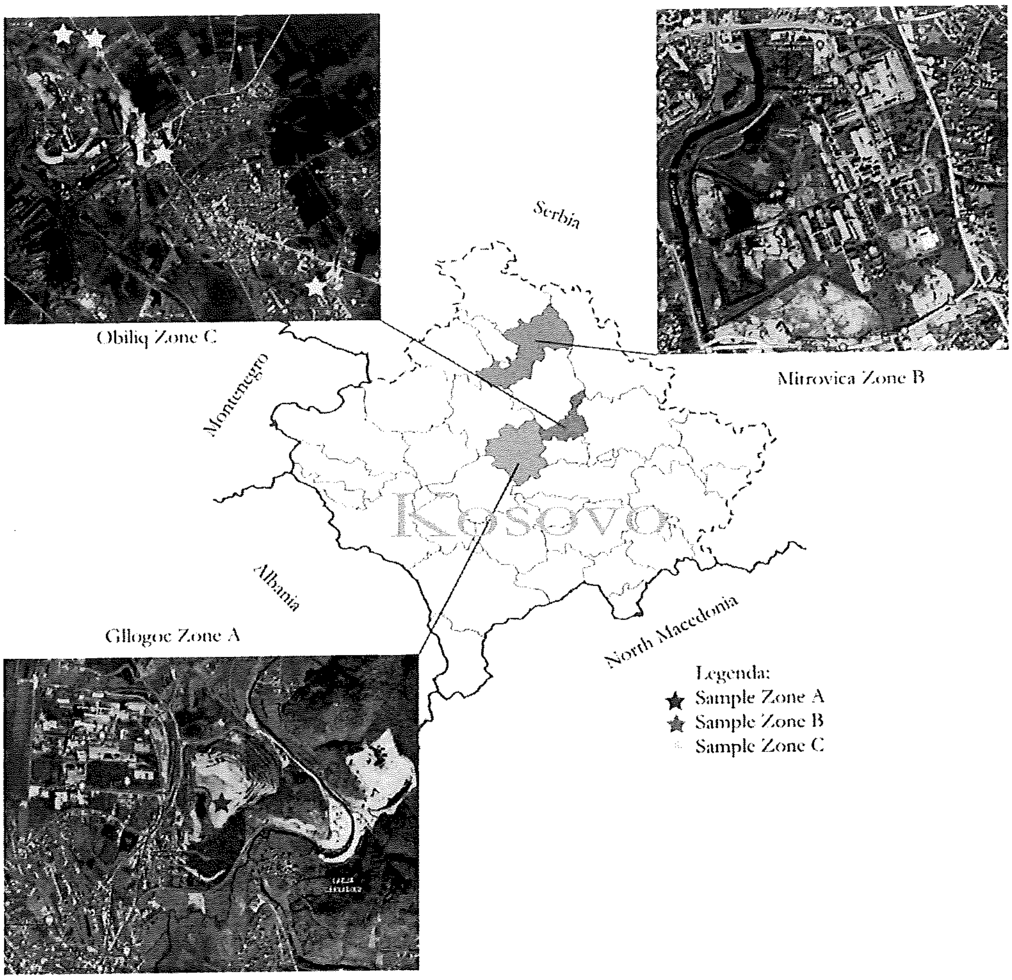

Fig. 1. The sampling site of scoria-sterile, toxic waste, ash, and soil at industrial zones of Obiliq, Mitrovica and Gllogoc

The Kosovo Power Plant generates power from lignite coal in two basins in the Kosovo and Dukagjini areas in an estimated 10–12 billion tons [4–7]. About 6 million tons of coal, which has a calorific content of 1800–2000 kcal, is produced each year, and the process results in the release of ashes [11]. These ashes could potentially contaminate groundwater and surface waters with harmful metals such as Pb, Ni, Cd, Al, and Cr [12].

Environmental samples for chemical analyses were gathered and prepared using modern analytical techniques. In December 2022, field sampling was carried out in the study regions. Samples of sterile material were collected from three sites in the New Co Ferronickeli (M1, M2), and soil samples were collected from a waste area close to Old Cikatovo Village (M3). Sterile samples were collected at the Kelmend (M4) landfill's toxic waste layer as well as in what is known as landfills but are known to the locals as IPM (Industrial Park of Mitrovica) (M5). Additionally, in the proximity of these zones, soil samples were collected in Shupkovc hamlet (M6). Toxic waste and soil samples were examined for the content of the following metals: Fe, Mn, Cr, As, Pb, Zn, Ni, Cu, Co and Cd.

