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Research Paper

Air Quality Prediction Using Programming Language in Konya

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Abstract: Air quality is a critical factor in terms of human health and environmental sustainability. The aim of this study is to examine the success of machine learning algorithms in air quality prediction. Using air quality data and meteorological data of Konya city, the performances of many algorithms such as Linear Regression, Random Forest, Ridge Regression, AdaBoost and Bayesian Ridge were compared. The results show that Extra Trees Regression model has the highest accuracy rate in predicting SO$_2$ pollutant, while Gradient Boosting Regression model is in second place. Gradient Boosting Regression model has the highest accuracy rate in predicting PM10 pollutant, while Extra Trees Regression model is in second place. This shows that Extra Trees Regression and Gradient Boosting Regression models can successfully learn long-term dependencies especially in time series data. Light Gradient Boosting Machine showed strong performance and ranked third in predicting both pollutants. It was observed that other machine learning algorithms have significant potential in air quality prediction but provide limited accuracy. The study emphasizes that the use of deep learning techniques will provide great benefits for the development of air quality prediction systems and that more generalizable models should be created. In addition, it is anticipated that future studies on larger data sets and different geographical regions will contribute more to air quality prediction.

Keywords: *Machine Learning, Air Pollution Forecast, Air Quality, Deep Learning*

Introduction

Air pollution poses a serious threat to human health and environmental sustainability on a global scale. According to the World Health Organization (WHO), millions of people die every year due to air pollution-related causes (WHO, 2024). In this context, predicting air quality is of critical importance both for taking protective measures at the individual level and for the timely implementation of public policies. With the development of machine learning (ML) techniques in recent years, higher accuracy results can be obtained as an alternative to traditional statistical methods in air quality prediction. In particular, machine learning algorithms are successfully used in short and medium-term predictions of pollutants such as PM$_{2.5}$, PM$_{10}$ and NO$_2$ (Xiang *et al*., 2016).

Machine learning algorithms have the capacity to model complex relationships by analysing many factors such as sensor data, meteorological variables (temperature, humidity, wind speed, etc.) and traffic density. This study examines the role of machine learning techniques in air quality prediction and aims to comparatively evaluate the accuracies of different algorithms (Xue *et al*., 2020). Studies on air quality prediction can be generally examined in two main groups: statistical methods and machine learning algorithms. In the early studies, time series analysis-based models such as ARIMA (AutoRegressive Integrated Moving Average) were frequently preferred. However, these models have achieved limited success in complex and variable air pollution data due to their dependence on linear relationships (Box *et al*., 2015).

With the development of machine learning, especially supervised learning techniques have begun to be used effectively in air quality prediction. Kaplan et al. (2014) in their study titled Estimation of PM10 and SO$_2$ substances that cause air pollution using artificial neural networks and calculation of error rate, it was aimed to predict PM$_{10}$ and SO$_2$ pollutants that cause air pollution using Levenberg-Marquardt learning algorithm. Levenberg-Marquardt algorithm, which is one of the learning algorithms of the feedback model in artificial neural networks, is a system that approaches the error surface parabolically at each iteration stage and the minimum parabola angle represents the result for that step. In this study, Wind, Humidity, PM$_{10}$ and SO$_2$ data taken every hour for 5 days belonging to Kütahya province were used. 96 of the data used were used as training and 24 as test data. A 3-layer feedback

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network structure was created using MATLAB artificial neural networks toolbox. The tangent sigmoid function was used as the activation function, and 30 neurons were selected in the intermediate layer, and the weights were changed in the feedback using the Levenberg-Marquart learning algorithm. As a result, because of using 5-day air pollutant concentration and meteorological data in Kütahya province, the pollutant estimate of the 6th day was realized and the estimates largely coincided with the real data. According to this model, the normalized PM10 root mean square error value was 0.0161 and the SO_2 root mean square error value was 0.0372 (Kaplan *et al*., 2014).

In the study Gültepe (2019) conducted on developing models to predict air pollution with various machine learning algorithms in Kastamonu province, Artificial Neural Networks (ANN), Random Forest, K-Nearest Neighborhood, Logistic Regression, Decision Tree, Linear Regression and Naive Bayes methods were used as prediction models. In the performance evaluations of the methods used on the Kastamonu DataSet, it was determined that there were statistically significant differences in terms of the Explanatory Coefficient (R2), Mean Squared Error (MSE), Root Mean Square Error (RMSE) and Mean Absolute Error (MAE) metrics. As a result of the study, it was seen that the correct prediction rate for the ANN model was 87% and the other machine learning models, Random Forest accuracy rate was 99% and Decision Tree accuracy rate was 99%, giving the most successful results in prediction. The Linear Regression method exhibited a very poor performance with an accuracy rate of 30% (Gültepe, 2019).

Garip's (2017) studied the estimation of CO2 emissions in 10 OECD countries with machine learning. 80% of the data was used for training and 20% for testing. Three methods; M5P, support vector machine (SVM) and artificial neural networks (ANN) were used as machine learning methods. After the estimations were made, statistical functions such as Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE) and Root Mean Square Error (RMSE) were used to evaluate the performance of the applied machine learning methods. As a result of the estimations, it was seen that the SVM machine learning method made quite successful estimations in 7 out of 10 countries. It was understood that SVM was more successful than ANN and M5P (Garip, 2017).

Dokuz et al. (2020) provided a study that can prevent selection confusion regarding the problem of which parameters should be examined with which method and how in machine learning, which is used as a tool in improving air quality. The study titled machine learning algorithms were introduced and many studies that performed air pollution estimation with machine learning were examined. As a result of the examinations, it was determined that the data volume to be used in algorithm selection significantly affects the algorithm success; pollutant parameter selection for the application area; the presence of a real air quality station to verify the algorithm result; a good data volume that can take meteorological variability into account; importance should be given to data regularity, quality and precision; The analysis technique should be determined according to the spatial distribution of the estimated concentration amounts obtained, whether it is an urban or rural area, the necessity of defining the topography and the type of land use. Paying attention to these headings will increase the accuracy percentage of the study to be conducted (Dokuz *et al*., 2020).

Methods such as random forest, support vector regression (SVR), k-nearest neighbour (k-NN) and gradient boosting algorithms (XGBoost) are also frequently preferred in multivariate air quality prediction problems (Dokuz *et al*., 2020). These algorithms can model the complex relationships between meteorological factors and air pollution and provide high accuracy rates, especially in short-term forecasts. However, current studies are mostly based on a single region or limited datasets. Therefore, it is necessary to develop models that are highly generalizable and tested in different geographical and climatic conditions. In addition, lightweight and fast models that can be integrated into real-time forecasting systems are also important for practical applications. Based on the findings of previous studies, this study compares different machine learning algorithms for air quality prediction and evaluates their performance on multivariate data.

Materials and Method

In this study, various machine learning algorithms were applied for air quality prediction and the prediction performances of these algorithms were comparatively examined. PM10 (Particulate Matter 10 micron) and SO_2 (Sulfur dioxide) concentration were selected as the prediction target. These components are considered to be the most critical indicators of air quality since they directly affect human health.

Dataset

The dataset used is the Konya PM10 and SO_2 dataset obtained from the General Directorate of Meteorology. The dataset includes air pollution data collected from an air quality monitoring station in Konya, Turkey, and meteorological data collected from a meteorological station between 01.01.2007 and 31.12.2024. The main features included in the dataset are:

- Year, month, day, hour
- PM10 ($\mu g/m^3$) – target variable
- SO_2 (mg/m3) – target variable
- Temperature (°C)
- Pressure (hPa)
- Wind speed (m/s)
- Humidity (%)
- Cloudiness

Missing values were completed by interpolation method in the data pre-processing stage.

Algorithms Used

The following machine learning algorithms were applied to create the prediction model.

- **Gradient Boosting Regression:** It combines weak learners (*e.g.* decision trees) in a sequential manner and each subsequent model focuses on correcting the errors made by the previous models. This iterative process helps in capturing nonlinear relationships effectively.
- **Extra Trees Regressor:** This class implements an estimator that applies a series of random decision trees (aka extra trees) to various subsamples of the dataset and uses averaging to improve prediction accuracy and control overfitting.
- **Light Gradient Boosting Machine:** Light gradient boosting machines (LightGBM) are new generation ensemble learning algorithms based on decision trees that work under the gradient boosting framework (Üstüner, Abdikan, Bilgin, and Şanlı, 2020).
- **Random Forest Regressor:** It is an ensemble learning method that combines multiple decision trees to make predictions. It can capture nonlinear relationships by summing the predictions of individual trees (Üstüner et al., 2020).
- **K Neighbors Regressor:** KNN is a simple nonparametric algorithm that estimates the target variable according to the average of the nearest neighbors in the input space. It can capture nonlinear relationships by taking into account the local structure of the data.
- **Linear Regression:** It is a data analysis technique that estimates the value of unknown data using another related and known data value. It mathematically models the unknown or dependent variable and the known or independent variable as a linear equation.
- **Ridge Regression:** Used to analyze multivariate regression data. The aim is to find the coefficients that minimize the sum of squared errors by applying a penalty to these coefficients.
- **Least Angle** Regression: In statistics, it is an algorithm used to fit linear regression models to multidimensional data (Aytekin, 2021).
- **Bayesian Ridge Regression:** BRR serves as a domain-oriented, supervised feature selection method that selects the main features by calculating the coefficients for each feature (Almutiri, Alomar, and Alganmi, 2024).
- **Lasso Regression:** Least Absolute Shrinkage and Selection Operator. It performs both variable selection and regularization to increase the predictive accuracy and interpretability of the model it produces (Ranstam and Cook, 2018).
- **Lasso Least Angle Regression:** A regularization method called LARS Lasso (Least Angle Regression Lasso) is used to reduce the number of features in linear regression and increase the predictive ability of the model. Here, certain regression coefficients are reduced to zero by penalizing the absolute values of the regression coefficients. By successfully eliminating unnecessary features from the model, the data is represented in a simpler and easier to understand manner.
- **Elastic Net:** The purpose is the same as ridge and lasso regression, but elastic net combines ridge and lasso regression. Ridge regression style penalization and lasso regression style variable selection.
- **Orthogonal Match Regressor:** It is a statistical method designed to help testers examine multiple variables, their interactions, and possible combinations (Jain, 2024).

- **Huber Regressor:** Huber Regressor optimizes the squared loss for samples with $|(y - Xw - c) / \text{sigma}| < \text{epsilon}$ and the absolute loss for samples with $|(y - Xw - c) / \text{sigma}| > \text{epsilon}$, where model coefficients w, intercept c, and scale sigma are the parameters to be optimized (Scikitlearn, 2025).
- **Dummy Regressor:** A dummy regressor is a simple machine learning model that predicts numerical values using basic rules without actually learning from the input data (Baladram, 2024).
- **Adaboost Regressor:** It is an ensemble classifier method that combines weak learners to form a strong learner. In each iteration, it calls a simple learning algorithm called a base learner and assigns a weight coefficient to the learner that is inversely proportional to its error. The solution is obtained as a result of weighted voting based on the weight coefficients (Acılar, 2020).
- **Passive Aggressive Regressor:** A category of machine learning where you train incrementally by feeding it examples sequentially, either one by one or in groups called mini-batches (Harwal, 2021).
- **Decision Tree Regressor:** A Decision Tree for regression is a model that predicts numerical values using a tree-like structure. It divides the data by basic features, starting from the root question and branching out. Each node asks a question about a feature and divides the data further until it reaches the leaf nodes, which have the final predictions. To get a result, you follow the path that fits the features of your data from the root to the leaf (Baladram, 2024).
- **LSTM (Long Short-Term Memory):** A type of recurrent neural network that can make powerful predictions on time series.

Assessment Criteria

The following performance metrics were used to evaluate model performance:

- **MAE (Mean Absolute Error):** Average of the absolute values of errors.
- **MSE (Mean Squared Error):** Average of the squared difference between the predicted values and the true value.
- **RMSE (Root Mean Square Error):** Root mean square of the error.
- **R^2 (Determination Coefficient):** The proportion of variance that the model can explain.
- **RMSL (Root Mean Square Deviation):** One of two closely related and frequently used measures of the difference between the true or predicted values and the observed values or an estimator.
- **MAPE (Mean Absolute Percentage Error):** Average of the absolute percentage values of errors.
- **TT (Terrestrial Time):** A modern astronomical time standard used for measuring the time of astronomical observations made from the Earth's surface.

The training of the models was performed with a data separation of 70% training and 30% testing. Due to the time series structure, the data was divided sequentially without mixing. In LSTM, the data sets were divided into 45 days and the 46th day was predicted. The model was trained in this way.

Table 1. Assessment of algorithms for PM10

PM10								
MODEL		MAE	MSE	RMSE	R2	RMSLE	MAPE	TT(Sec)
lstm	Long Short-Term Memory	5.9148	76.8823	8.7683	0.9168	0.3393	0.3296	0.1658
gbr	Gradient Boosting Regression	23.2587	1155.0933	33.9474	0.3557	0.5111	0.5137	0.1740
et	Extra Trees Regressor	23.5310	1169.7608	34.1679	0.3470	0.5138	0.5179	0.2550
lightgbm	Light Gradient Boosting Machine	23.2645	1172.8358	34.2291	0.3429	0.5076	0.4999	0.0780
rf	Random Forest Regressor	23.5947	1180.0147	34.3234	0.3404	0.5160	0.5196	0.4310
knn	K Neighbors Regressor	24.7402	1327.2976	36.3886	0.2595	0.5375	0.5281	0.0230
lr	Linear Regression	27.6477	1511.2190	38.8066	0.1608	0.6258	0.6502	0.9430
ridge	Ridge Regression	27.6474	1511.2181	38.8066	0.1608	0.6258	0.6502	0.0160
lar	Least Angle Regression	27.6477	1511.2191	38.8066	0.1608	0.6258	0.6502	0.0180
br	Bayesian Ridge	27.6388	1511.2050	38.8063	0.1608	0.6254	0.6500	0.0190
lasso	Lasso Regression	27.5956	1515.5887	38.8063	0.1586	0.6163	0.6494	0.0190
llar	Lasso Least Angle Regression	27.5956	1515.5872	38.8062	0.1586	0.6163	0.6494	0.0200
en	Elastic Net	27.6358	1540.1677	39.1688	0.1455	0.6011	0.6558	0.0170
omp	Orthogonal Matching Pursuit	28.1598	1560.5229	39.4336	0.1334	0.6304	0.6543	0.0160
huber	Huber Regressor	26.2501	1603.1199	39.9490	0.1118	0.5825	0.5387	0.0240
par	Passive Aggressive Regressor	27.7870	1780.4937	42.0832	0.0082	0.6186	0.5780	0.0160
dummy	Dummy Regressor	30.1717	1807.5494	42.4330	-0.0027	0.6434	0.7222	0.0150
ada	Adaboost Regressor	38.9266	2181.1274	46.2900	-0.2091	0.7490	1.0761	0.0820
dt	Decision Tree Regressor	31.5549	2186.2003	46.7293	-0.2262	0.6818	0.6491	0.0230

Experimental Results

In this section, the performances of different machine learning algorithms on the test dataset are presented comparatively. All models were subjected to the same data preprocessing steps and feature set, and their prediction performances were evaluated on seven basic metrics (MAE, MSE, RMSE, R2, RMSL, MAPE, TT).

Performance Comparison

Various calculations were made to evaluate the performance of the test algorithms applied for the estimation of PM10 and $S0_2$ parameters. The decision on which algorithm to choose was made based on these values. Table 1 and Table 2 show the algorithms applied to PM10 and SO_2 parameters and the error metrics frequently used to measure the performance of regression models in machine learning.

Table 2. Assessment of algorithms for SO_2

SO_2								
MODEL		MAE	MSE	RMSE	R2	RMSLE	MAPE	TT(Sec)
lstm	Long Short-Term Memory	5.9148	76.8823	8.7683	0.9168	0.3393	0.3296	0.1658
et	Extra Trees Regressor	6.3378	115.2323	10.6718	0.2539	0.6734	0.9925	0.2530
gbr	Gradient Boosting Regression	6.2792	122.5207	11.0091	0.2112	0.6636	0.9695	0.1760
lightgbm	Light Gradient Boosting Machine	6.3256	120.5423	10.9272	0.2103	0.6673	0.9464	0.0870
rf	Random Forest Regressor	6.4059	124.7666	11.1120	0.1855	0.6780	0.9989	0.4650
knn	K Neighbors Regressor	6.5757	131.5452	11.4035	0.1444	0.6937	0.9691	0.0250
br	Bayesian Ridge	6.5439	140.9541	11.7477	0.1270	0.7095	1.0367	0.0160
v	Linear Regression	6.5490	140.9539	11.7481	0.1269	0.7101	1.0364	1.0510
ridge	Ridge Regression	6.5487	140.9537	11.7480	0.1269	0.7100	1.0364	0.0150
lar	Least Angle Regression	6.5490	140.9539	11.7481	0.1269	0.7101	1.0364	0.0160
lasso	Lasso Regression	6.5492	145.9085	11.9380	0.1009	0.7117	1.1030	0.0180
llar	Lasso Least Angle Regression	6.5492	145.9085	11.9380	0.1009	0.7117	1.1030	0.0150
en	Elastic Net	6.5817	146.6456	11.9695	0.0960	0.7161	1.1199	0.0170
huber	Huber Regressor	6.1340	148.5570	12.0475	0.0841	0.6594	0.8279	0.0180
omp	Orthogonal Matching Pursuit	6.7588	150.1936	12.1185	0.0726	0.7325	1.1540	0.0190
dummy	Dummy Regressor	7.1748	161.9809	12.5909	-0.0020	0.7788	1.2806	0.0160
par	Passive Aggressive Regressor	7.7043	167.2623	12.8040	-0.0458	0.8357	1.2377	0.0170
dt	Decision Tree Regressor	8.5676	233.6124	15.1608	-0.5141	0.8861	1.2196	0.0290
ada	Adaboost Regressor	16.9601	405.3060	20.0504	-1.7660	1.2437	3.4807	0.0840

Interpretation of Results

According to the obtained results, LSTM model showed the best prediction performance among all the algorithms. Thanks to its ability to deal directly with time series data, LSTM proved to be a powerful model in the prediction of PM10 and SO_2 levels.

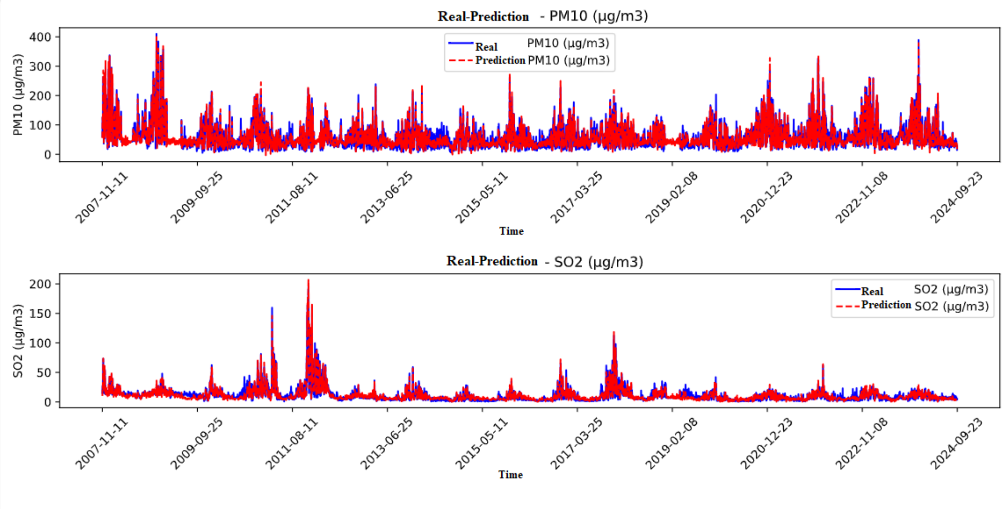
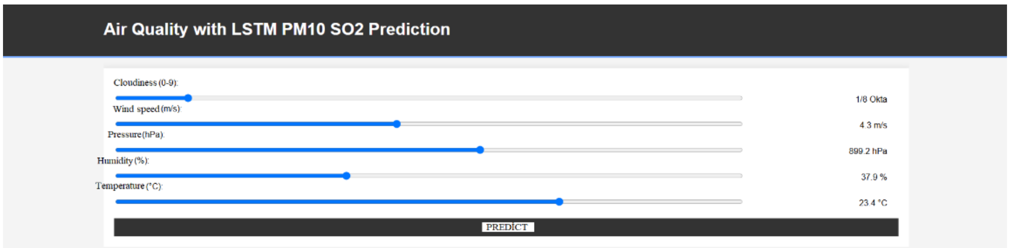


Figure 1. Overlap of real and predicted data for PM10 and SO_2.