Lignite combustion releases hazardous gases such as sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon dioxide, hydrocarbons, ammonia, and hydrogen sulfide in the form of smoke and dust. Ash samples were gathered in two places. Additionally, ash dumps contain inorganic substances, the most significant of which are hazardous metals like Pb, Ni, Cd, Al, and Cr [2-5]. Two locations – TC Kosovo A (M7) and TC Kosovo B (M8) provided ash samples for analysis. 5 km from TC Kosovo, at the town of Plemetin (M9), soil samples were collected.

Sample digestion. 1 g samples of the soil, waste toxic, ash, and scoria-sterile were placed in Teflon containers. After the addition of 10 cm^3 of aqua regia, the samples were heated in a microwave. Following digestion, the components were filtered (quantitative filter paper) and diluted with distilled water to create a 100 cm^3 solution [13–15].

Instrumentation and statistical analyses. With the aid of inductively coupled plasma-optical emission spectrometry (Optima 2100 DV), the quantities of heavy metals were calculated (ICP-OES). For each group of analytical samples, two technique blanks and two spiked blanks were simultaneously processed. Statistics charts created using the Minitab 19 program were displayed separately for each component [16].

Pollution indices analyses. Müller's geoaccumulation index (I_{geo}) [17–19], established to measure contamination of sedimentary bottoms, was used to assess soil contamination. Soil pollution assessment can also be done by comparing the current toxic metal presence with preindustrial levels of concentration [8, 24]. I_{geo} has been widely used to comprehend the pollution levels of toxic metals in the soils [24], that is, for the calculation to assess the toxic metal pollution status of soil [17]. The I_{geo} was computed as follows:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \qquad (1)$$

where C_n is the metal concentration in soil, mg/kg, B_n geochemical background concentration of the corresponding metal, mg/kg.

The contamination factor (CF_i) was established following the Tomlinson model [19] as the ratio of the maximum metal concentration in soil, waste, or ash to the reference value:

$$CF_i = \frac{C_n^i}{C_0^i} \tag{2}$$

where C_n^i is the metal concentration in soil (waste, ash), mg/kg, C_0^i – its pre-industrial concentration (the reference value), mg/kg.

According to international regulations, the following reference values for the analyzed metals in soil were used, mg/kg: Pb 100, Cr 100, Ni 100, Zn 300, Cu 100, Co 50, Fe 56.9, Mn 26, As 50, and Cd 5 [25, 27]. As the reference values vary from country to country, the CF_i values may be different, even if the metal concentrations are similar [8]. The CF_i is an important factor that is used to monitor metal contamination in the soil [22]. It has four categories according to the degree of contamination in the soil. $CF_i < 1$ indicates a low degree of contamination, $1 \leq CF_i < 3$ moderate pollution, $3 \leq CF_i < 6$ considerable pollution, and $CF_i \geq 6$ very high degree of contamination [24, 25].

The pollution load index (*PLI*) was calculated based on contamination factors calculated for each considered heavy metal. The *PLI* can assess the level of metal contamination and the actions that must be taken. The *PLI* was calculated according to:

$$PLI = \left(CF_1 CF_2 \times \cdots \times CF_n\right)^{1/n} \tag{3}$$

The potential ecological risk index (*ERI*) put forward by Hakanson [17] was used to evaluate the soil ecological risk [17, 24]:

$$ERI = T_r CF_i \tag{4}$$

where T_r is the toxic response factor and CF_i the contamination factor. T_r values for metals are: Pb 5, Cr 2, Ni 5, Zn 1, Cu 5, Co 5, As 4, and Cd 7. The soil classification concerning ecological risk values involves five classes: $ERI < 40$ corresponds to low ecological risk, $40 < ERI < 80$ moderate ecological risk, $80 < ERI < 160$ appreciable ecological risk, $160 < ERI < 320$ high ecological risk, and $ERI > 320$ serious ecological risk [17, 24].