Figure 1 shows that the estimated values in the study are in high agreement with the actual values. As a result of the study, an interface was designed, and users are asked to enter current or future meteorological data. Input data is restricted. Here, it is aimed to keep the accuracy rate high by preventing the entry of extremely low or extremely high data. In Figure 2, you can see the home page of the designed interface. After the data entered the interface is completed, when the "Prediction" button is clicked, the "Prediction Results" page opens and PM10 and SO_2 results can be seen on the page. In Figure 3, you can see the results page of the designed interface.



Air Quality with LSTM PM10 SO2 Prediction

Cloudiness (0-9): 1/8 Okta
Wind speed (m/s): 4.3 m/s
Pressure (hPa): 899.2 hPa
Humidity (%): 37.9 %
Temperature (°C): 23.4 °C

Figure 2. Data entry page in the application where air quality forecasting is done.

Prediction Results

Tahmin Sonuçları

PM10: 13.18 µg/m³
SO2: 2.32 µg/m³

Figure 3. Prediction results page in the application where the air quality forecast is made.

Discussion and Comments

The machine learning algorithms used in this study have shown varying success in air quality prediction. The best performance of the LSTM model is related to its ability to learn long-term dependencies in time series data. Since air quality data fluctuates over time due to environmental factors and atmospheric conditions, it is extremely beneficial for LSTM to learn long-term relationships in such data.

Although this study compares machine learning methods for air quality prediction, it offers several important opportunities for improvement:

1. **Real-Time Applications:** The developed forecast models can be integrated into real-time air quality monitoring systems. Such systems not only provide users with instant air quality information, but also can recommend preventive health measures by predicting short-term changes in air quality.
2. **Larger and More Diverse Data Sets:** The data set used in the study is limited to data from Konya city only. In the future, models can be tested with data from different geographical regions and various climatic conditions to obtain more generalizable results.
3. **Deep Learning and Hybrid Models:** The strong performance of LSTM shows the potential of deep learning techniques in air quality prediction. In future studies, more efficient predictions can be made by using hybrid approaches of LSTM and other deep learning networks. In addition, networks such as Convolutional Neural Networks (CNN) can be used in spatial data analysis as well as time series data.
4. **Data Expansion and Feature Selection:** New features can be added to the data set to increase success in air quality prediction. For example, social media data (such as Twitter or Weibo) or dynamic factors such as traffic density can be important factors affecting air quality. In addition, more meaningful features can be obtained by using feature engineering and dimensionality reduction techniques.
5. **Adaptability of the Model and Fast Response Time:** The model used for real-time air quality predictions must be able to adapt quickly to new data. For this reason, continuous updating and adaptation of the model can be provided with techniques such as online learning or transfer learning.

This study has some limitations. First, the fact that the dataset used is limited to only one city limits the generalizability of the model. Air pollution has different dynamics in different geographical regions, so studies conducted in other regions should be evaluated. In addition, the performance of the model may experience accuracy losses in some predictions, especially since it does not consider the effects of external factors (e.g. sudden weather events, disasters or human activities).

Conclusions

This study compared various machine learning algorithms for air quality prediction and found that the LSTM model successfully analysed time series data and achieved the highest accuracy. The results show that machine learning is an important tool in air quality monitoring and prediction systems and that the development of more sophisticated models offers great potential for research in this area. In the future, air quality prediction systems are expected to be developed with algorithms that can make faster and more accurate predictions with larger data sets.

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Research Paper

Optimal Surface Exploitation Planning for the New Lignite Mine in Sibovc, Kosovo

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Abstract: Coal remains a major classical primary energy source and is expected to maintain a dominant role in electricity generation throughout the first half of the 21st century, particularly in Europe. The Balkan Peninsula, and Kosovo in particular, holds significant lignite reserves over 12 billion ton placing the country among the most resource-rich globally. Despite this geological potential, Kosovo's current lignite production remains modest, underscoring the opportunity for expansion to meet growing domestic energy demands and contribute to the regional energy market. The Kosovo Energy Corporation (KEK) plans to increase production to 15 million ton annually by modernizing existing infrastructure and developing new mines, notably the New Sibovc Mine under the N1 alternative. This approach emphasizes efficient resource exploitation, avoids economically marginal areas, and aims to reduce operational losses. As lignite currently supplies approximately 97% of Kosovo's electricity, the further development of the coal sector is vital for ensuring long-term national energy security.

Key words: *Lignite, exploitation, Sibovc, New mine, Kosovo.*

Introduction

Coal belongs to the group of classical primary energy sources. Energy resources represent the fundamental basis for planning and implementing a country's energy strategy. The European Union of Coal Producers (EUROCOAL) predicts that coal in the future, namely until the first half of this century, will be a significant and dominant factor within the framework of energy sources for the production of electricity, and that with the increase in electricity needs there is a tendency for coal production to increase. With the modernization of existing capacities and the implication of new innovative technologies in the coal production process, the own needs of our country, as well as the wider European market region, will be met.

Coal basins are widespread in the Balkan Peninsula and Central Europe, and represent a major contribution to the total balance of coal reserves at European and global levels. During the Tertiary geological period, the largest accumulation of plant material for the formation of major coal reserves occurred in Europe. Of these reserves, the largest amount, about 70%, belongs to lignite-type coal, while about 30% to coal, which in the near future, precisely until the first half of this century, coal will be an important and determining factor in the framework of sources for the production of electricity, and the continuous increase in the need for electricity also conditions the trend of increasing coal production. Lignite coal production in Europe is presented according to data from Euro Coal (Figure 1).

According to available data for 2023 (Figure 2), global lignite production has reached around 337.3 million ton (Mt), with Germany taking the first place as the main producer, followed by Turkey and Poland (IEA). Meanwhile, Kosovo has contributed with a modest amount of 6.9 Mt, despite having large lignite reserves, estimated at over 12 billion ton. This discrepancy between the geological potential and the current level of production indicates an untapped opportunity in the further development of the energy sector in the country (Hyseni & Muzaqi, 2021). In this context, it is reasonable to aim for an increase in production to 15 Mt per year, relying on existing technical capacities and identified resources, in order to meet the strategic objectives of the Kosovo Energy Corporation (KEK). The young Republic of Kosovo sits atop the fifth largest geological lignite reserve on the planet (Arifi & Spath, 2018). Kosovo, in relation to the area and the number of inhabitants with its coal potential of over 12 billion ton of lignite, is the country with the greatest perspective of developing energy capacities for its own and wider needs (Ymeri, 2015).

The Kosovo Basin represents one of the largest and most extensive coal basins of the Balkan Peninsula. Due to its importance and colossal reserves, over the years it has been the subject of study

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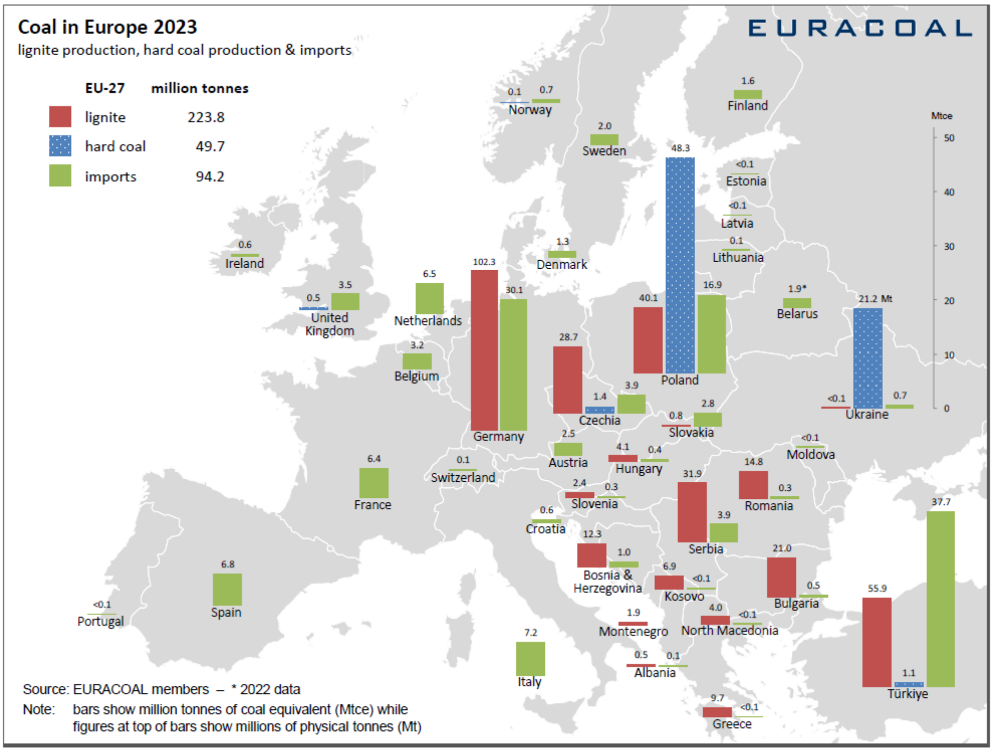
for many local and foreign researchers from various fields. The first studies during the Second World War were of a general geological nature, within the framework of compiling geological maps covering this basin. The most complex and voluminous studies began after the Second World War, around 1950 and continue to this day, mainly in the central and northern part where the main concentrations of coal reserves were located (Mirash, Bardhe and Sibovc coal fields).



Source: EURACOAL members – * 2022 data
Note: bars show million tonnes of coal equivalent (Mtce) while figures at top of bars show millions of physical tonnes (Mt)

Figure 1. Coal (lignite) production in Europe for 2023

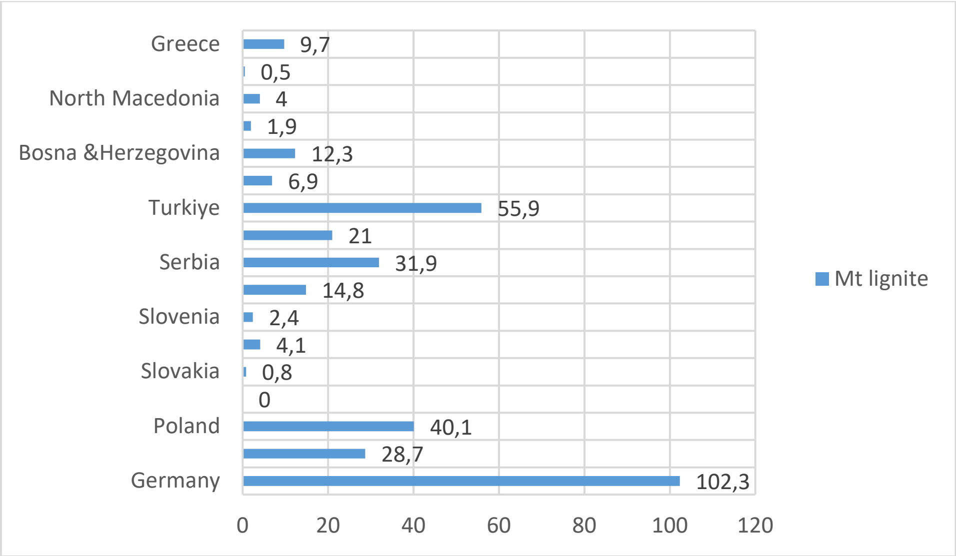


Figure 2. Lignite production by country for year 2023

Considering that the Republic of Kosovo secures about 97% of its electricity needs from the existing The Kosovo A and Kosovo B power plants, which use lignite as raw material, the strategic and development plans of the Kosovo Energy Corporation (KEK) foresee the opening of new surface mines in the Kosovo coal basin. The main goal of these plans is to ensure a stable supply of raw materials for existing power plants, as well as for new planned capacities for thermal energy production. To achieve this goal, it is required to increase lignite production capacities and build new plants for its processing and enrichment. Kosovo possesses significant reserves of lignite, with over 12 billion ton of identified geological reserves, making it the main source of electricity for the country, despite its negative impacts on the environment (Hajra, 2014). According to geological research data, four coal basins have been identified in the territory of Kosovo: the Kosovo Coal Basin, the Dukagjini Basin, the Drenas Basin and the Skenderaj Basin (Figure 3). Among them, the Kosovo Coal Basin is the largest both in terms of surface area and the amount of lignite reserves it contains.

Within this basin, three main fields with high potential for exploitation have been identified: Sibovci Field, Jug Field and D Field (Bytyqi & Goskoli, 2012). In these areas, the opening of three new surface mines is foreseen, where advanced technologies for excavation, transport and storage of lignite will be applied.

In this paper, the focus will be on the treatment of the Kosovo Coal Basin, namely the new mine planned in the Sibovci area. This basin represents the largest and most important area in terms of lignite reserves in the Republic of Kosovo, as well as the most studied from a geological-mining and practical perspective, because several mining sectors have been opened and exploited within it over the years.

The Kosovo Coal Basin contains over 12 billion ton of lignite, formed in the geological time of the Pliocene (Morina et al., 2012). Its central area, known as the "Kosovo Coal Basin", extends over an area of about 270 km². The thickness of the coal seams in this basin reaches up to 100 meters, while the average thickness is about 45 meters (Haxhiu et al., 2013).

The average discovery coefficient for this basin is 1:1.85, indicating a favourable ratio between the amount of cover (overburden) and the mineral body. The depth of occurrence of lignite seams varies from surface outcrops to 310 meters below ground level.

The average quality parameters of lignite in this basin are as follows:

- Low energy value (ETU): 7,400 kJ/kg
- Sulphur content (S): less than 1%
- Non-combustible matter (L): 45-47%
- Moisture (H): 18%

These data show that lignite from this basin represents an energy source of strategic importance for the energy sector of Kosovo, justifying investments in opening new mines such as the one in the Sibovc Field.

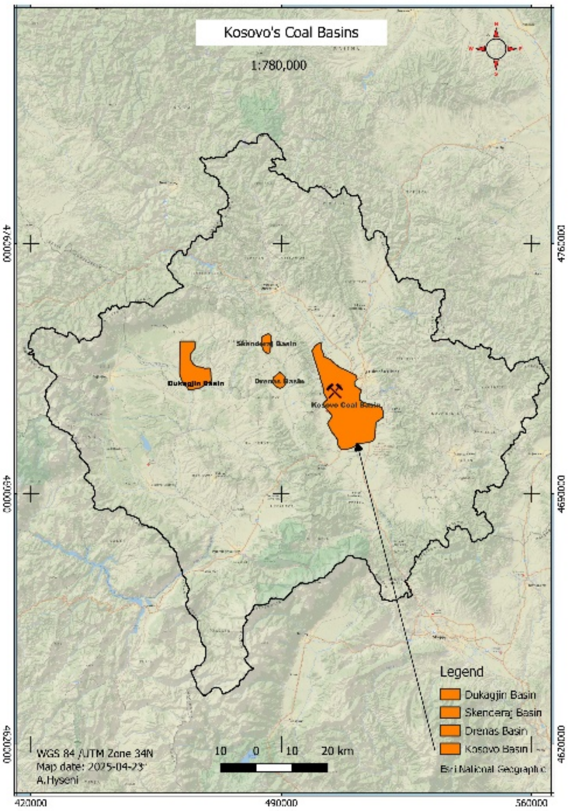


Figure 3. Main coal basins in Kosovo

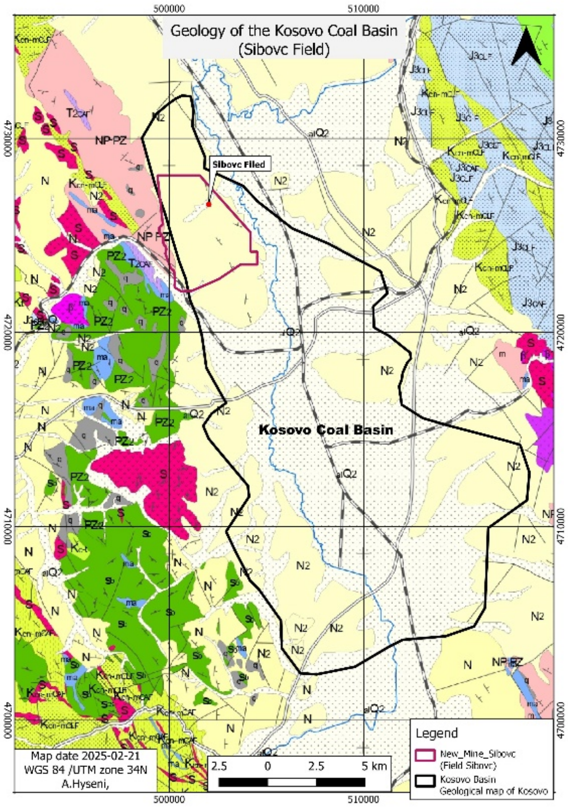


Figure 4. Geology of the Kosovo and Sibovc basin

Geology of the Sibovc deposit

The Sibovc opencast mine or deposit belongs to the Kosovo Coal Basin, which can be identified with the Kosovo Plain, which has a longitudinal north-south extension and a rise towards the west, while the general extension of the basin is northwest - south southeast.

The Sibovc deposit is located on the western side of the Kosovo Tertiary Basin ((Figure 4). This deposit is currently undergoing geological research and assessment for the development of a new opencast mine for the extraction of lignite (Mirena, 2022).

Geologically, the Sibovc coal basin is a Pliocene formation created by freshwater sedimentation, resulting from the displacement between two parallel faults. Tectonic structures in this region lie in a NNW-SSE direction (Mirena, 2019).

The Sibovc mine represents the largest coal deposit in Kosovo, with total reserves of 990 million ton (Mt), of which 830 Mt are considered exploitable. The deposit covers an area of 19.7 km² (Figure 5). The overburden layer reaches a thickness of up to 50 meters, while the coal layer exceeds 55 meters in thickness. The overburden to coal ratio is favourable at 0.9:1 (m^3/t), making extraction efficient. The exploitation of these coal reserves represents a significant challenge for the next 50 years, with an expected annual production of up to 15 Mt (Authors' Group, 2019). Geological and exploration studies conducted so far in this basin have revealed that the lignite layers that represent its geological structure are in fact horizontal or almost horizontal layered deposits and are characterized by a low discovery coefficient, which makes the exploitation of the balanced reserves available in the basin very profitable (Ahmeti & Duraku, 2023). The depletion of lignite reserves in the South-West Sibovci Field Surface Mine has led to the necessity of opening the new Sibovci North Mine to meet consumer demands for lignite. For this, a detailed mining project was drafted in 2019.

The New Sibovc deposit has an average altitude of 620 m above sea level and fluctuates between 500 m and 750 m. The angle of dip of the lignite layer ranges from 100÷40 with a general dip in the direction from southeast to southwest. The floor of the coal layer consists of non-layered clays with a high content of sand and clayey sandstones in the deepest part up to the vicinity of the coal layer. The direct floor consists of green clays with the presence of oily clays and sands. The thickness of the clay is about 50 m. The Sibovc mining field in the west direction generally follows the border of the lignite deposit. In the Northeast direction it is defined by the diagonal orientation North-West-Southeast in the main direction of the Sitnica River flow and is curved in the Southeast in the southern direction along the border of the exploited mine Brandi. The southern border is along the exploited mines Bardhi and Mirashi (Figure 6). Within the surveyed area several geological landslides have been identified and additional cracks have been presented. Most of these structural failures have been observed on the western border of the northern field.

Current use of the Sibovci deposit area There are a number of villages, the most important being Hadja, Shipitull, Leshkoviqi and Sibovci. Most of the surface of this field is used for agricultural purposes.

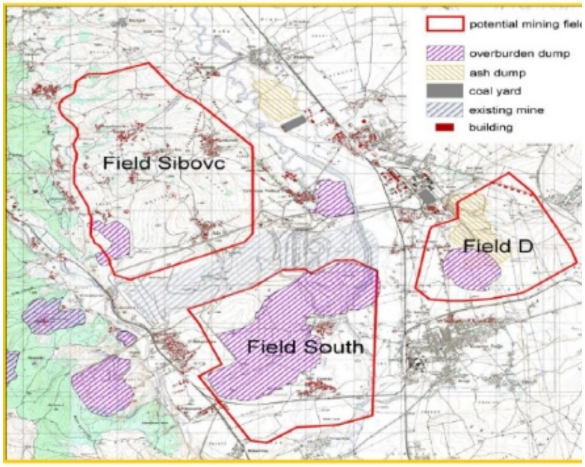


Figure 5. Sibovc Field, South Field and D Field

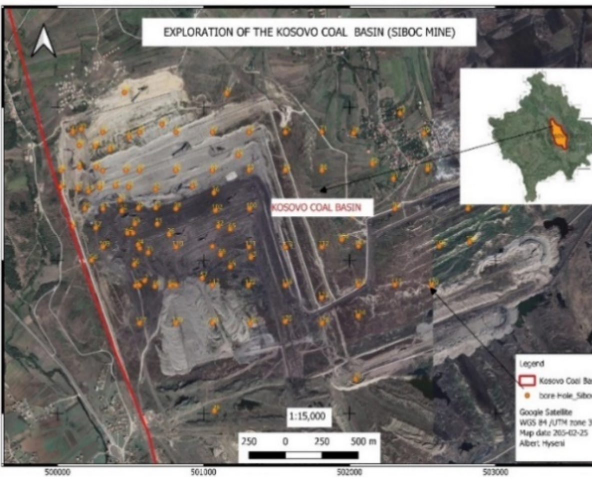


Figure 6. Deep drilling exploration in Sibovc

Material and methods

The exploitation of mineral raw materials in the Sibovc Mining Field is carried out on the basis of the mining project documentation, which includes a series of technical and engineering solutions in accordance with legal requirements and professional standards. The documentation is divided into two main phases: conceptual and operational. The conceptual documentation includes conceptual studies, elaborates and expertise that provide approximate estimates of the exploitation method, the life of the works, the costs and the economic feasibility of the project. The operational documentation contains concrete and detailed solutions for each segment of the mining facility, including: mine contouring, exploitation methods, technical and technological parameters, protective measures, drainage and transportation.

Results and Discussions

Alternatives for the exploitation of the new mine in Sibovci

In this paper, we focus on the Sibovc lignite deposit and its surface exploitation system with the aim of optimizing lignite production (Hyseni & Haliti, 2025). In the Master Plan for the Sibovc Mining Field, it is emphasized that: "If the consumption of raw coal is clearly reduced, the basic project including long ladders would no longer be optimal and would result in a specific increase in production costs". For the opening, preparation and exploitation of the new Sibovc Field mine according to the documentation (Technical Planning, KEK, 2019), three alternatives have been considered:

Alternative N1

- Continued development of the Sibovc-JP mine in a northerly direction;
- No relocation of the southern part of Hada is required from a technological point of view, but planned in time for social reasons;
- No additional equipment is required in the first five years except for necessary repairs to existing excavation, transport and stacking equipment,
- Planning the equipment of the career with additional conveyors with belt widths of 1600 and 1800 mm for all grades due to the progress of the mine,
- Replacement of obsolete coal excavators and conveyor belts in the normal process of purchasing two or three compact excavators with digging capacity and technical and constructional characteristics similar to the SR 1300 and SchRs 650 type excavators;
- Relocation of parts of the village of Sibovc and land acquisition in accordance with the development of the mine.

Alternative N2

- Opening the Hada section in parallel with the continuation of the Sibovc - JP mine. The objective is to develop a mine with a long Sibovc-Jug front;
- Immediate relocation of the entire village of Hade is required;
- Start with mobile or discontinuous equipment (contractor) for heavy overburden management for coal discovery in the Hada region;
- Urgent provision of overburden excavators and conveyor systems
(First commissioning in 2025) due to the required parallel work of Sibovc-JP and the opening of the Hada section).

Alternative N3

- Additional conveyor systems for overburden transport in 2025/2026 due to the required redesign of the Sibovc-JP overburden transport (from the eastern to the western border);
- Application for submission of a permit request prior to the commencement of any mining activities;
- Replacement of obsolete coal excavators and conveyor belts through the normal process of purchasing two or three compact excavators of similar capacity such as SRs 1300/ SchRs 650 (2026/28).
- Relocation of parts of the villages of Sibovc and Leshkoshik and acquisition of land in accordance with the development of the mine.

Considering the potential development of the Sibovc mining field and the current development of the Sibovc South-West mine, for the future development of mining activity we have selected Alternative N1 with the above-mentioned characteristics for the detailed study.

Exploitation of surface lignite ore according to Alternative N1

The exploitation of the New Sibovci Mine according to alternative N1 actually represents the continuation of the exploited Sibovci-J-P mine in the north direction (Figure 7). All main (front) conveyors should be extended with the advancement of mining works in the career. In the center of the 1st system in the cover, the height of the step is higher than the technical height of the excavator excavation. In this part, auxiliary equipment should be engaged in the work processes, i.e. discontinuous shovel-truck excavator system, to clean possible concrete and other waste from the houses and shorten the block height to a maximum of 21 m. The material will be stacked in the western part of the former Bardhi mine. The length of the first step in the cover of the existing mine is 1600 m (Sector 0).

The development of the mine will continue in a Northerly direction (Sectors 0 to 3) exploiting the best part which results in very favourable geological coefficients or cover/lineage ratios (prevailing with a value of 1.0, while in sector 3 it is only 0.6) throughout the life of the mine. It is not necessary to excavate the hills north of Hade and furthermore it is not necessary to relocate the village of Leshkoshik and most of the village of Hade.

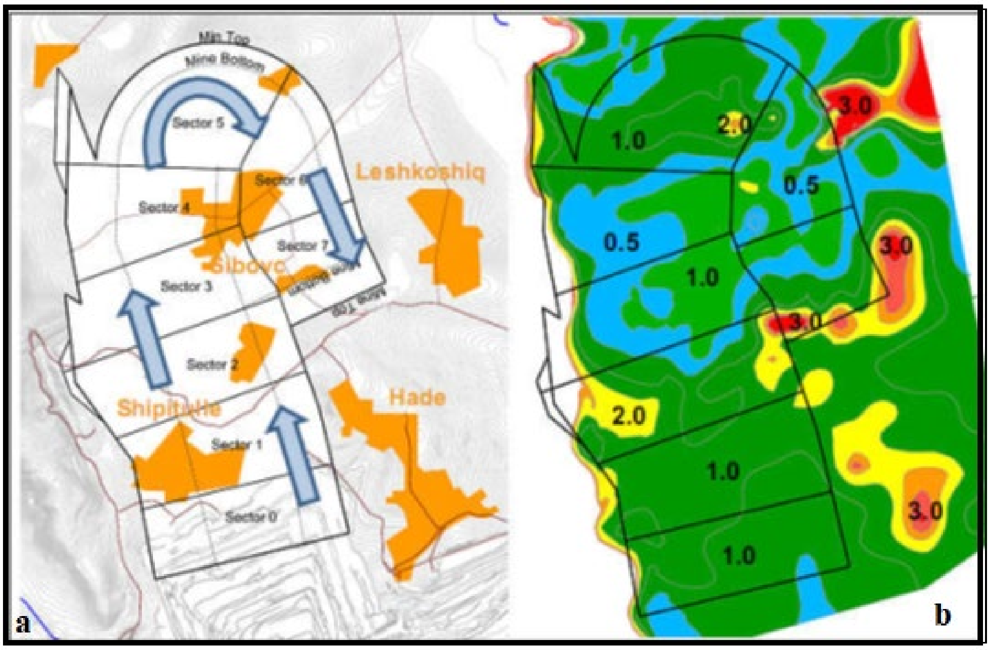


Figure 7. Alternative N1- Mine Development and Discovery Coefficient in the Sibovci Field
a. *Mine development* **b.** *Geological coefficient of discovery*

Starting from Sector 0 which is like the existing Sibovci–SW open pit mine, the mine will be operated with parallel mining operations until the beginning of Sector 4. At the end of Sector 4 the mine switches to clockwise rotation operations. In Sector 6 the mine operation switches from circular front mining operations to longitudinal or parallel front mining operations in the South direction. The discovery coefficient varies between 0.8 and 1.0. The western boundary of the mine in sectors 6 and 7 has already been excavated within sectors 3 and 4. For this reason the cover systems will only excavate the pillar which is blocked under the main conveyors. During the first 5 sectors the mine will not be extended in the east direction (due to the eastern ring slope system with the front conveyors in place). Starting from the completion of sector 5, the mine can be expanded in the east direction. Then, the front conveyors will be installed in the western edge slope system, which will enable the expansion of the mine in the east direction.

The annual mine advancement of the N1 mining alternative on average is 100 meters. The general plan for the advancement of the mining works is given in Figure 8. In this alternative, it is not necessary to exploit the mine in the economically unfavourable parts of the deposit, as well as in the area of the previous underground exploitation. Within the framework of alternative N1, it is also not necessary to excavate the hills north of the Hade village and, moreover, it is not necessary to relocate the village of Leshkoshik and most of the Hade village. Considering the annual demand for coal for Kosovo's total thermal energy capacity is 400 Mt by 2065. For this reason, in the described scenario N1 of mine exploitation, 378 Mt m^3 of waste must be removed, which leads to an excellent average discovery coefficient of 1.0.

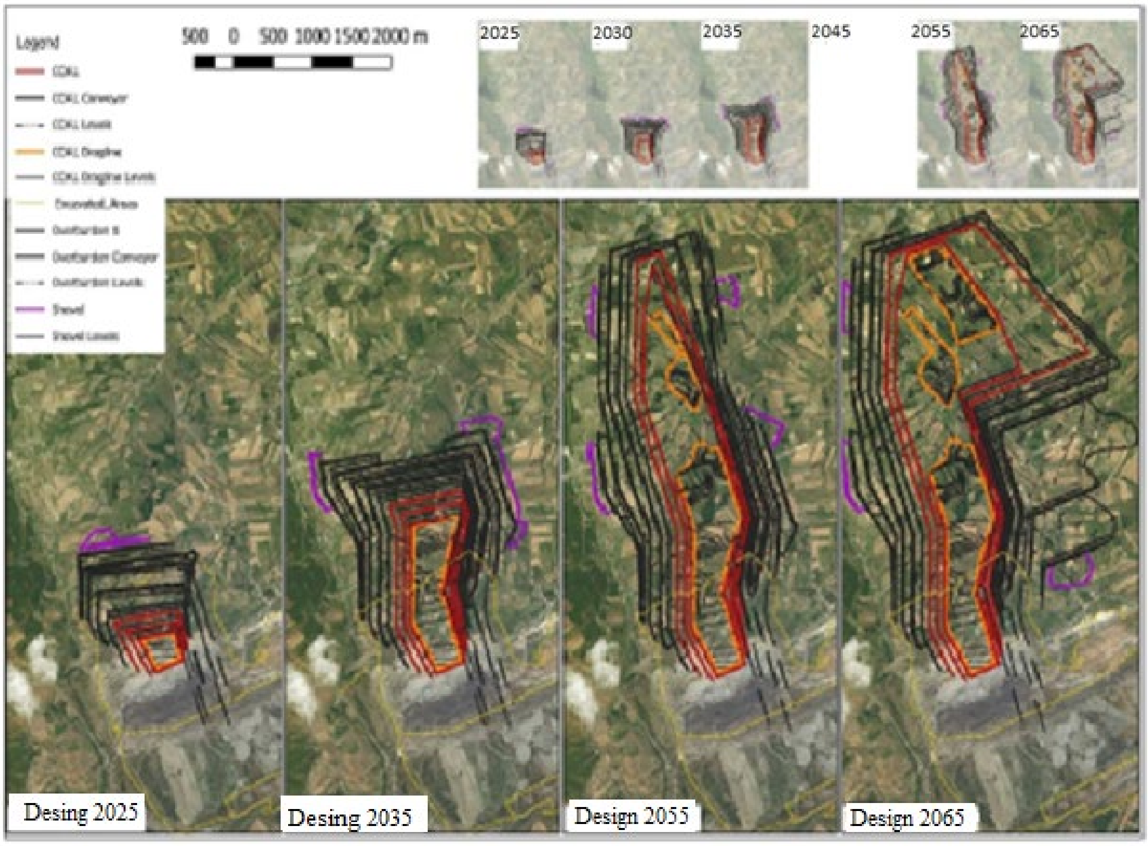


Figure 8. Mining works advancement plan

Conclusion

The Republic of Kosovo possesses one of the largest lignite reserves in Europe, with over 12 billion ton located mainly in the Kosovo Coal Basin. Despite this large geological potential, current production levels remain relatively modest. As Kosovo relies on lignite for approximately 97% of its electricity production, the sustainable and strategic development of this resource is essential for national energy security. This study has highlighted the importance of the Sibovc deposit, particularly the New Sibovc Mine, as a major potential for future energy production.

Through comprehensive geological assessments, the Sibovc deposit has been identified as economically and technically viable for long-term exploitation. Among the proposed development strategies, Alternative N1 has been selected for its efficiency, minimal environmental impact and optimal exploitation ratio. This alternative allows for continuous expansion without the need for major village relocations or excavation of economically unsustainable areas, thus balancing economic development with social responsibility.

The implementation of Alternative N1, supported by modern mining technologies and infrastructure investments, is expected to ensure a stable supply of lignite until at least 2065, ensuring the reliable operation of existing and future thermal power plants. Furthermore, the strategic exploitation of the Sibovc field will strengthen Kosovo's role in the regional energy market, while providing a model for the responsible development of mineral resources in the Western Balkans.

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Research Paper

Evaluation of Pesticides in Soil and Dry fruits (Hazelnuts) of Mallakastra Region, Albania

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Abstract: Dried fruits such as hazelnuts, walnuts, almonds, *etc*. grow naturally in Albania due to suitable climatic conditions. They are widely distributed from coastal to mountainous areas of the country. Recent years the consumption of dried fruits has increased significantly due to the good qualities that these products present for the body. Hazelnuts contain high percentage of vitamins, minerals and antioxidants. Before 2000, dried fruits, including hazelnuts, have been limited on their use (mainly to sweets). Last years, many agricultural lands have been planted with hazelnut fruits due to the economic benefits. For these important food products (dry fruits), analyses of pesticides and other pollutants are important because can directly affect population health. Hazelnut fruits and soil samples were taken in six stations in Mallakastra area. Pesticide analysis was performed in hazelnut fruits according to the EN ISO 15662:2018 Foods of plants origin method which is a multi-residue method for the determination of pesticides using GC/MS/MS and LC/MS/MS techniques. The method allows the simultaneous determination of more than 600 individuals. Sample treatment is based on acetonitrile extraction/partitioning and clean-up by dispersive SPE. The procedure is a modular QUEChERS-method recommended for the analysis of pesticides in samples with lower percentage of water (such as dry fruits). Almost the same procedure was used for treatment of soil samples. Extraction in ultrasound by using acetonitrile and QUECHERS salt for clean-up procedure were used for pesticide analyse from soil samples. It was observed that pesticides were not detected (N.D) or their levels were lower than the limit of defect (LOD < 10 ug/kg) in all analyzed hazelnut samples. Some traces of organochlorine pesticides were found in hazelnut fruits (always below LOD level). The same pesticides were found in soil which could be the main source of pesticides to the fruit. Their presence will not exceed the permitted level for analysed samples but their presence (even in trace level) should encourage the responsible institutions for continuous analysis for both matrices, food products and soil samples.

Keywords: *Dry fruits, Food safety, multi-residue analyse, Soil, Pesticides, GC/MS/MS and LC/MS/MS*

Introduction

Albania has a suitable climate for the growth of many fruit trees including hazelnuts, walnuts, almonds, etc. The suitable climate allows them to grow from coastal areas to mountainous areas. The fruits grown in the country are well-known by their quality due to the autochthonous seeds that are best adapted to the country's climate. Before the 90s, the planting of fruit trees was mainly carried out on poor soils because good soils were mainly used for planting cereals. After the 90s, many agricultural lands (of good categories) were left unplanted due to the fragmentation of lands in small fields (private one) and the emigration of population from rural areas. After the 2000s, the situation changed because many immigrants returned to invest in their homeland and many of the agricultural lands were planted by fruit trees (mainly olives, apples, grapes, etc). Recent years the consumption of dried fruits plays an important role in a balanced diet due to the high content of vitamins, minerals and antioxidants. Dried fruits, including hazelnuts, have been part of Albanian diet since ancient times, but their use was limited

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**Corresponding: E-Mail: aurel.nuro@fshn.edu.al,* mainly to sweets. Hazelnut is a tree that is found almost throughout the territory of Albania, mainly in its wild (natural) form. In recent years (after 2010), hazelnuts and other nuts (walnuts, chestnuts, almonds, etc.) are being cultivated by farmers in many plantations in all Albanian territory, but many of these plantations have been established in agricultural areas where pesticides have been used frequently in the past (Nuro et al, 2007). This was the reason why the level of pesticides in fruit and soil samples must be evaluated. In general, pesticides are not directly applied to hazelnuts, but accumulation processes (from pesticides accumulated in soil) can affect the presence of pesticides to fruits. In September 2024, hazelnut samples were taken from different plantations in Mallakastra area. Samples were selected in this region because Mallakastra is part of Myzeqeja Field, which is the main agricultural area on the country. In this field the application of pesticides has been very frequent from 1946 to 1992 because there has developed a large scale of agricultural activity. Although after the 1990s this activity declined, it revived after the 2000s. Even today this area is one of the most important agricultural areas of the country where large quantities of cereals, fruits, vegetables, medicinal plants, etc. are grown. Also, in this area, the largest hazelnut plantations (and other trees) can be found.

The hazel tree includes any of the nuts deriving from species of the genus Corylus, especially the nuts of the species *Corylus avellana*. Wild hazelnuts are traditionally grown as multi-trunk trees where the rootstock is formed by the variety itself. To enhance the possibility for mechanization and to prevent suckering, a single-trunk tree can be formed by grafting process. Hazelnuts are used as secondary food, mostly as a snack food, in baking and desserts but many studies have shown that their fruits contain high amounts of protein, dietary fibre, vitamin E, iron, thiamine, phosphorus, manganese, and magnesium (Gruine & Correia, 2020; Santillo *et al*, 2004). Also, they contain B vitamins have appreciable content, significant amounts are vitamin K (low levels but necessary for the body), calcium, zinc, and potassium. Hazelnuts are a rich source of dietary fat. The fat components are monounsaturated fat as oleic acid (75% of total), polyunsaturated fat mainly as linoleic acid (13% of total), and saturated fat, mainly as palmitic acid and stearic acid (together, 7% of total) (Gruine & Correia, 2020). Its nutritional value and market demand for this product have made hazelnuts one of the fruits whose production has increased several times higher than their production/consumption before the year 2000. This important fruit should receive the attention of the authorities regarding its quality. Although pesticides are not applied directly to the hazelnut fruit and moreover it is protected by the peel that surrounds it, the transfer of pesticides from the roots to the fruit may be possible (Skibniewska and Smoczynski, 2000). When soils contain high levels of pesticides, they can be the main source of contamination of the fruit with pesticides or other pollutants (Santillo *et al,* 2004; Sefiloglu *et al*, 2021, Silva *et al*, 2019; Wilhelm *et al*, 2002).