3. RESULTS AND DISCUSSION

3.1. HEAVY METAL CONTENTS IN THE STUDY AREA

The focus of this study was to evaluate the presence of Pb, Zn, Fe, Ni, Co, Cr, Mn, As, Cd and Cu in scoria-sterile material (M1, M2) and soil (M3) in sampling zone A (Gllogoc, New Co Ferronickeli), in the concentrate Pb-Zn toxic waste (M4, M5) and soil (M6) in sampling zone B (Mitrovica, Trepça), and in ash (M7, M8) and soil (M9) in sampling zone C (Obiliq, TC Kosovo A and B, Power plant) (Table 1) as possible pollution sites.

Table 1

Heavy metal concentrations in zones A, B and C [mg/kg]

Sample	Pb	Zn	Fe	Ni	Co	Cr	Mn	As	Cd	Cu
Sampling zone A – Gllogoc, New Co Ferronickeli										
M1	47.5	422.2	36400	922.6	46.6	6575	2541	21.1	39.9	18.3
M2	49.9	410.6	36340	1257	30.8	1792	326.2	65.3	31.4	29
M3	43.7	344.5	21280	766.4	39.5	635.5	762.9	13.8	15.1	19.1
Sampling zone B – Mitrovica, Trepça										
M4	3364	2394	4043	36.6	8.8	25.8	8683	4739	61.8	297.6
M5	90.3	428.3	913.6	7.4	0.2	16.2	59.6	13.4	2.1	21
M6	693	1847	2241	88.8	19	125.2	1657	41.7	27.3	76.1
Sampling zone C, Obiliq, TC (power plant)										
M7	65.5	235.7	28370	349.4	10.1	2839	1302	278.5	20.2	82.9
M8	50.5	238.4	25940	318.8	9.7	4262	1272	74.1	22.1	36.9
M9	96.26	460.14	23685	346.14	16.71	971	1054	58.14	8.29	51.57

It is important to note that the metal concentrations can change over time and location and also depend on the agency. The official documents for the soil quality guidelines are: *Soil quality – urban technical note No. 3* (established by EPA) [24] and *Dutch target and intervention value* [27]. These databases contain soil quality guideline values for a variety of contaminants, including heavy metals, as well as information on how the values were derived (mg/kg, As – 22, Cd – 0.4, Cr – 100, Cu – 1500, Pb – 400, Hg – 0.2, and Ni – 100 mg/kg).

The EU countries may have different soil quality guidelines for heavy metals than the EPA and the US [26]. However, in general, for essential elements such as Zn, Fe, Co, and Mn, guideline values are not usually set, as these elements are important for plant and animal growth and are beneficial (effects in small amounts). However, excess amounts of these elements can be harmful, so it is important to consider other factors such as pH, organic matter, and the presence of other contaminants when assessing soil quality. It is suggested to check the guidelines of each specific country, as they may have different rules and values.

The concentration of some heavy metals (Table 1), such as Fe (36 400 mg/kg) and Ni (922.6 mg/kg) was higher in study zone A than in sites B and C. Long-term use of minerals (scoria-sterile), machine tools, paints, pigments, and industrial equipment in study zone C may have caused the highest concentration of Fe and Ni in the soil samples in this area [9, 10].

The Trepça complex's ongoing toxic waste disposal (sampling zone B) which enriches the ore Pb-Zn, is to blame for the high concentration of heavy metals in toxic waste and soil. Our findings suggest that mining operations have a significant impact on the presence of metal contamination in study zone B (M4). A high metal concentration was observed for Mn (8683 mg/kg), As (4739 mg/kg), Fe (2241 mg/kg), Pb (3364 mg/kg), and Zn (2394 mg/kg).

Study zone C is located very close to settlements, whereas ash waste contains natural magnetic minerals, which can raise heavy metal concentrations [4–7]. At study zone C, the contents of Fe (28 370 mg/kg) (M7), Cr (4262 mg/kg) (M8), and Mn (1302 mg/kg) (M7) were higher than those of other elements, which are suspected to be from the wasteland ash, agricultural fertilizers [9–11], as well as traffic waste. This is known because of the proximity of zone C to the power plant TC Kosovo factory.

3.2. CORRELATION ANALYSIS

A strong correlation between the Ni with Pb, and Cr with Pb (Table 2) indicates that their base arises from toxic waste and ash landfill side [19–23]. These toxic metals in the soil are a very common occurrence in the vicinity of landfill toxic waste and power plants (coal-fired), and lignite combustion and its unburned residuals are responsible for this situation [18–23]. Correlations between As with Pb and Cd with Ni (in zone C), shown for the level of significance $p < 0.05$, are negative. The results for Ni and Pb have a strong positive correlation, which means that high x-variable scores go with high y-variable scores (and vice versa). Whereas, As, Cr, and Cd have a negative moderate correlation.