Material and Methods

Study Area and Sampling Stations

Hazelnut fruits and soil samples were taken in September 2024 in six different plantations of Mallakastra area (Fig. 1). In this area there is many hazelnut, walnut and almond plantations. This area is included in the Myzeqe Field which is the largest agricultural area in the country. In this agricultural area before the 90s, mainly cereals and vegetables were planted, and pesticides were also constantly used frequently. After the 90s the situation changed due to the division of lands into small plots and the emigration processes of the population. Many lands were not planted and turned into barren (Nuro, 2007). After the 2000s many of these lands were replanted mainly with fruit trees such as olives, apples, grapes, walnuts, almonds and hazelnuts. Their planting in agricultural lands where pesticides had been used earlier prompted us to think about a study both in the soil and in dried fruits to observe the possibility of their passage and the risk to the population (Skibniewska & Smoczynski, 2000; Santillo *et al*, 2004; Sefiloglu *et al*, 2021, Silva *et al*, 2019). Hazelnut samples were dried and closed to the plastic bags. Soil samples were taken at a depth of 0 – 50 cm in the same plantations where the hazelnut samples were taken. The soil samples were left to air dry initially and then ground in a porcelain mortar. They were sieved and only the 63-micron fraction was taken for analysis which has a porosity suitable for pesticide absorption. They were stored in a dry place before their analyses.

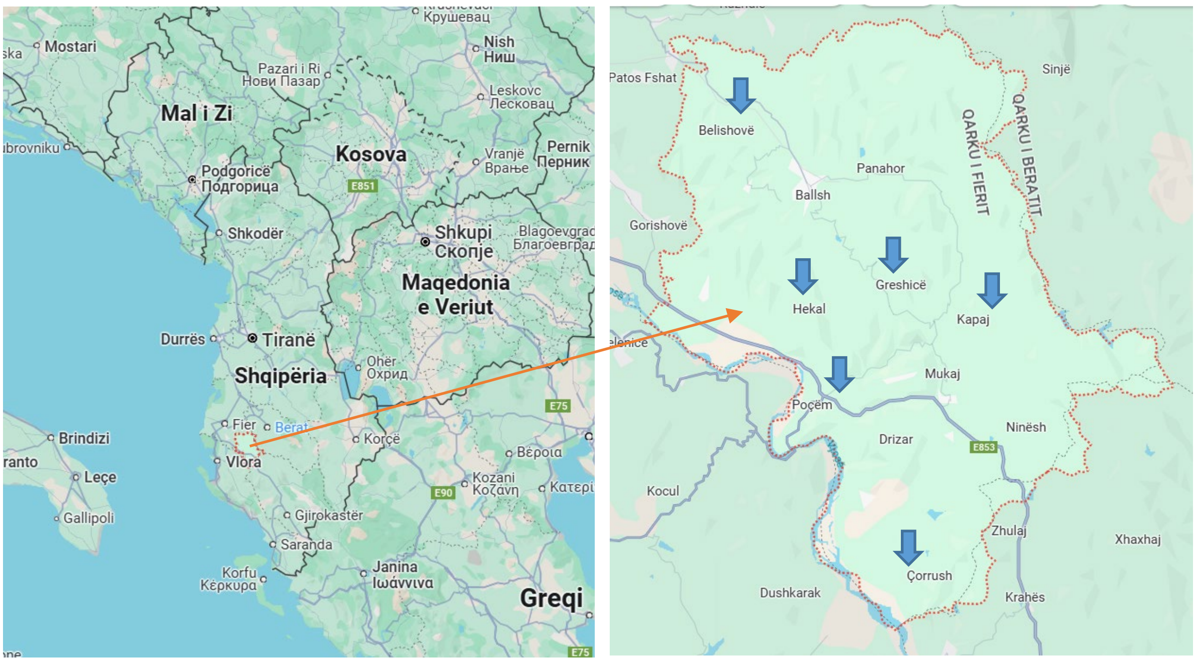

Figure 1. Sampling sites at Mallakastra area, Albania

Sample treatment for multi-residue analyses of pesticides in dry fruits

Pesticide analysis was performed in hazelnut fruits according to the EN ISO 15662:2018. This is a method for foods of plants origin which is a multi-residue method for the determination of pesticides using GC/MS/MS and LC/MS/MS techniques. The method allows the simultaneous determination of more than 600 individuals in a run (in both techniques). Sample treatment is based on acetonitrile extraction/partitioning and clean-up by dispersive SPE. The fruit samples were stored at +4ºC before analysis. The samples were left for about 1 hour at room temperature before analysis. Hazelnut fruits were previously ground in a mill 2 gram of ground dry fruit sample were taken in a Teflon tube. 8 ml of MilliQ distilled water are added and mixed in a vortex. It was left to stand for 10 minutes and then 10 ml of ACN were added to it. It was mixed again in a vortex and after being left to stand for 2 minutes. After that it was treated with citrate tube salt (Quercher 1). The container was placed on an automatic shaker for 5 minutes and then in a centrifuge at 8000 Rpm, at 4oC, for 5 minutes. A quantity of 6 ml of supernatant were taken and transferred to a PSA tube with C18 (Quercher 2) and mixed to a vortex (2 min). After this, the centrifuge was used again at 8000 Rpm, for 5 minutes, at +4ºC. The supernatant was filtered through a 0.45 um filter using a syringe and collected in two different chromatographic vials. The vial to be analysed in the LC/MS/MS technique was injected directly while the vial to be injected into the GC/MS/MS apparatus was first dried completely under a nitrogen stream and then recovered with 1 ml of the mixture Ethyl acetate/n-Hexane (3/7). In addition, the calibration curve were built for pesticides in concentrations of 1, 5, 10, 25 and 50 ug/l for both devices (Silva et al, 2019; Nshimiyimana et al, 2014; Mahdavi et al, 2021; Lozowicka et al, 2017; Homazava et al, 2014; Hvezdova et al, 2018, Accosta-Dacal et al, 2021; Asensio-Ramos et al, 2010; Beltran et al, 2000).

Treatment procedure of soil samples for analyses of pesticides

Soil samples were sieved and fraction of 63 micron was considered for the study. The treatment procedure of soil sample was almost the same with treatment of dry fruit samples by using modular acetonitrile (for extraction) and modular SPE (Quercher salts) for clan-up procedure. The analysis allows complete extraction of pesticides from soil samples and SPE removes compounds that may interfere in the pesticide analysis such as fats, carbohydrates or other macromolecules. 5 grams of soil (sieved sample) were taken in a Teflon tube. 8 ml of MilliQ distilled water are added and mixed in a vortex. It was left to stand for 10 minutes and then 10 ml of ACN were added to it. It was mixed again in a vortex and after being left to stand for 2 minutes. After that it was treated with citrate tube salt (Quercher 1). The container was placed on an automatic shaker for 5 minutes and then in a centrifuge at 8000 Rpm, at 4ºC, for 5 minutes. A quantity of 6 ml of supernatant were taken and transferred to a

PSA tube with C18 (Quercher 2) and mixed to a vortex (2 min). After this, the centrifuge was used again at 8000 Rpm, for 5 minutes, at +4ºC. The supernatant was filtered through a 0.45 µm filter using a syringe and collected in two different chromatographic vials. The vial to be analyzed in the LC/MS/MS technique was injected directly while the vial to be injected into the GC/MS/MS apparatus was first dried completely under a nitrogen stream and then recovered with 1 ml of the mixture Ethyl acetate/n-Hexane (3/7). The same calibration curves were used for both devices (Silva *et al,* 2019; Nshimiyimana *et al*, 2014; Mahdavi *et al*, 2021; Lozowicka *et al*, 2017; Homazava *et al*, 2014; Hvezdova *et al*, 2018, Accosta-Dacal et al, 2021; Asensio-Ramos et al, 2010; Beltran *et al*, 2000).

GC/MS/MS analyses of pesticides

For the analysis of pesticides, the Agilent GC/MS/MS-7000D GC/TQ instrument was used. Also, the instruments were equipped with an auto-sampler and a vacuum system. The BP5-Ms capillary column with dimensions of 30 m x 0.25 mm x 0.25 um I.D. was used for pesticide separation. The qualitative/quantitative method of pesticide determination with GC/MS/MS was optimized before the analysis of both samples (dry fruits and soil samples). The parameters of the GC/MS/MS apparatus were evaluated before analyses of samples. Qualitative analytical data for each pesticide (222 individuals, see Table 1) were provided by the retention time (RT) and by the selection of two specific ions (qualitative and quantitative ions) for everyone. The selection of ions is based on the pesticide database and the NIST spectral library. Quantitative analysis of pesticides was performed using the internal standard technique (ISTD) where triphenyl phosphate (TPP with a concentration of 10 ppb). Spectral and numerical data for the sample were generated by the “Mass Hunter” software provided by Agilent for this instrument model (Silva *et al*, 2019; Nshimiyimana *et al*, 2014; Mahdavi *et al*, 2021; Lozowicka *et al,* 2017; Homazava *et al*, 2014; Hvezdova *et al,* 2018, Accosta-Dacal *et al*, 2021).

LC/MS/MS analyses of pesticides

The Agilent LC/TQ instrument (LC Model 1290/TQ Model 6470) was used for determination of pesticides (425 individuals, see Table 2) in hazelnut and soil samples. Note, that some pesticides were determined in both apparatuses. A C18 Zorbax model column (240 x 4 mm) was used for the separation of pesticides in the LC/MS/MS apparatus. Two types of mobile phase were used: Phase A - water with 5 mM sodium formate/formic acid buffer and Phase B - MeOH with 5 mM sodium formate/formic acid buffer. Before analyses, the column was rinsed with a mixture of 25% isopropanol and methanol/water solutions (1/3) to clean the column and the chromatographic system. Qualitative data for each compound were provided by the retention time (RT) and by the selection of two specific ions (one for qualitative and the other for quantitative analyses) for each individual. The selection of ions is based on the pesticide database and the NIST spectral library. The quantitative analysis of pesticides was based in internal standard technique (ISTD) using triphenyl phosphate (TPP at a concentration of 10 ppb). Spectral and numerical data for the sample were generated by the “Mass Hunter” software provided by Agilent for this device model (Silva *et al*, 2019; Nshimiyimana *et al*, 2014; Mahdavi *et al,* 2021; Hvezdova *et al*, 2018, Accosta-Dacal *et al*, 2021).

Results and Discussions

The analysis of pesticides in products dry fruits (samples with low water level) and soil samples from hazelnut plantations of Mallakastra were performed by using GC/MS/MS and LC/MS/MS techniques, based on the EN 15662:2018 method. The method allows the simultaneous determination of more than 600 individuals (646 pesticides and their residues) in a run (in both techniques). Table 1 shown the pesticide list obtain by GC/MS/MS and Table 2 pesticide list analysed by LC/MS/MS. Sample treatment for dry fruits and soil samples is based on acetonitrile extraction/partitioning and clean-up by dispersive SPE. The procedure is a modular QUEChERS-method recommended for the analysis of pesticides (multi-residue) mostly in food samples. The method can be used for other matrices such as soil, sediment, biota, etc., because the extraction of pesticides with acetonitrile (a recommended solvent) and the clan-up procedure performed by QUERChERS salt are appropriate steps for the analyses of pesticides (Silva *et al,* 2019; Nshimiyimana *et al,* 2014; Mahdavi *et al*, 2021; Lozowicka *et al*, 2017; Homazava et al, 2014; Hvezdova et al, 2018, Accosta-Dacal *et al*, 2021).

Table 1. List of pesticides analysed by GC/MS/MS analyse

2, 4-D-Isopropyl	Chlorbufam	Ditalimfos	Ioxynil - Octanoate	Pirimiphos-Ethyl
2,4,5-T-Isobutyl	cis-Chlordane	Edifenphos	Iprodione	Pretilachlor
2,4,5-TP	trans-Chlordane	alpha-Endosulfan	Isazofos	Profenofos
2,4'-DDD	Chlordecone	beta-Endosulfan	Isodrin	Prometon
2,4'-DDE	Chlorfenapyr	Endosulfan-Ether	Isofenphos	Propetamphos
2,4'-DDT	Chlorfenson	Endosulfansulfate	Isopropalin	Prosulfocarb
2,4-D-Methyl	Chlorfluazuron	Endrin	Isopyrazam	Prothiofos
4,4'-DDD	Chlormephos	Endrin aldehide	Leptophos	Pyraclostrobin
4,4'-DDE	Chlorobenzilate	EPN	Mancozeb	Pyraflufen-Ethyl
4,4'-DDT	Chloroneb	Epoxiconazole	MCPA Ethyl	Pyrazophos
Acetochlor	Chloropropylate	Esfenvalerate	MCPA- Methyl	Pyridalyl
Acibenzolar-S-Methyl	Chlorothalonil	Ethalfluralin	MCPA, 1-butyl	Pyroquilon
Aclonifen	Chlorpropham	Ethiofencarb	MCPA, 2 Ethylhexyl	Pyroxsulam
Acrinathrin	Chlorpyrifos_Dursban	Ethiolate	Butotyl-MCPA	Quinalphos
Alachlor	Chlorsulfuron	Etridiazole	MCPP, 1-OCTYL	Quinclorac
Aldrin	Chlorthal-Dimethyl	Etrimfos	MCPP-Methyl	Quintozene
Ametryn	Chlorthion	Fenchlorphos	Mecoprop - 2- Octyl	Sebuthylazine
Amitraz	Chlorthiophos	Fenitrothion	Mecoprop - 2,4,4-Trimethylpentyl	Secbumeton
Ancymidol	Chlozolinate	Fenoxycarb	Mecoprop -2- Butoxyethyl	Simazine
Anthraquinone	Cinidon-Ethyl	Fenpropimorph	Mecoprop-2-Ethylhexyl	Simeconazole
Atraton	Clethodim	Fenson	Methoxychlor	Sulfotep
Atrazine	Crufomate	Fensulfothion	Metiram	Sulprofos
desethyl-Atrazine	Cyanophos	Fenthion	Mirex	Tebupirimfos
Benazolin	Cycloheximide	Fenvalerate	Naled	Tebutam
Benfluralin	Cyfluthrin (SUM)	Fipronil	Nitrofen	Tecnazene
Bensulide	beta-Cyfluthrin	Fipronil- Desulfinyl	Nitrothal-Isopropyl	Tefluthrin
alpha-BHC	lambda-Cyhalothrin	Flamprop-Methyl	Norflurazon, Desmethyl	Terbacil
beta-BHC	Cypermethrin	Fluazifop-P-Butyl	Orthophenylphenol	Terbumeton, Desethyl
delta-BHC	Deltamethrin	Flucarbazone Sodium	Oxadixyl	Tetradifon
gamma-BHC	Demeton O	Fluchloralin	Oxychlordane	Tetramethrin
Bifenox	Demeton-S-Methyl	Flucythrinate	Oxyfluorfen	Tetrasul
Bioallethrin	Demeton-S-Methylsulfone	Fluthiacet-methyl	Paraoxon-Methyl	Thiocyclam-Oxalate
Bioresmethrin	Dialifos	tau-Fluvalinate	Parathion	Thiometon
Biphenyl	Dichlobenil	Folpet	Parathion-Methyl	Thionazin
Bromophos-Ethyl	Dichlofenthion	Fonofos	Pebulate	Tolylfluanide
Bromophos-Methyl	Dichlofluanid	Formothion	Penoxsulam	Transfluthrin
Bromopropylate	Dichlormid	epsilon-HCH	Pentachlorbenzene	Tributylphosphate
Bromoxynil-octanoate	2,6 -Dichlorobenzamide	Heptachlor	Pentachloroaniline	Trichlorfon
Butafenacil	Diclofop-Methyl	cis-Heptachlorepoxid	cis-Permethrin	Trifluralin
Butralin	Dicloran	trans-Heptachlorepoxid	trans-Permethrin	Trinexapac - Ethyl
Captafol	Dicofol	Heptenophos	Perthane	Vamidothion
Captan	Dieldrin	Hexachloro-1,3butadien	Phenothrin	Vinclozolin
Carbophenothion	Diphenylamine	Hexachlorobenzene	Phorate	
Chinomethionat	Dipropetryn	Iodofenphos	Pinoxaden	
Chlorbromuron	Disulfoton	Ioxynil - Methyl	Piperophos	

Table 2. List of pesticides analyzed by LC/MS/MS analyze

2.4.5-T	Cyflufenamid	Fenthion sulfon	Mefenpyr-diethyl	Propham
2.4-D	Cyhalofop-Butyl	Fenthion-Oxonsulfoxide	melathion	Propiconazole
Abamectin	Cymiazol	Fenuron	Mepanipyrim	Propoxur
Acephate	Cymoxanil	Fipronil	Mepronil	Propyzamide (Pronamide)
Acequinocyl	Cyproconazole	Fipronil sulfone	Mesosulfuron-methyl	Proquinazid
Acetamiprid	Cyprodinil	Flamprop-isopropyl	Metaflumizone	Prothioconazole
Acifluorfen	Daimuron	Flazasulfuron	Metalaxyl	Prothioconazole desthio
Alanycarb	Dazomet	Flonicamid	Metamitron	Pymetrozin
Aldicarb sulfoxide	DEET	Florasulam	Metazachlor	Pyracarbolid
Allidochlor	Demeton S	Fluazifop	Metconazole	Pyributicarb
Ametoctradin	Desmedipham	Fluazinam	Methabenzthiazuron	Pyridaben
Amidosulfuron	Desmetryn	Flubendiamide	Methacrifos	Pyridafenthion

Aminocarb	Di-allate	Flucarbazone Sodium	Methamidophos	Pyridat
Amisulbrom	Diazinon	Fludioxonil	Methidathion	Pyrifenox
Anilazine	Dichlorvos	Flufenacet	Methiocarb	Pyrimethanil
Atrazine Desisopropyl	Diclobutrazol	Flumetralin	Methiocarb-sulfoxide	Pyriproxyfen
Avermectin B1a	Dicrotophos	Flumetsulam	Methomyl	Quinalphos
Azaconazole	Diethofencarb	Flumioxazin	Methoprene	Quinclorac
Azamethiphos	. N.N- Diethyl-m-toluamid	Fluometuron	Methoprotryne	Quinmerac
Azinphos-ethyl	Difenoconazole	Fluopicolide	Methoxyfenozide	Quinoclamin
Azinphos-methyl	Difenoxuron	fluopyram	Metobromuron	Quinoxyfen
Azoxystrobin	Diflubenzuron	Fluoxastrobin	Metolachlor	Quizalofop-ethyl
Barban	Diflufenican	Fluquinconazole	Metosulam	Quizalofop-P
Beflubutamid	Dimefox	Fluridone	Metrafenon	Resmethrin
Benalaxyl	Dimefuron	Flurochloridon	Metribuzin	Rotenone
Bendiocarb	Dimepiperate	Fluroxypyr -meptyl	Metsulfuron-methyl	Saflufenacil
Benfuracarb	Dimethachlor	Flurprimidol	Mevinphos	Secbumeton
Benodanil	Dimethenamide	Flusilazole	Mexacarbate	Sethoxydim
Benoxacor	Dimethoate	Flutolanil	Molinate	Silthiofam
Bensulfuron-methyl	Dimethomorph	Flutriafol	Monocrotophos	Simetryn
Bentazone	Dimethylvinphos	Fluxapyroxad	Monuron	Spinetoram
Benthiavalicarb-isopropyl	Dimetilan	Fomesafen	Moxidectin	Spinosad A
Benzoximate	Dimoxystrobin	Foramsulfuron	Myclobutanil	Spinosad D
Benzoylprop-ethyl	Diniconazole	Forchlorfenuron	Napropamide	Spirodiclofen
Bifenazate	Dinitramine	Fosthiazate	Naptalam	Spiromesifen
Bifenthrin	Dinotefuran	Fuberidazol	Neburon	Spirotetramat
Bispyribac	Dioxacarb	Furalaxyl	Nicosulfuron	Spiroxamine
Bitertanol	Diphenamid	Furathiocarb	Nicotine	Sulfadiazole_Ethidimuron
Bixafen	Disulfoton Sulfone	Griseofulvin	Nitenpyram	Sulfallate
Boscalid	Disulfoton-sulfoxid	Halofenozide	Nitralin	Sulfentrazone
Bosclid (Nicobifen)	Diuron	Halosulfuron-methyl	Norflurazon	Sulfosulfuron
Bromacil	dmst	Haloxyfop	Novaluron	Tebuconazole
Bromfenvinphos	Doramectin	Haloxyfop-ethotyl	Nuarimol	Tebufenozid
Bromuconazole	Emamectin - Benzoate	Haloxyfop-methyl	Ofurace	Tebufenpyrad
Bupirimate	Epoxyconazol	Hexaconazole	Omethoat	Tebuthiuron
Buprofezin	Eprinomectin	Hexaflumuron	Omethoate	Teflubenzuron
Butachlor	EPTC	Hexazinone	Orbencarb	Temephos
Butamifos	Esprocarb	Hexythiazox	Oryzalin	Tepraloxydim
Butocarboxim	Etaconazole	Hydramethylnon	Oxadiargyl	Terbufos
Butoxycarboxim	Ethametsulfuron-Methy	Imazalil	Oxadiazon	Terbufos sulfone
Buturon	ethidimuron	Imazamethabenz methyl	Oxamyl	Terbumeton
Butylate	Ethiofencarb sulfone	Imazapyr	Oxasulfuron	Terbuthylazine
Cadusafos	Ethiofencarb sulfoxide	Imazaquin	Oxycarboxin	Terbuthylazine desethyl
Carbaryl	Ethion	Imazethapyr	Paclobutrazol	Terbutryn
Carbendazim	Ethiprole	Imibenconazole	Paraoxon - ethyl	Tetrachlorvinphos (Dietreen T)
Carbetamide	Ethirimol	Imidacloprid	Penconazole	Tetraconazole
Carbofuran	Ethofumesate	Indanofan	Pencycuron	Thiabendazol
Carbosulfan	Ethoprophos	Indoxacarb	Pendimethalin	Thiacloprid
Carboxin	Ethoprophos_Ethoprop	iodosulfuron-methyl sodium	Penthiopyrad	Thiamethoxam
Carfentrazone-ethyl	Ethoxyquin	IOXYNIL	Pethoxamid	Thidiazuron
Carpropamid	Etofenprox	Ipconazole	Phenmedipham	Thiobencarb
Chlorantraniliprole	Etoxazole	Iprobenfos	Phenthoate	Thiodicarb
Chlorfenvinphos	Famoxadone	Iprovalicarb	Phorate sulfone	Thiofanox
Chlorfluazuron	Famphur (Famophos)	Isocarbamide	Phosalone	Thiofanox sulfon
Chloridazon (Pyrazon)	Fenamidon	Isocarbophos	Phosmet	Thiram
Chlorotoluron	Fenamiphos	Isofenphos methyl_1 TS	Phosphamidon	Tolclofos-methyl
Chloroxuron	Fenamiphos sulfone	Isoprocarb	Picloram	Tolylfluanide
chlorpyrifos - ethyl	Fenamiphos sulfoxide	Isoprothiolane	Picolinafen	Tralkoxydim
Chlorpyrifos	Fenarimol	Isoproturon	Picoxystrobin	Tralomethrin
Chlorpyrifos-Oxon	Fenazaquin	Isoxaben	Piperonyl butoxide	Triadimefon
Chlorpyriphos-methyl	Fenbuconazole	Isoxadifen-ethyl	Pirimicarb	Triadimenol
Chlorthiamid	Fenhexamid	Isoxaflutole	Pirimicarb-desmethyl	tri-allate
Cinosulfuron	Fenobucarb	Isoxathion	Pirimiphos methyl	Triazamate
Clethodim	Fenoprop (2.4.5- TP; Silvex)	Ivermectin B1b	Primisulfuron-Methyl	Triazophos

Climbazole	Fenothiocarb	Ivermectin B1a	Prochloraz	Tribenuron-methyl
Clodinafop-Propargyl	Fenoxaprop-P-Ethyl	Kresoxim-methyl	Procymidon 1TS	Tricyclazol
Clofentezin	Fenpiclonil	Lenacil	Promecarb	Trietazin
Clomazone	Fenpropathrin	Linuron	Prometryn	Trifloxystrobin
Cloquintocet-mexyl	Fenpropidin	Lufenuron	Propachlor	Triflumizol
Coumaphos	Fenpyrazamine	Malaoxon	Propanil	Trimethacarb
Cyanazine	Fenpyroximat	Malathion	Propaphos	Triticonazole
Cyazofamid	Fensulfothion	Mandipropamid	Propaquizafop	Uniconazole-P
Cycloate	Fensulfothion sulfone	MCPA	Propargite	Vamidothion
Cycloxydim	Fenthion oxon	Mecarbam	Propazine	XMC
Cycluron	Fenthion oxon sulfone	Mefenacet	Propetamophos	Zoxamide

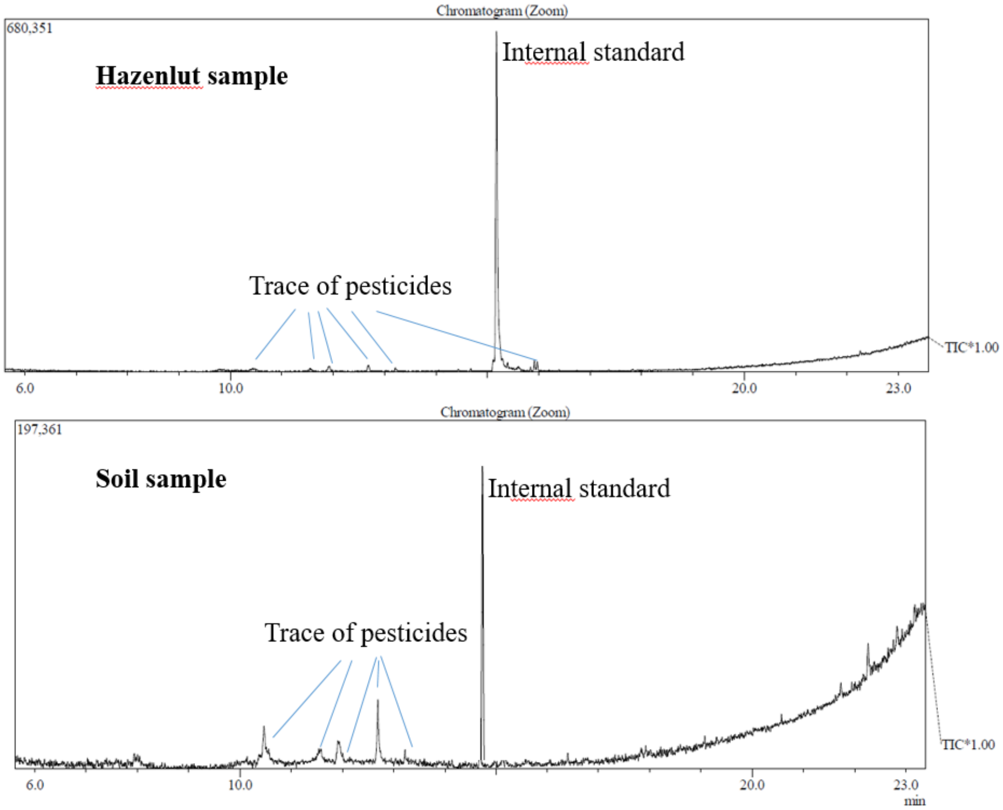

Figure 2. GC/MS/MS analyses of pesticides in hazelnuts and soil samples from Mallakastra, Albania

Figure 2 shown GC/MS/MS chromatograms for hazelnut and soil samples from Mallakastra area. All analyses of hazelnut fruits from Mallakastra area shown that pesticides were not detected (N.D) or their levels were lower than the limit of defect (LOD < 10 ug/kg) in all analysed samples. For hazelnut samples were identified traces of some pesticides such as d-HCH (LOD < 10 ug/kg), Heptachlor (LOD < 10 ug/kg), Heptachlor epoxide (LOD < 10 ug/kg), Aldin (LOD < 10 ug/kg), Dieldrin (LOD < 10 ug/kg), Pyretin (LOD < 10 ug/kg) and Endosulfan I (LOD < 10 ug/kg). Note, that, their levels were always below than allowed level for each of them based on Codex Alimentarius and Albanian norm. Almost the same pesticides were found in soil samples, in a quantity of higher than in hazelnut fruits such as Heptachlor epoxide (22 ug/kg) and Dieldrin (12 ug/kg). Their presence could be because of previous use of pesticides for agricultural purposes in this area. Note that, pesticides found in soil samples could be there because of their previous use of them for other plants/vegetables/cereals not because of their use for hazelnut plants. In addition, it was a fact that generally were found organochlorine pesticides that were regularly used until the 90s in the Myzeqe Field for the treatment of many agricultural crops/fruits/vegetables that grew in this area. Due to their stability, they continue to be reported even today in many studies (Nuro *et al*, 2007; Hvezdova *et al,* 2018; Silva *et al*, 2019). Fortunately, their levels are constantly decreasing due to degradation processes and also the fruits have negligible levels (much lower than the allowed norm for each individual). The way from the soil to the fruits could be a possible source of them but because even in the soil their presence is low then their levels in the fruits are even lower. Another source of pesticides could be their transport from irrigation water or other atmospheric factors such as rain. Presence of pesticides even in trace level should encourage the responsible institutions for the monitoring of products and soil samples from agricultural areas where pesticides have been used regularly/massively for a long time.

Conclusions

In this study, analyse of pesticide in hazelnut fruits and soil samples from Mallakastra region were performed by using GC/MS/MS and LC/MS/MS techniques. Treatment steps for both samples type was based on the EN ISO 15662:2018 method for foods of plants origin. The method allows determination of more than 600 pesticides and pesticide residues in only run. The procedure is a modular QUEChERS-method recommended by SANTE for the analysis of pesticides in fruits with low water percentage but it is also could be used for soil samples because extraction and clean-up steps are favourable for analyses of pesticides in these samples. Fortunately, it was not observed pesticide levels above the LOD (< 10 mg/kg) which is also the allowed level in EU and Albanian norm. Also, their limit was lower than ADI (Acceptable Daily Intake) based on Cedex Alimentarius levels. For hazelnut samples were identified traces of HCHs, Heptachlors, Aldrin's and Endosulfane. Almost the same pesticides were found in soil samples but in higher level (maximum level up to 20 ug/kg). All these pesticides were organochlorine type. Their presence could be mostly because of their previous use in the same areas where now are built hazel plantations. Even pesticide levels will not exceed the permitted level for any hazelnut and soil sample, their presence (even in trace levels) should encourage the responsible institutions for continuous analysis of fruits, vegetables, cereals, soil samples from areas when in the past pesticides were used widely and for a long time.

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Research Paper

A Comparison Study on Chemical Profile of *Laurus Nobilis* Leaves by Using Different Extraction Techniques

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Abstract: The essential oil of *Laurus nobilis* leaves were analyzed from natural population of Tirana, located in Central Albania by using two different extraction techniques: hydro-distillation with Clevengar apparatus (HD) and Head space technique by using PDMS fiber (HS-SPME). *Laurus nobilis* can be found easy (naturally) in western lowlands of Albania up to altitudes of 1500 m (for areas with warm climates). It is easy to harvest (their leaves), and it is very popular in Albania in culinary and traditional medicine. Essential oils derived from *Laurus nobilis* have valuable pharmacological properties that have been used and continue to be investigated due to their interest properties. The samples of *Laurus nobilis* (their leaves) were taken in different stations (6 stations) of Tirana, at June 2024. The fresh and air-dried samples were the subject of two extraction processes: hydro-distillation by using Clevenger apparatus and Head space technique. The chemical composition of the essential oils for both methods were determined by using a gas chromatograph model Varian 450 GC equipped with split/spitless injector and flame ionization detector. VF-1ms capillary columns (30 m x 0.33 mm x 0.25 um) were used for separation of compounds. Monoterpenes (especially oxygenated monoterpenes) were in higher percentage in all *Laurus nobilis* samples. Terpenes that were found in higher percentage were: Cineole, Linalool, Menthol, Pulegon, Carvone, Piperthone, Thymol, beta-Caryophyllene. The chemical profile between fresh and dry leaves of Laurus nobilis was almost the same. Small differences were observed between two extraction techniques. Head space technique showed a higher percentage for compounds with lower boiling point. Also between stations there were some differences between the main compounds because of atmospheric conditions and soil composition. Chemical profile of *Laurus nobilis L.* samples from Tirana, was similar with other reported studies from Albania as well as Balkan and Mediterranean areas.

Keywords: *Laurus nobilis*, Essential oil, Hydro-distillation, Head space GC/FID

Introduction

Laurel (*Laurus nobilis*) is a large evergreen tree or shrub with green leaves. It is part of the flowering plant family Lauraceae. It grows naturally in the Mediterranean region. Laurus nobilis forests covered most of the Mediterranean countries when the climate of the region was wetter, but with the increase of temperatures during the Pliocene, the laurel forests gradually retreated and were replaced by populations of drought-tolerant plants, which are still found today. Some laurel forests can be still found today in some areas of the Mediterranean (Anzaro *et al*, 2022; Asllani, 2004; Burnie, 1995; Dafera *et al*, 2010; Kathe *et al*, 1999; Mikail *et al.,* 2013). Laurel is one of the earliest plants known and used by humans. In ancient times, the laurel was a symbol of glory, peace and security. Its leaves have been used in culinary spices to give characteristic flavors to foods. Laurel was used widely in traditional medicine because it has for treatment of some illness. Among the compounds present in laurel leaves are Eugenol (1,8-Cineole) and Limonene, which are known as active substances useful due to their antiseptic, antioxidant, digestive and anti-carcinogenic properties (Dafera *et al.,* 2010; Asllani, 2004). Fresh leaves of *Laurus nobilis* are an important source of vitamin C, which is one of the most powerful natural antioxidants capable of combating

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Corresponding: E-Mail: aurel.nuro@fshn.edu.al, the action of free radicals. Vitamin C also has antiviral effects, stimulates the immune system and promotes wound healing. Also, when laurel leaves are fresh, they are a good source of folic acid, which is important for DNA synthesis and during pregnancy it prevents the appearance of birth defects in children (Anzaro *et al*, 2022; Asllani, 2004; Burnie, 1995; Dafera *et al,* 2010; Dobrosslavic, 2021). Laurel leaves also contain vitamin A, essential for maintaining vision, skin and mucous membranes. Consumption of foods rich in vitamin A protects the lungs from cancer. Also, they contain a mixture of vitamins B, such as niacin and riboflavin. Vitamin B regulates metabolism, contributes to enzyme synthesis and the functioning of the nervous system (Naser *et al*, 2020; Paparella *et al*, 2022). The mineral content it contains should be considered. Among them, in fact, can be found potassium, copper, calcium, manganese, iron, selenium, zinc and magnesium. Potassium is important for keeping blood pressure and heart rate under control. Iron is necessary to produce red blood cells. In herbal medicine, laurel leaves are known as laxative, diuretic and appetite stimulant. Bay leaf tea has been used to relieve stomach pain or abdominal pain [3-7]. The lauric acid content in its leaves is a natural remedy for insects and parasites. The components present in laurel leaves have been used to produce medical products for the treatment of arthritis, muscle pain, bronchitis and flu symptoms. Tea obtained from laurel leaves aids digestion and removes gas from the gastrointestinal tract, and it is also a useful remedy in cases of sciatica (Mikail *et al*, 2013; Stefanova, 2020)

The hydro-distillation technique is one of the most common methods used both in the laboratory and on an industrial scale to produce essential oils from aromatic and medicinal plants. For research purposes and also recognized by the Pharmacopoeia, Clevenger model hydro-distillation apparatus, is the most used. In this apparatus, continuous extraction is applied by continuously enriching the organic phase with the compounds found in the plant being extracted. When the amount of organic matter is small, an organic solvent such as toluene or hexane is used to dissolve the compounds in the organic phase. Now, this method has been modified with gases in a critical state (instead of water), such as carbon dioxide, which is more efficient than water vapor. Other methods used in the extraction of essential oils include maceration, squeezing, ultrasonic baths, and more recently, Head space techniques. These techniques are based on the isolation (extraction) of volatile compounds (flavonoids) from plants or other substances in a bottle closed at its head. Air sampling from this bottle can be done directly using a syringe (classic Head space) or using a high-porosity polymer fiber that binds organic compounds well (absorbs) (Anzaro *et al*, 2022; Asllani, 2004; Burnie, 1995; Naser *et al*, 2020; Paparella *et al*, 2022; Dafera *et al,* 2010; Dobrosslavic, 2021). In this study hydro-distillation (by using Clevenger apparatus) and HS-SPME (by using PDMS fiber) was used to determine the chemical profile of *Laurus nobilis* leaves from Tirana area, Albania.

Material and Methods

Sampling of laurel leaves

The leaves of *Laurus nobilis* were collected at 6 different stations in the Tirana area (Farkë, Mullet, Artificial Lake, Linzë, Sharrë and Kashar). The plants were collected in June 2024. At each station, the leaves of the plant were collected. The leaves were dried in the shade so as not to lose their morphological characteristics. After drying, the plant material was chopped into small pieces of 0.5-2 cm for further analysis.

Materials and reagents

High purity n-Hexane and toluene, suitable for gas chromatography, were provided by Merck (Darmstadt, Germany). Also, the mixture of n-alkanes from n-octane (C8) to eicosanes (C20) that was used to calculate the Kovats indices (KI) was provided by the Merck catalog.

Chemical profile of *Laurus nobilis* by using HS/SPME technique

5 g of the laurel leaves were placed in a SPME bottle with a volume of 10 ml. The bottles are equipped with Teflon stoppers suitable for their analysis by means of the Head-space technique. The manual SPME syringe equipped with a 100 um PDMS (Polydimethyl siloxane) fiber was inserted through the Teflon stopper into the top of the sample. The bottle was placed in Banjo Mari at a temperature of 50oC for 40 minutes. After the adsorption process, the syringe (PDMS fiber) is transferred to the Varian 450 gas

chromatograph equipped with FID detector where their injection is performed (desorption process at 280oC for 20 seconds). The separation of volatile compounds of sage will be carried out in the VF-1ms column (Paparella *et al*, 2022).

Isolation of essential oils by using Clevenger apparatus

Dried and crushed laurel leaves from the Tirana area (50 g of plant material) were subjected to hydro-distillation for 4 hours without interruption using a Clevenger-type apparatus (recommended by European Pharmacopeia, 2014) for the isolation of the essential oil. The essential oil was collected in 2 ml of toluene as the extraction solvent. The extract was dehydrated by adding 1 g of anhydrous sodium sulfate. It was stored in dark vials at +4oC. The essential oil of *Laurus nobilis* was subjected to analysis using the GC/FID technique (Awada *et al*, 2023; Daferra *et al*, 2000; David *et al*, 2010).