Table 2

Heavy metal correlation analyses in zones A, B, and C

Sampling zone A – Gllogoc				
↓ x	Pb	Ni	Cr	As → y
Ni	0.944			
Cr	0.309	–0.022		
As	0.867	0.983	–0.206	
Cd	0.74	0.476	0.869	0.306
Sampling zone B – Mitrovica				
Ni	0.012			
Cr	–0.267	0.96		
As	0.986	–0.156	–0.425	
Cd	0.966	0.269	0.01	0.91
Sampling zone C – Obiliq, TC (power plant)				
Ni	0.684			
Cr	–0.993	–0.766		
As	–0.258	0.528	0.142	
Cd	–0.98	–0.526	0.95	0.445

3.3. CONTAMINATION FACTOR (CF_i) AND POLLUTION LOAD INDEX (*PLI*)

The soil was classified as having a high contamination degree in three tested regions, with middle contamination degree due to Pb, Ni, As, and especially high contamination degree by Cd and As (M4) (Table 3, according to criteria given in Table 6). As a result, the contamination factor may provide a thorough assessment of the overall enrichment and contamination impact of various pollutant groups in the soil and toxic waste. Significant correlations indicate that they are thought to be industrial, originating from industrial activities such as the production of Fe-Ni and Pb-Zn ores. The three analyzed areas are about 20 km of airlines the one from other, which is thought to contribute to the accumulation of heavy metals in soil and toxic waste in these areas [3–8].

Table 3

Contamination factors (CF_i) and pollution load indices (*PLI*) of heavy metals in toxic waste, ash and soil in zones A, B and C

Sample	CF_i					*PLI*
	Pb	Ni	Cr	As	Cd	
Sampling zone A – Gllogovc – New Co Ferronickeli						
M1 (scoria)	0.48	9.23	65.75	0.42	7.98	1.18
M2 (scoria)	0.50	12.57	17.92	1.31	6.28	1.13
M3 (soil)	0.44	7.66	6.36	0.28	3.02	1.10
Sampling zone B – Mitrovica						
M4 (waste)	33.64	0.37	0.26	94.78	12.36	1.20
M5 (waste)	0.90	0.07	0.16	0.27	0.42	1.00
M6 (soil)	6.93	0.89	1.25	0.83	5.46	1.09
Sampling zone C – Obiliq TC (power plant)						
M7 (ash)	0.66	3.49	28.39	5.57	4.04	1.14
M8 (ash)	0.51	3.19	42.62	1.48	4.42	1.16
M9 (soil)	0.96	3.46	9.71	1.16	1.66	1.10
Baseline reference value, mg/kg	100	100	100	50	5	*PLI* > 1 (contaminated)

The *PLI* was derived from the CF_i values to calculate the toxic metal pollution [18–23]. In all toxic waste, ash, and soil samples, the analyzed *PLI* > 1 (Table 3) indicates the presence of sample pollution.

3.4. ECOLOGICAL RISK ASSESSMENT (*ERI*)

The *ERI* index stands for the potential ecological risk factor of toxic metals [21, 24, 26]. The estimated *ERI* values for chosen metals (Pb, Ni, Cr, As, and Cd) are presented in Table 4. From the obtained results and criteria (Table 6), all toxic waste, ash, and soil samples showed a high ecological risk [17, 18, 26]. The maximum *ERI* value (379.12) was observed for As and the lowest one (0.32) was noted for Cr. This study revealed that Cd in all zones posed the highest ecological threat, whereas, in zone A (M1), Cr exhibited the highest ecological risk (*ERI* amounted to 131.50). As (M4) and Pb (M4) in zone B posed the highest ecological threat (the *ERI* values reached 379.12 and 168.20, respectively). The study also revealed that Cr in zone C (M8) posed the highest ecological threat (*ERI* amounted to 85.24).