Apparatus and gas chromatographic analysis

Gas chromatographic analysis of the essential oil of *Laurus nobilis* was performed on a Varian 450 GC apparatus, equipped with a PTV injector and a flame ionization detector (FID). The injector and detector temperatures were set at 280 ºC and 300 º C, respectively. 2 µl of the essential oil dissolved in toluene was injected in split mode (1:50). Nitrogen was used as carrier gas (1 ml/min) and as 'make-up gas' (25 ml/min). Hydrogen and air were detector flame gases at 30 ml/min and 300 ml/min respectively. A VF-1ms capillary column (30 mx 0.33 mm x 0.25 mu) was used to isolate the essential oil compounds. The identification of the compounds was based on the comparison of the exit times (RT) with the Kovats indices, which together with the literature data were used to identify the main compounds of laurel. The quantitative data of the analyzed compounds are given in % against the total peak areas without calculating the toluene peak area (Adams, 1995; Asllani, 2014; Dafera *et al,* 2000; Koing et al, 1999). Figure 1 shown chromatograms of essential oils for laurel leaves obtained by hydro-distillation and Head space techniques.

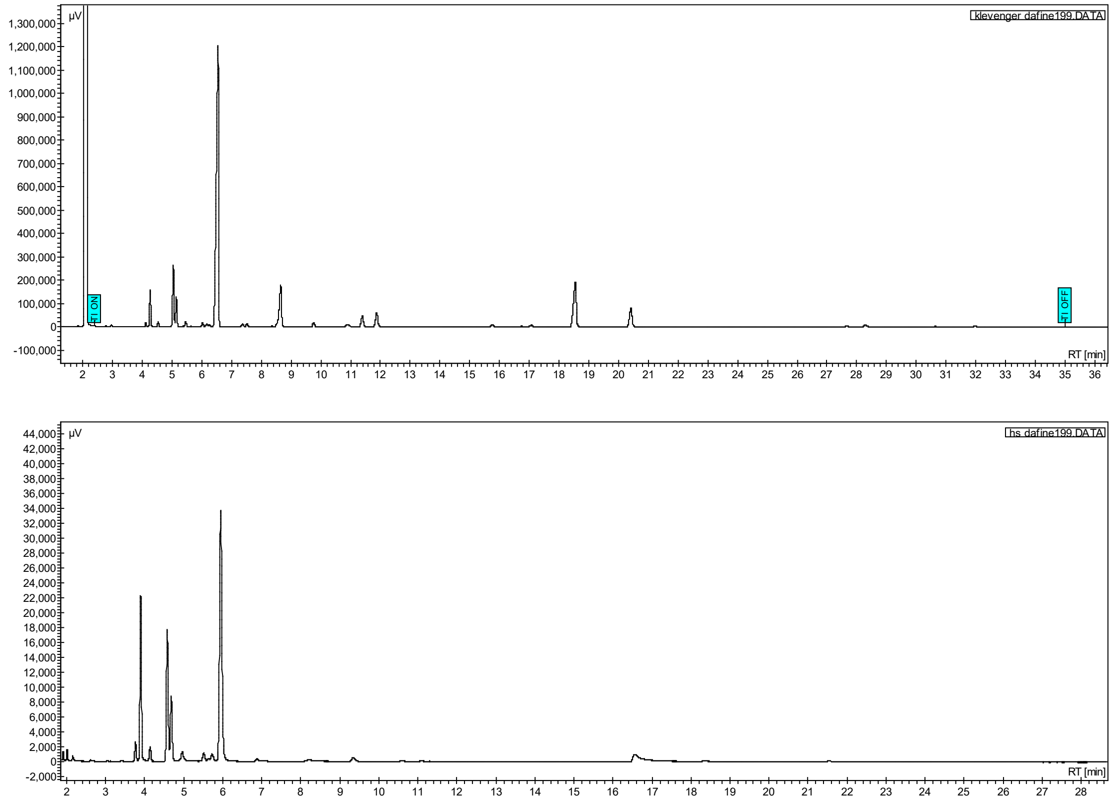

Figure 1. Chromatograms of essential oils for laurel leaves using the hydro-distillation method (above) and Head space (below)

Results and Discussions

The GC/FID analyses of laurel leaves by using the hydro-distillation technique (Clevenger apparatus), it showed that in the chromatograms were 40-60 compounds, while for the same samples but analyzed with Head space technique, their number was 75-100 compounds. The analysis included 28 main compounds that constitute about 95.6% of the total compounds using the Clevenger technique and 93.5% of the total compounds using the Head space technique. The main compounds that were identified in the majority in all samples, for both methods, were: Cineol (Eucalyptol), Sabinene, alpha-Pinene, beta-Pinene, and alpha-Terpinyl acetate. Table 1 gives the average percentages of the components analyzed from laurel leaves for both methods. Piks (compounds) with an area lower than 0.01% were not considered in this study.

Table 1. Average percentages of main components for *Laurus nobilis* leaves from Tirana area

	Clevenger (Hydro-distillation)				**Head space – Solid Phase Micro-Extraction**			
	Mean	**Min**	**Max**	**STDEV**	**Mean**	**Min**	**Max**	**STDEV**
alfa-Thujene	0.59	0.34	0.73	0.21	1.17	0.45	1.89	1.02
alfa-Pinene	4.97	3.32	6.21	1.49	9.75	3.63	15.87	8.65
Camphene	0.68	0.51	0.95	0.24	1.03	0.45	1.61	0.82
Sabinene	8.78	6.53	12.01	2.87	7.34	0.02	14.66	10.35
beta-Pinene	2.18	0.88	3.17	1.18	6.95	6.03	7.87	1.30
Myrcene	0.43	0.18	0.80	0.33	1.49	0.83	2.15	0.93
alfa-Felandrene	0.44	0.09	1.12	0.59	0.02	0.02	0.02	0.00
alfa-Terpinene	0.22	0.07	0.52	0.26	0.17	0.11	0.22	0.08
para-Cymene	0.27	0.00	0.58	0.29	1.02	0.67	1.37	0.49
Limonene	0.27	0.00	0.72	0.39	1.14	0.47	1.80	0.94
1,8-Cineole	48.40	44.84	50.49	3.10	31.58	25.38	37.77	8.76
gama-Terpinene	0.59	0.00	0.98	0.52	0.53	0.40	0.65	0.18
Cis-Sabinenehydrat	0.17	0.00	0.47	0.26	0.25	0.25	0.25	0.00
Linaleol	0.38	0.07	0.95	0.50	0.19	0.15	0.22	0.05
Terpinen-4-ol	0.90	0.08	2.36	1.27	0.18	0.12	0.24	0.08
alfa-Terpineol	1.54	0.58	2.21	0.85	0.81	0.35	1.26	0.64
Acetat bornili	0.39	0.12	0.65	0.27	0.97	0.51	1.42	0.64
alfa-Terpinil acetat	8.04	3.94	12.44	4.26	7.34	5.62	9.06	2.43
Timol	0.92	0.31	2.08	1.00	0.32	0.31	0.32	0.01
Eugenol	2.27	1.47	2.80	0.71	0.65	0.14	1.16	0.72
Aceatt Nerili	0.25	0.14	0.33	0.10	0.43	0.25	0.60	0.25
beta-Elemene	1.27	0.47	2.57	1.13	0.27	0.24	0.29	0.04
Metil eugenol	7.96	5.32	10.32	2.51	2.51	0.91	4.11	2.26
beta-Kariofilene	1.71	0.45	4.15	2.11	0.19	0.17	0.21	0.03
Germacene D	0.46	0.11	0.78	0.34	0.16	0.12	0.19	0.05
Biciklogermacene	0.45	0.25	0.56	0.18	0.48	0.11	0.85	0.52
delta-Cadineen	0.16	0.14	0.18	0.02	6.15	1.05	11.25	7.21
Cariophyllen oksid	0.84	0.23	1.93	0.95	10.51	3.21	17.81	10.32
Total	95.57	90.04	99.73	4.99	93.55	87.53	99.56	8.51
Bicyclic monoterpenes	17.20	11.58	23.07	5.99	26.24	10.58	41.90	22.15
Monocyclic monoterpene	1.52	0.16	3.34	1.75	1.85	1.00	2.69	1.20
Aliphatic monoterpene	0.43	0.18	0.80	0.33	1.49	0.83	2.15	0.93
Oxygenated Monoterpene	60.09	49.77	69.90	10.60	41.73	32.63	50.82	12.86
Aromatic Monoterpene	11.42	7.10	15.78	4.51	4.50	2.03	6.96	3.49
Sesquiterpenes	4.06	1.42	8.24	3.78	7.24	1.69	12.79	7.85
Sesquiterpenes oxide	0.84	0.23	1.93	0.95	10.51	3.21	17.81	10.32

Hydro-distillation method with the Clevenger apparatus showed fewer compounds compared to the HS technique (Figure 1). This difference in the analyzed compounds should be mainly related to the selectivity of Toluene, the solvent used for extraction. The Head space technique has lower sample discrimination because the number of compounds with this technique is 2 – 3 times higher. The HS technique allows the analysis of a larger number of compounds.

Figure 2 shows the chemical profile of the main compounds obtained by the hydro-distillation and Head space methods for dried laurel leaves from the Tirana area, July 2024. It is noted that the main compound found for both methods was Cineol. It was found in a higher percentage in the hydro-distillation extracts with 48.4% compared to 31.6% obtained with HS. The compounds found in higher percentages by the HD method were: Cineol, Sabinene, alpha-Terpinyl acetate, Methyl eugenol and alpha-Pinene while their profile for the HS technique was: Cineol, alpha-Pinene, Caryophyllene oxide, Sabinene, beta-Pinene, alpha-Terpinyl acetate and delta-Cadinene. It is noted that HS provides higher levels not only for compounds with low boiling points but also for compounds that have relatively high molecular mass (high boiling points) compared to HD. This should also be related to the discrimination of water vapor or toluene used during HD. Figure 2 provides chemical profiles for the classes of terpenes found in *Laurus nobilis* leaves from the Tirana area. For both extraction techniques, the highest level was for oxygenated terpenes, respectively with 60.1% for HD and 41.7% for HS. Their high level was due to the high percentage of Cineole. For HD the profile of the terpene classes was: Oxygenated monoterpenes, bicyclic monoterpenes, aromatic monoterpenes, sesquiterpenes (monocyclic, aliphatic and oxygenated sesquiterpenes) were at levels lower than 1%). For the HS technique their profile was different because after the oxygenated and bicyclic monoterpenes were oxygenated sesquiterpenes, sesquiterpenes and aromatic monoterpenes (also for this technique the percentages of monocyclic and aliphatic monoterpenes were lower than 1%). This is related to the preference/discrimination that the different extraction techniques have for some of the compounds and the classes to which they belong. In Figure 4 the respective percentages for bicyclic monoterpenes (alpha-Thujene, alpha-Pinene, Camphene, Sabinene and beta-Pinene) for both HD and HS methods are given. For the HS method it should be said that there is a higher percentage of them of 26.2% compared to HS with 17.2%. This is expected because these compounds are the first to appear in the chromatogram due to their low boiling points and have high evaporation which favors the HS technique. Their profile was also different, for HD it was: Sabinene, alpha-Pinene, beta-Pinene, camphene and alpha-Thujen while for HS it was: alpha-Pinene, Sabinene, beta-Pinene, alpha-Thujen and Camphene. These differences are also not directly related to their percentages but to the extraction techniques, their preferences/discrimination towards some compounds and the way of reporting the result in percentage against the total points (We recall that for HD the number of identified compounds was smaller than HS). Similarly, differences were also observed in the profiling of monocyclic monoterpenes (Figure 5). Their profile for HD was: gamma-Terpinene, alpha-Phelandrene, Limonene and alpha-Terpinene while for HS their profile was: Limonene, gamma-Terpinene, alpha-Terpinene and alpha-Phelandrene. Methyl Eugenol was found as the most abundant aromatic monoterpene both in the HD technique and in the HS technique. Its presence in HS was much greater, a fact that can be justified by the solubility of phenols in water while their boiling points are relatively high and could be less preferred in the HS technique which is obvious from the levels of Thymol and Eugenol. The situation changes for para-Cymene which has a lower boiling point and does not have an OH group making it more preferred for HS versus HD. The polarity that the OH group gives to the molecule makes it more attractive for HD. This is also reflected for the oxygenated monoterpenes (Figure 7) which have higher levels of Cineol, alpha-Terpinyl acetate, alpha-Terpineol, Terpinen-4-ol, linaleol, Neryl acetate, Sabinen hydrate. Also the presence of this group affects the increase of boiling points making them less volatile and more discriminated by the HS technique. The increase of molecular mass for sesquiterpenes makes them less volatile and in general (beta-Elemene, beta-Caryophyllene, Germacene, Bicyclogermacene) appear in higher percentage in the HD technique. The only difference is delta-Cadinene identified at a higher level for the HS technique. As for Myrcene (representative of aliphatic terpenes) it was found in an amount less than 0.5% for both methods and without a substantial impact on the overall profile. Data obtained from HD and HS analyses of dried laurel leaves from the Tirana area showed that their chemical composition was the same as those reported in other works from other areas of Albania, the Balkans or the Mediterranean (Asllani, 2014; Caputo et al, 2017; Daferra et al, 2000; Hajlauoni et al, 20008; Fantasma et al, 2024; Fidan et al 2019; Stefanova et al 2020; Naser et al, 2020).

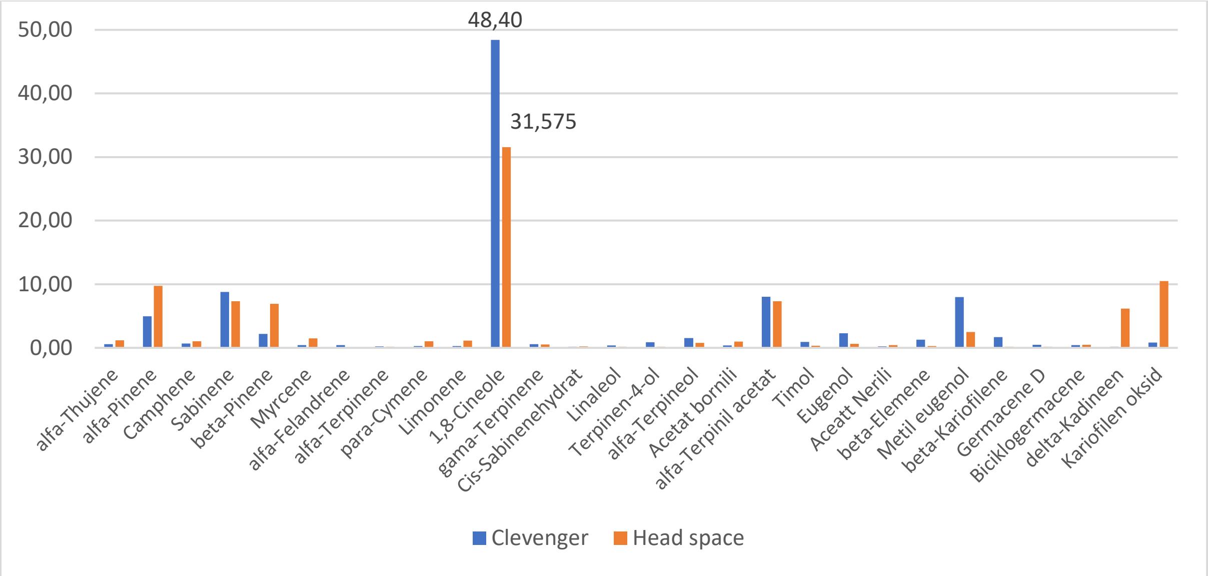

Figure 2. Chemical profile of terpenes in laurel leaves from Tirana area, June 2024

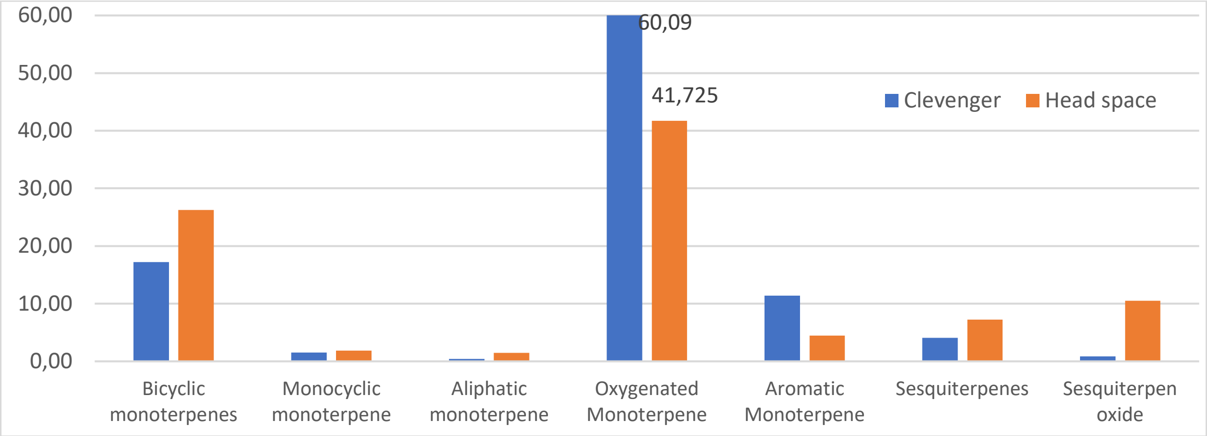

Figure 3. Terpene classes in laurel leaves from Tirana area, June 2024

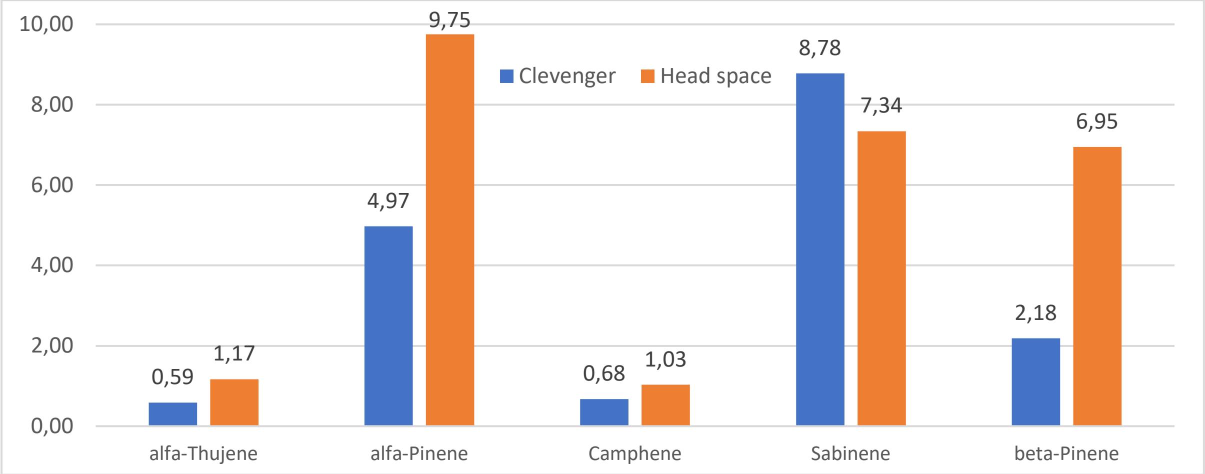

Figure 4. Bicyclic monoterpenes in laurel leaves from Tirana area, June 2024

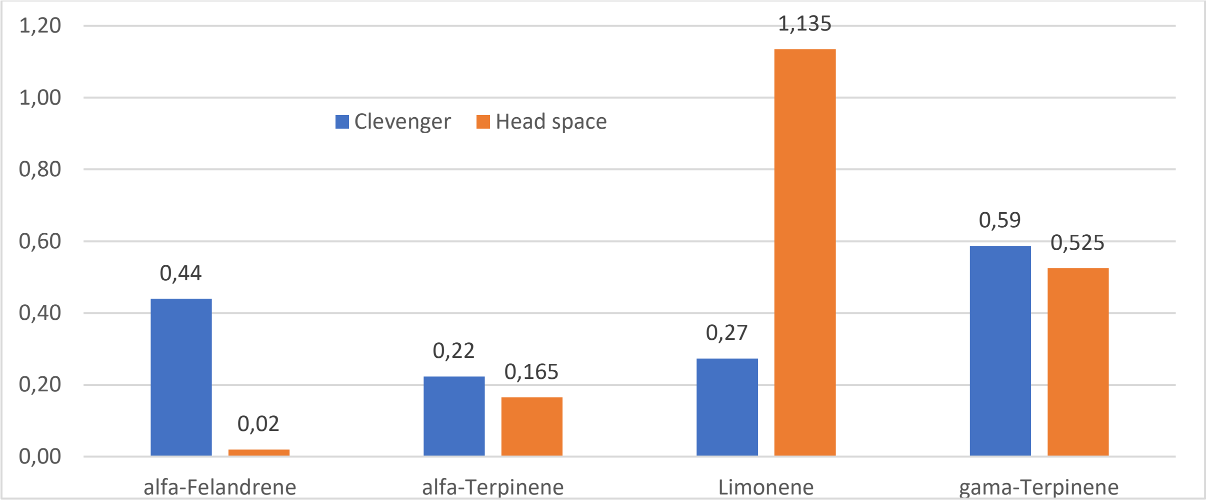

Figure 5. Monocyclic monoterpenes in laurel leaves from Tirana area, June 2024

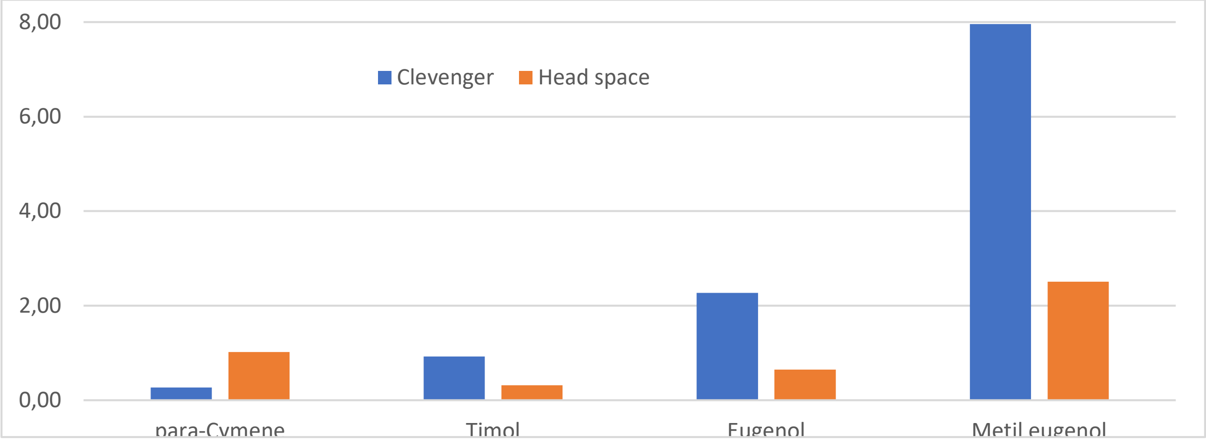

Figure 6. Aromatic monoterpenoids in laurel leaves from Tirana area, June 2024

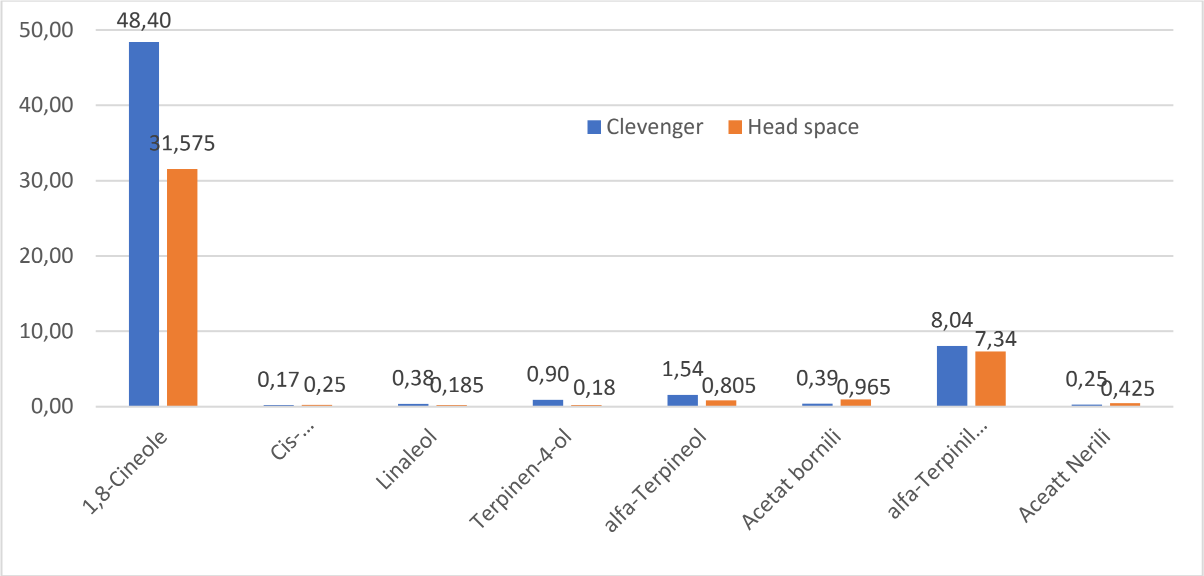

Figure 7. Oxygenated monoterpenes in laurel leaves from Tirana area, June 2024

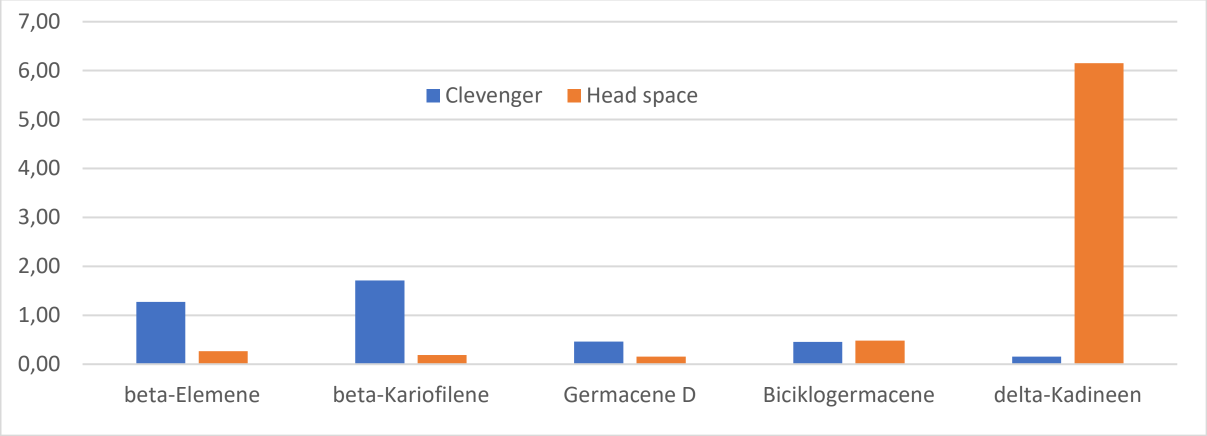

Figure 8. Sesquiterpenes in laurel leaves from Tirana area, June 2024

Conclusions

In this study, leave samples of *Laurus nobilis* L. from the Tirana area were analyzed. Laurel is an aromatic/medicinal plant widely used in cooking as a spice and its active compounds have been found to have very good pharmacological effects and are therefore often used in traditional medicine to treat many symptoms and to increase the quality of life. The chemical analysis of the essential oils extracted from these plants was performed using two different extraction techniques, hydro-distillation and Head space followed by GC/FID quantification. The HS technique had a greater advantage in the number of identified compounds (up to 100) compared to the HD technique (up to 60). This should be related to the preference/discrimination of compounds and their different classes from water vapor, toluene or from their boiling points. This is also evident from the fact that the bicyclic monoterpenes that appear in the first part of the chromatogram due to their low boiling points are in higher percentage in HS while alcohols and phenols (polar compounds, with higher solubility in water and higher boiling points) are in higher percentage in HD technique. However, it should be said that the chemical profile for both methods was similar where Cineole, alpha+beta-Pinenes, Sabinene, alpha-Terpinyl acetate and Methyl Eugenol were the main compounds. Both methods are suitable for determining the chemical profile of essential oils including dried laurel leaves. Some advantages of HS-SPME method are: it is a green method (organic solvents are not used), has good reproducibility and repeatability (low values for STDEV in parallel measurments), low cost, the analyze time is shorter, etc. The chemical profile for *Laurus nobilis* was the same as those reported in other works from other areas of our country and wider from the Balkans and the Mediterranean.

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Research Paper

Investigation Ion Balance, Enrichment and Neutralization Factors in Iskenderun Gulf's Precipitation

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Abstract: The purpose of this study was to investigate the ion balance, enrichment (EFc) and neutralisation (NF) factors of precipitation in the Gulf of Iskenderun. There are several different industries in the Gulf region. pH, conductivity, anion, cation and trace element analyses were performed in precipitation samples (n=153) from five different locations. Ion chromatography (IC) was used for quantitative analysis of anions (sulphate, nitrate, chloride) in rainwater samples. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used for cation and trace element (Ca, Ba, Mg, K, Ca, Li, Fe, Mn, Na, Cr, Ni, Cu, Al, Pb) analysis. Among the anthropogenic elements, the highest concentrations were found for Mn, Pb, and Fe. The ratio of cations to anions was found to be 1.0. The enrichment and neutralization factors of elemental concentrations also revealed the change in 10 years. In all locations, EFc values decreased within 10 years, indicating a decrease in pollutant concentrations. However, ion and element values are still high in precipitation in the region. To prepare a clean air plan in the region, it is suggested that the number of sampling sites where rainwater is taken should be increased, continuous measurements should be made with automatic devices and regular reports should be obtained on a yearly basis. On 6 February 2023, two earthquakes with magnitudes of 7.8 and 7.5 occurred in Türkiye and caused major damage in Iskenderun Gulf. This study provides valuable information on the use of post-earthquake rainwater analyses in Iskenderun Gulf.

Keywords: *Precipitation, Gulf of Iskenderun, enrichment factor, neutralisation factor, ion balance.*

Introduction

Ecosystems are being destroyed by atmospheric deposition, which has gained focus in recent years. Anthropogenic sources include sewage effluent, traffic emissions, mining and manufacturing processes, metal furnaces, waste processing facilities, air pollution contamination, and rainfall from cities (Morais *et al.*, 2012). Acid rain, soil pollution, and water pollution are the effects of wet deposition, which is caused by pollutants from particulate matter and certain gases, such as sulphur dioxide and nitrogen oxides, rainout and washout (Michalska *et. al.*, 2020). Heavy metals are also an important pollutant. The elements classified as heavy metals (HMs) have an atomic number higher than 20 and an atomic density higher than 5 g/cm^3. Because of their great bioaccumulation abilities *(e.g.*, Pb, Cu, Zn, and Ag) and non-degradability (*e.g.*, Hg, Pb, and As), HMs are known to be increasingly concerning in our environment (Jaishankar *et al.*, 2014). Water, soil, and environmental sediments serve as HM sinks (Shou et al., 2022). Numerous emission sources, both natural and man-made, including fuel burning, dust storms, road transportation, agriculture, pharmaceuticals, and manufacturing processes, were responsible for the release of heavy metals into the atmosphere. The pristine environment can be identified as areas with minimal levels of trace metals (Honório *et al.*, 2010).

Alkaline species are present in the atmosphere. The source of aerosol calcite from alkaline species in the atmosphere is mineral dust in the earth's crust. Mineral dust originates mainly from arid regions. They are also transported over very long distances by atmospheric means and deposited on land and sea surfaces. The Sahara Desert is known to be the most important potential source region affecting the structure of Eastern Mediterranean aerosols (Dulac *et al.*, 1992). Ca, K, Mg elements are generally originated from the earth's crust and the concentration of these elements increases with the dust carried from the soil in summer months.

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The Amanos Mountains are located to the east of Iskenderun Gulf and Iskenderun is established on a 5 km plain at the foot of these mountains. It is also protected from strong lodos winds. Since 1950, Iskenderun Gulf has been involved in shipping and international transport, import and export, petroleum, fertilizer, iron and steel enterprises and ports. Shipping is an important source of pollutants in the form of petrol and petroleum derivatives in the sea. The largest inland area of the Mediterranean Sea is Iskenderun Gulf. In Iskenderun, the Iron and Steel Factories, fertilizer and cement factories and nearly 50 small and large factories belonging to the public and private sectors are important pollutant sources. Iskenderun Iron and Steel factory (ISDEMIR) is one of the three integrated iron and steel plants in Türkiye and is located on an area of 1750 hectares (Sarıhan *et al.*, 2006). Iskenderun is a city that does not allow air pollutants to escape due to its topographical structure. The high Amanos Mountains surround the city and do not allow polluting gases and dust to escape from the city, thus changing the chemical composition of precipitation.

The port in the city of Iskenderun is Türkiye's third largest port on the Mediterranean coast. The reason for the selection of Iskenderun Gulf in the study is that it is one of the regions with the largest population density in Türkiye and the region is also important in terms of tourism. It is very important to determine the composition of pollutant sources in precipitation water in the region where the industry is also very intense. In this study, pH, conductivity, anion, cation and trace element concentrations were determined in precipitation samples collected from five different locations in Iskenderun Gulf. With the data obtained, ion balance, enrichment and neutralization factors were calculated and pollution sources in rainwater were investigated.

Material and Method

The Study Area

Industrial establishments in İskenderun are generally located on the seashore. When looking from south to north, there are primarily fertilizer factory, organized industrial zone and ISDEMIR (Iskenderun iron and steel factory). Five sampling points were established to investigate the chemical composition of precipitation water in Iskenderun Gulf as shown in Figure 1. The first sampling location (L1) is 2 km. away from the seashore and in ISDEMIR (the largest iron and steel factory in the region) where is located North of İskenderun industrial zone, there are many industrial establishments as well as arc furnaces, fertiliser factory *etc*. The coordinates of sampling site L1: N 36° 42.419° E 036° 13.033° and altitude 40. In the second sampling location at Payas (L2), which is 2 km. north of ISDEMIR, highly polluting electric arc furnace plants, integrated iron and steel plants, rolling mills, foundries as well as residential area are located. Coordinates of L2: N 36° 45.301° E 36° 12.235° and altitude 12. The third sampling zone (L3) is mainly affected by traffic and rural influences. The coordinates of sampling site L3: N 36° 32.514°E 036° 08.730° and altitude 180. The L3 sampling location is also located close to the main route in the Amanos Mountains, which gates from Iskenderun to the Amik plain. The fourth sampling area (L4) is the city centre, which is highly populated and under the influence of traffic and domestic fuels. The coordinates of L4: N 36° 35.313° E 036° 10.232° and altitude 9. The fifth sampling site (L5) is only under the influence of the sea and the rural area and there is no industrial activity. The coordinates of L5: N 36° 32.058° E 036° 02.612° and altitude 10. In 1999 and 2009, a total of 153 samples were analysed for each year between January and May at the same sampling sites.

Collection of sample and preparation

Precipitation samples were collected using 2 1L HDPE (high density polyethylene) bottles. The bottom of one of the bottles was cut and 2 bottles were mounted on the neck. Rainwater collected from 5 different sampling sites shown in Figure 1, taken into HDPE (high density polyethylene) containers. The samples were divided into 3 parts for measurement of pH and conductivity, and analyses of ion-cation. After the samples were collected, pH and conductivity were measured immediately. The precipitation sample for anion analysis was filtered through 0.22μm cellulose-acetate filter paper using Milipore filtering apparatus before being transferred to the storage container. For cation analysis, precipitation samples were filtered on blue band filter paper and the transferred containers were kept in 10% HNO_3 washing solution and rinsed with distilled water before use. Before the analysis, 5-6 drops of HNO_3 were added. Samples were stored in 50 - 100 mL HDPE bottles at +4 °C until analysis.

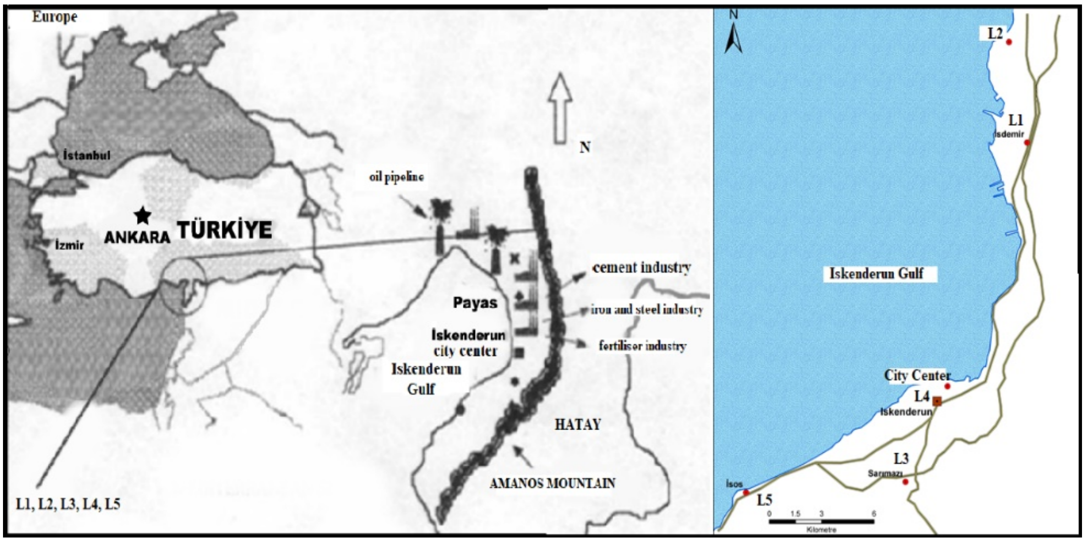

Figure 1. Map of the Precipitation sampling points in Iskenderun Gulf

pH and Conductivity Measurement

The acidity of the rainwater was measured with a Hanna 211 pH-meter. The pH-meter was calibrated against pH 4.01, 7.01 and 10.01 buffer solutions before measurement if not used at regular intervals. Calibration liquids; Merck pH 4 1.09435.1000, Merck pH 7 1.09439.1000. During pH measurement, the electrode immersed in the sample in the glass beaker was gently stirred continuously and the reading was recorded after the electrode reached a completely stable state. Electrical conductivity of precipitation water was measured with Hanna H I7031. Additionally, a conductivity standard of 1.413 µS/cm was employed, which is prepared in comparison to a potassium chloride solution that is traceable by NIST.

Analytical Methods pH and Conductivity Measurement

Sodium carbonate, Nitric acid 65%, were purchased from Merck. And also Merck certipur ICP multi-element standard solution and reference material from the World Meteorological Organization were used for ICP-AES. DIONEX ICS-3000 was used for basic anion analyses (sulphate, nitrate and chloride). The cation analyses in the samples were performed with Varian Liberty-II Model Plasma 96, ICP-AES system controlled by PC Pentium III. The device is flamed by axial torch and the plasma power is 1.0 kW. The integration time is 1.5 s and gives the average of 3 readings for each sample. 4-5 drops of nitric acid were added to the filtered samples before they were fed into the ICP-AES device. Standard solutions of different concentrations for cations (minimum 5) were prepared by diluting from Merck ICP multi-element standard solution of 1000 mg/L concentration. Trace element analysis was carried out with Varian Liberty-II Model Plasma 96, ICP-AES system in Mustafa Kemal University Central Laboratory. The standard solutions used in the calibration were prepared by dilution from Merck ICP multi-element standard solution with a concentration of 1000 mg/L. The parameters used in the ICP-AES device for the analyses are given in Table 1. The wavelength of the elements whose concentrations will be determined in the ICP-AES device and the determination limit (LOD) of the device are given in Table 2.