Table 4

Ecological risk assessment (*ERI*) of heavy metals in scoria, waste, soil and ash samples

Sample	Pb	Ni	Cr	As	Cd
Sampling zone A – Gllogovc – New Co Ferronickeli					
M1 (scoria)	2.40	46.15	131.50	1.68	55.86
M2 (scoria)	2.50	62.85	35.84	5.24	43.96
M3 (soil)	2.20	38.30	12.72	1.12	21.14
Sampling zone B – Mitrovica					
M4 (waste)	168.20	1.85	0.52	379.12	86.52
M5 (waste)	4.50	0.35	0.32	1.08	2.94
M6 (soil)	34.65	4.45	2.50	3.32	38.22
Sampling zone C – Obiliq, TC (power plant)					
M7 (ash)	3.30	17.45	56.78	22.28	28.28
M8 (ash)	2.55	15.95	85.24	5.92	30.94
M9 (soil)	4.80	17.30	19.42	4.64	11.62

3.5. GEOACCUMULATION INDEX (I_{GEO}) OF TOXIC METALS IN SOIL

The calculated values of the geoaccumulation indices (I_{geo}) for toxic metals in soils at the industrial zones A, B, and C are presented in Table 5. I_{geo} is highly variable, implying that the soil surrounding the sampling area was from strongly to moderately contaminated with the metals tested. The average values obtained for I_{geo} (zone A) were as follows: Pb 9.61, Ni 16.00, Cr 17.61, As – 11.31, and Cd – 10.21. It can be seen that the maximum value has been reached by Cr (17.61). For values of $I_{geo} > 5$ (Table 6) [22, 23] soil is extremely contaminated. Based on the average values of all toxic metals (zone A) it can be concluded that the soil belongs to the class extremely contaminated (Table 5). For zone B, the average values obtained for I_{geo} were as follows: Pb 1.20, Ni –1.76, Cr –1.43, As 5.60, and Cd 5.66. It can be seen that the maximum value has been reached for Cd (5.42). Based on the average values for all toxic metals in zone B, it can be concluded that the soil belongs to the partially contaminated class. As for zone C, for the same elements, their values were Pb .08, Ni 1.17, Cr 4.16, As – 2.05, and Cd – 4.81 (strongly to extremely contaminated). Also, this zone is practically contaminated.

The distribution of items that were compared throughout the three research topics is shown in Fig. 2. The letters A, B, and C are included in brackets to denote the research area. The metals are divided into three categories by the first main component [24] (at different zones).

Table 5

Geoaccumulation index (I_{geo}) of heavy metals in soils

Sampling zone A – Gllogovc, New Co Ferronickeli		
Metal	I_{geo} value	I_{geo} class
Pb	9.61	extremely contaminated
Ni	16.00	extremely contaminated
Cr	17.61	extremely contaminated
As	11.31	extremely contaminated
Cd	10.23	extremely contaminated
Sampling zone B – Mitrovica		
Metal	I_{geo} value	I_{geo} class
Pb	1.20	uncontaminated to moderately contaminated
Ni	−1.76	practically uncontaminated
Cr	−1.43	practically uncontaminated
As	5.60	extremely contaminated
Cd	5.66	extremely contaminated
Sampling zone C – Obiliq, TC (power plant)		
Metal	I_{geo} value	I_{geo} class
Pb	−3.08	practically uncontaminated
Ni	1.17	uncontaminated to moderately contaminated
Cr	4.16	strongly contaminated
As	2.05	moderately to strongly contaminated
Cd	4.81	strongly to extremely contaminated

Table 6

Pollution/ecological indices, classification, and interpretation [17–26]

Index	Classification	Interpretation
I_{geo}	$I_{geo} < 0$	uncontaminated
	$I_{geo} < 2$	between uncontaminated and moderately contaminated
	$2 < I_{geo} < 3$	between moderately and strongly contaminated
	$3 < I_{geo} < 4$	strongly contaminated
	$4 > I_{geo} < 5$	between strongly and extremely contaminated
	$I_{geo} \geq 5$	extremely contaminated
CF_i	$CF_i < 1$	low contamination
	$1 \leq CF_i < 3$	moderate contamination
	$3 \leq CF_i < 6$	considerable contamination
	$CF_i \geq 6$	very high contamination
PLI	$PLI = 0$	perfection
	$PLI < 1$	baseline level
	$PLI > 1$	contaminated
ERI	$ERI < 40$	low ecological risk
	$40 \leq ERI < 80$	moderate ecological risk
	$80 \leq ERI < 160$	considerable ecological risk
	$160 \leq ERI < 320$	high ecological risk
	$ERI \geq 320$	very high ecological risk

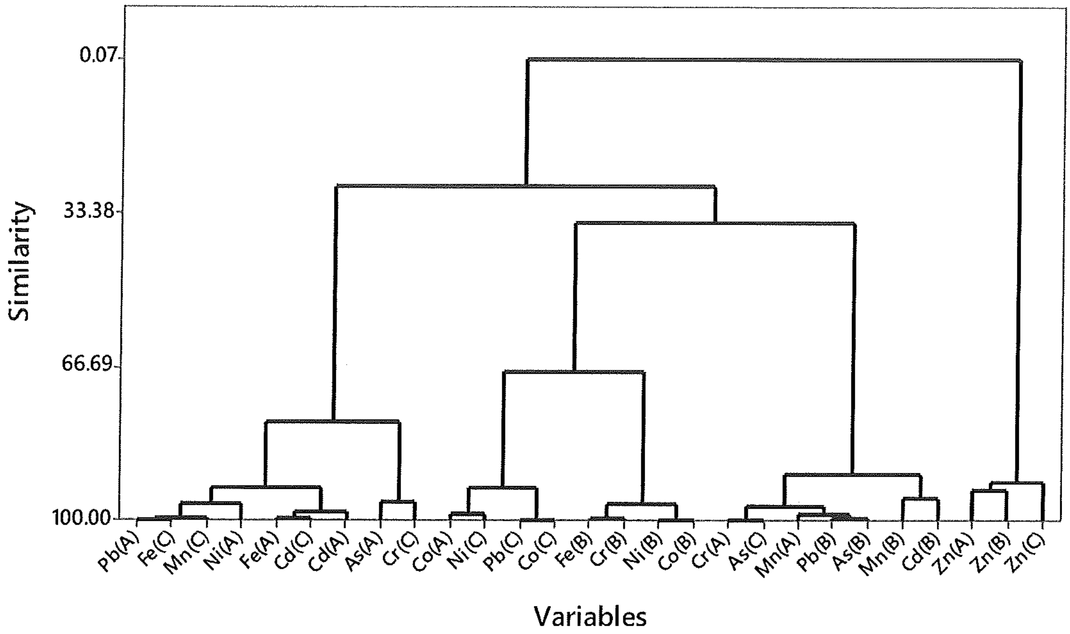

Fig. 2. Dendrogram analysis of the elements present in the locations zone (zone A, B and C)

The group consists of three component groups for metals: Cr, As, Mn, Cu, Pb, Cd, and Co, and one element, Zn. The first basic component group for metals is Pb, followed by Fe, Ni, Mn, Cu, Cd, As, and Cr. The second basic component group which comprises the metals is made up of the following elements: a) Pb, Fe, Ni, Mn, Cu, Cd, As, and Cr, b) Cr, As, Mn, Cu, Pb, Cd, and Co, and c) Zn. This supports the regression results, confirming their pollution source. Generally, the above results show the metal pollution distribution within the different sampling positions. The study confirms that the use of toxic waste, scoria-sterile material, ash and soil, can serve to monitor heavy metals [25–28].

4. CONCLUSIONS

A vital part of the biosphere is the soil, and any deterioration in its quality can have negative effects on human life. Heavy metals in the soil pose a serious hazard to human health, especially when they enter the food chain. Fe, Ni, Cr, Mn, Cu, Zn, and Pb contamination levels were significantly higher than those recommended by the Dutch Target and Intervention Values 2000 and Environmental Protection Agency.

Mining activities that can release substantial amounts of heavy metals into the environment have a significant impact on the occurrence of metal contamination in the study zones. The soil around the test site was contaminated with heavy metals, according to the highly variable geoaccumulation index, a measure of soil contamination. In zone A, heavy metal concentrations were 2–3 times higher than those in zones B and C. Based on the average values of the geoaccumulation index for all toxic metals (zone B) it can be concluded that the soil belongs to the partially contaminated class. Also, zone C is practically contaminated.

The obtained results call for mandatory and long-term monitoring of toxic metals in the soil, as well as comprehensive research about adverse environmental and health factors. The national government and the local residents in general need to acknowledge the grave risks of toxic metal contamination and prioritize the work on sustainable solutions to mitigate the current risks.

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