Table 1. Parameters used in the ICP-AES

Torch: Demountable Qrtz Torch	Nebulizer: Concantric Glass Nebulizer
Plasma gas speed:15 L/min	Auxiliary gas speed :15 L/min
PMT Voltage:750 V	Power:1 W
Integration time:1 s	Pump speed:15 rpm
Sample Dilution Time: 25 s	Replication:3

Enrichment and Neutralization Factors of Elements

One of the methods used to obtain qualitative information about the sources of components in the atmosphere is the enrichment factor. Enrichment factor (EFc) is the value that shows to what extent the elements are enriched or impoverished in rainwater or aerosol compared to the earth's crust or marine sources. This calculation, which was first used in atmospheric studies and to which the normalization technique was applied, is expressed by equations (Equation 1) and (Equation 2) (Yufei et al., 2020). If the concentration of a constituent in rainwater is entirely due to the Earth's crust, the value of the EFc for this ion will be 1.0. In general, values above 10.0 indicate that the component is enriched relative to the Earth's crust because of the contribution of different sources.

$$EFc = (x / Al)\ \text{precipitation} / (x / Al)\ \text{crust} \qquad (1)$$

Table 2. For the elements, the wavelength (λ) studied and the limit of detection (LOD)

	λ (nm)	**LOD µg/ L**		**λ (nm)**	**LOD µg/ L**		**λ (nm)**	**LOD µg/ L**
Ca	317.933	0.08	**Ba**	413.066	0.08	**Li**	610.362	0.08
Fe	259.94	0.04	**Mg**	383.826	0.08	**Mn**	403.076	0.08
K	766.49	0.08	**Ca**	345.35	0.08	**Ni**	352.454	0.08
Na	588.995	0.08	**Cr**	357.869	0.08	**Al**	396.152	0.08
Pb	405.783	0.08	**Cu**	224.7	0.04			

If all the concentrations of nitrate and non-sea salt (nss) sulphate in rainwater were present in the form of free acid, the pH value should be much lower. From the difference between the total average concentrations of nitrate and non-sea salt sulphate and the average concentration of H^+ ions, it can be concluded that the acidity is neutralized to a large extent. To understand the extent to which Ca^{2+}, Mg^{2+} and Na^+ ions contribute to the neutralization of acidity, the Neutralization Factor (NF) for each cation was calculated using formula by equations (Equation 2,3,4).

$$NFCa = Ca^{2+} / (NO_3^- + SO_4^{2-}) \qquad (2)$$

$$NFMg = Mg^{2+} / (NO_3^- + SO_4^{2-}) \qquad (3)$$

$$NFNa = Mg^{2+} (NO_3^- + SO_4^{2-}) \qquad (4)$$

Results and Discussion

Results of analysis of precipitation

The meteorological conditions (wind direction and speed, amount of precipitation) and the industrial establishments of the sampling regions greatly affect the acidity of precipitation. The lowest pH values were found as 5.23 in L2 and 5.35 in L1, and the highest pH values were found as 7.12, 7.06 and 7.16 in L3, L4 and L5, respectively. The pH in the range of 5.0-6.0 was measured only in L2 and L1 where industrial establishments are situated. It was also determined that the pH value did not exceed 7.0 in this region. It was observed that the electrical conductivity varied between 37.3 – 171.1 µS cm^{-1} according to the regions. The arithmetic mean conductivity value of 153 samples was 86.77 µS cm^{-1}. It was observed that the increase and decrease in conductivity values were similar in all sampling areas. The pH and electrical conductivity changes according to the regions are shown in Figure 2.

Results of samples analysed in 1999 and 2009 are given in Table 3. In 1999, the highest concentrations of Pb, Mn, Ca, Mg, Li, K were found in L1. The reason for this is that this company is the largest iron and steel plant in Türkiye and at that time it emitted 43 tonnes of heavy metals per day. In 2009, Mn, Li and Ca were found at the highest concentrations in L1, while Pb, Mg and K were found to be high in L2, and no daily heavy emission data could be obtained. It was observed that sulphate concentration decreased in the last 10 years but nitrate concentration increased and also chlorine ion increased in L1 and L5 and decreased in other sampling sites. In 1999, sulphate concentration was the highest at L1 with 97.7 mg/L, while it decreased to 11.46 mg/L in 2009. This shows that the amount of SO_2 released to the atmosphere has decreased. It was also found that there was a decrease in sulphate concentration and all metal ions except K, Ba and Al. This may be due to the increase in sensitivity to environmental pollution and taking precautions within 10 years. The increase in K^+ and Cl^- ions shows that the salinity in the sea has increased.

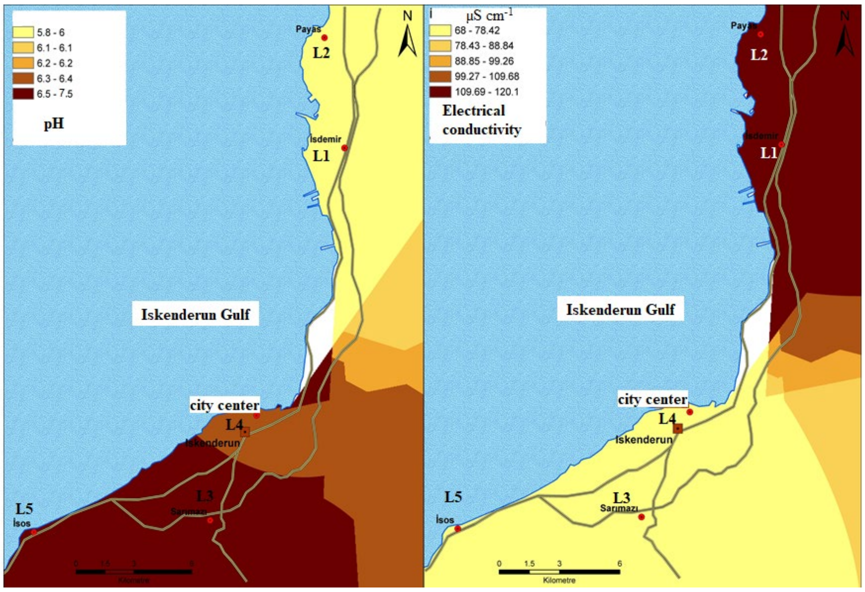

Figure 2. The pH and electrical conductivity changes according to the regions

Table 3. Results of samples analyzed in 1999 and 2009.

		L1	L2	L3	L4	L5			L1	L2	L3	L4	L5
Cl^-	*	6.67	8.43	11.31	12.10	12.22	Ba	*	16.46	13.96	19.55	22.04	21.19
mg/L	**	8.46	7.68	2.78	4.45	13.55	µq/L	**	17.98	13.25	12.09	10.55	6.52
SO_4^{2-}	*	97.07	64.55	34.81	33.91	27.44	Mn	*	26.27	17.72	3.87	4.83	1.12
mg/L	**	11.46	9.05	4.26	3.94	3.11	µq/L	**	7.78	6.84	5.65	6.02	5.15
NO^-_3	*	2.50	1.72	0.05	0.03	0.39	Pb	*	6.87	4.16	5.22	6.63	5.52
mg/L	**	8.07	7.58	2.13	2.49	2.47	µq/L	**	6.54	6.81	3.27	4.04	4.42
Mg	*	2.32	2.18	1.41	1.31	1.12	Fe	*	12.35	13.91	18.06	14.55	16.05
mg/L	**	1.2	1.38	1.02	0.94	1.02	µq/L	**	10.98	9.21	8.51	7.56	7.09
Ca	*	16.69	14.58	14.33	10.00	12.34	Cr	*	4.11	3.77	3.27	5.16	3.95
mg/L	**	7.62	7.21	5.68	6.22	6.54	µq/L	**	2.47	1.47	0.59	0.73	0.72
Na	*	4.03	4.12	4.60	4.40	4.89	Cu	*	4.28	6.24	5.28	4.26	5.04
mg/L	**	3.67	2.89	2.37	2.68	3.6	µq/L	**	3.09	4.69	0.65	0.92	1.16
K	*	0.95	0.99	0.98	1.03	0.97	Ni	*	5.00	6.79	6.62	4.97	3.40
mg/L	**	0.73	1.11	1.0	1.07	1.37	µq/L	**	1.17	1.25	1.18	1.17	1.21
Al	*	32.59	29.07	35.97	30.04	22.64	Li	*	0.91	0.82	0.89	0.76	0.89
µq/L	**	54.22	54.13	47.09	48.08	53.61	µq/L	**	0.41	0.31	0.32	0.47	0.46
Co	*	5.08	5.43	3.44	3.09	2.60							
µq/L	**	3.54	3.66	2.81	2.43	2.01							

* For the year 1999, ** For the year 2009

Significant metal concentration was found in previous research on heavy metals (HMs) in precipitation from nations such as Korea, Greece, China, Mexico, Iran, USA, and Tibet (Cherednichenko *et al.*, 2021, Báez et al., 2007, Koulousaris *et al.*, 2009, Kim *et al.*, 2012, Koulousaris et al. 2013). Samples from Kazakhstan's Mynzhilki Mountains had high amounts of Cu, Pb, Cd and As (7720, 1520, 206 and 275 µg/L, respectively) (Cherednichenko *et al.* 2021). Pb and Cd values in northwest France were reported to be 142 and 9 µg/L, respectively (Koulousaris *et al.* 2013). Zn, Ni, Cr, Pb, and Cd levels of 89, 4, 5, 10, and 13 µg/L were measured in Denizli, Türkiye (Cukurluoglu et al. 2017). In Iran, the results for the mean concentrations of As, Cd, Cr, Cu, Ni, Pb, Zn, and Na were fewer than 6.4 µg/L (Hosseinpoor *et al.*, 2023).

Trace elements

The percentage distribution of trace elements measured in rainwater samples collected in Iskenderun Gulf is given in Figure 3. Concentrations of trace elements are in the order of Al> Ba> Fe> Mn> Pb>

Co> Cu> Cr> Ni> Li and the highest concentrations are Al and Ba, which are soil-derived elements. Among the anthropogenic elements, the highest concentrations belong to Ba, Mn, Pb and Fe.

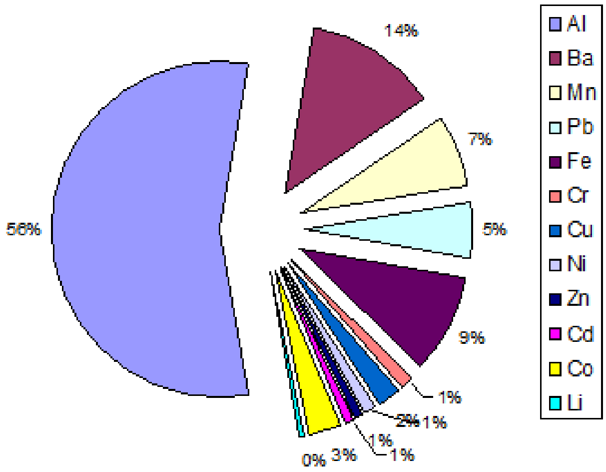

Figure 3. Percentage distribution of trace elements.

Ion Balance

The ratio of the total concentration of anions to the total concentration of cations (∑Cation / ∑Anion) is an indication that the analyses are complete and the measurements are complete. In case all the basic anions and cations are measured, this ratio should be 1.0. Deviations from 1.0 indicate that some basic ions were not measured or that the analyses were performed incorrectly when all ions were measured (Özsoy *et al.*, 2009). The ratio (∑Cation / ∑Anion) of total cation concentrations (Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, H^{+}) to total anion concentrations (SO_4^{2-}, Cl^{-}, NO_3^{-}) measured in Iskenderun Gulf was calculated as 1.3 in 1999. The fact that this ratio is above 1.0 suggests that there is an essential anion not included in the analyses. These anion is thought to be HCO_3^{-}. Therefore, for 2009, the HCO_3^{-} ion concentration was calculated as 163.93µeq/L using the pH of the rainwater in the sampling sites. As a result, the ratio (∑Cation / ∑Anion) of total cation concentrations to total anion concentrations was found to be 1.0.

Enrichment Factors

The enrichment factors of the elements measured in the Iskenderun Gulf precipitation were calculated according to aluminium, which is used as a reference element and assumed to originate entirely from the soil, and EFc values were found based on the average total concentrations of the elements. The EFc values of elements in for each sampling site are given in Table 4. In this calculation, the average composition of the upper crust given by Rudnick and Gao (2003) was used as reference values.

Table 4. EFc values of elements in precipitation

	L1	L2	L3	L4	L5	L1	L2	L3	L4	L5
	For the year 1999					For the year 2009				
Ca	1015	997	782	737	1048	278	264	239	256	242
Ba	97	93	105	142	171	64	47	49	42	23
Na	430	493	440	506	1524	235	186	175	194	233
Co	519	624	318	343	376	217	225	198	168	12
Cr	105	108	75	143	143	37	22	10	12	11
Cu	195	320	219	190	327	85	129	20	28	32
Pb	1405	1880	966	1474	1492	804	830	462	560	549
Li	116	117	103	105	161	31	23	28	40	35
Mg	256	265	247	154	203	78	90	76	69	67
Mn	67	92	9	13	4	11	10	9	10	8
Ni	168	256	202	182	162	23	25	27	26	24
Fe	0.55	0.62	0.73	0.71	1	0.30	0.25	0.26	0.23	0.19
K	114	133	106	133	161	53	80	83	87	100

The highest EFc values were found in L1 and L2 regions. The reason for this is that L1 and L2 are located the North of the İskenderun industrial zone where there is intensive industrialization such as iron-steel, cement factories, arc furnaces, fertilizer factory etc. In addition, pollutants are transported more to L1 and L2 region with the wind blowing from the southwest.

Table 4 shows that Fe element with EFc values between 1-10 is not enriched by anthropogenic sources and are of crustal origin. Ca, Na, Co and Pb metals with EFc values greater than 100 have high anthropogenic contributions. EFc values of Ba, Cr, Cu, Li, Mn, Ni and K metals between 10 and 100 indicate moderate anthropogenic contribution. Especially Mn was found to be of anthropogenic origin in L1 and L2 regions where the industry is intensive, and of crustal origin in other regions. According to the calculated enrichment factors, Pb enrichment factor is the highest among the anthropogenic elements with EFc=1492, followed by Co. When the enrichment factors calculated in 1999 and 2009 are compared, the decrease in 10 years is clearly seen. In 1999, the EFc value of the anthropogenic Pb element with a maximum EFc value of 1492 decreased to 549 after 10 years. There is a noticeable decrease in the EFc values of all elements.

When the enrichment factors (EFc) for Fe, V, Ni, and Cr in Kuwaiti rainwater were less than 10, it was suggested that the sources could only be crustal. Furthermore, results for Ni, Zn, Cu, and Mn ranged from 10 to 100 in the research, indicating pollution from industrial sources. Since the contribution from anthropogenic sources exceeded 100, the EFc for Sr exceeded 100 (Samayamanthula *et al.*, 2021). The enrichment factor analysis of precipitation in Iran showed that whereas Cd, Zn, Cr, Pb, Ni, and Cu were considerably enriched, indicating major contributions from anthropogenic sources, Na and As exhibited relatively low enrichment factors, suggesting natural origins (Hosseinpoor et al., 2023).

Neutralisation Factors

The neutralization factors (NF) for Ca^{2+}, Mg^{2+} and Na^{+} ions are given in Table 5 for each sampling site.
Table 5. NF values for the sampling sites. This result shows that Ca^{2+} ion is the main factor that plays a role in the neutralization of acidity in the Gulf of Iskenderun precipitation.

	L1	L2	L3	L4	L5
NF_{Ca}	0.39	0.43	0.88	0.96	1.17
NF_{Mg}	0.06	0.08	0.15	0.14	0.18
NF_{Na}	0.04	0.06	0.13	0.12	0.19

Salinity

The samples belonging to L5, which is located on the coast, have high concentrations of Na^{+} and Cl^{-} ions. In this sampling area, especially Na^{+} and Cl^{-} ion concentrations are high in rainwater due to the effect of salts in the sea. The fact that the Cl^{-} concentration in the L1 sampling area reaches and exceeds the value in the L5 area from time to time shows that the Cl^{-} source in this region is not only the sea but also industrial processes. Na^{+} and Cl^{-} concentrations were measured in the samples taken for L1, L2, L3, L4 and L5 respectively and the Cl^{-} / Na^{+} ratio in rainwater was calculated and the results of 2.3; 2.65; 1.17; 1.66; 3.76 were obtained respectively. These ratios indicate how high the salinity of the sea is. Since sea salt particles are formed by the bursting of bubbles on the surface of the sea, the concentration of sea salt elements depends on the wind speed. Most of the storms in the Mediterranean region are frontal and increase their effects on rainy days.

Conclusions

The average pH of the rainwater collected in 5 different regions in Iskenderun Gulf was found to be 5.95, 5.81, 6.53, 6.3 and 6.5 in L1, L2, L3, L4 and L5, respectively. The average pH of 6.22 indicates that the rains in Iskenderun Gulf are alkaline in character. The reason for this is the mineral dust with high limestone ($CaCO_3$) content present in the local atmosphere. Carbonate and/or bicarbonate anions formed by the dissolution of limestone buffer the rainwater and neutralize its acidity. In all sampling sites, pH increased in the ranges where sulphate and nitrate concentrations decreased, and pH decreased in the ranges where they increased for both years. It is understood that calcium ion is one of the factors that play a role in neutralizing the acidity of rainfall in the Gulf of Iskenderun.

Ca, which is generally originated from the earth's crust, was found to be very high in all sampling areas. The biggest factor in the high concentration is the abundant $CaCO_3$ content of the soil due to meteorological factors and the dolomite deposits in the region. Crustal and marine elements showed a similar decrease and increase at all sampling sites.

At the end of March and the beginning of April, dusts from Africa were observed intensively. Ca and Al concentrations were high in all sampling sites during these periods. During the furnace smelting of scrap metals, a significant amount of gas and dust is generated and these gases cannot be collected efficiently and can be uncontrollably discharged into the atmosphere through the air gaps in the roofs and walls of the facilities. In all five sampling sites, the average concentrations of the major ions were $Cl^- > Ca^{2+} > SO_4^{2-} >$ NO3- > N+ > $Mg^{2+} > K^+$, respectively. The ions with the highest concentrations are calcium cation, mainly from soil and anthropogenic sources, and chloride anion from sea salt. The sum of these two ions constitutes 46.6% of the total ion concentration, while sulphate and nitrate ions constitute 36.02% of the total ion concentration. This shows that anthropogenic sources are effective in the atmosphere of Iskenderun Gulf. A significant amount of gas and dust is generated during the melting of scrap metals. Since these gases cannot be collected efficiently, they can be uncontrollably discharged into the atmosphere through the gaps in the roofs and walls of the plants.

Within 10 years, the reason for the decrease in sulphate concentration is thought to be the use of natural gas as fuel in industrial establishments. The order of trace element concentrations in the collected precipitation is Al> Ba> Fe> Fe> Mn> Pb> Co> Cu> Cr> Ni> Li and the highest concentrations were found in the L1 and L2 regions where both soil and anthropogenic elements were found to be high in the precipitation water. Among the anthropogenic elements, the highest concentration belongs to Pb element and the highest concentration of this element was measured in L1 and L2 region. The highest concentrations of Ni, Co, Cu were measured in L2 region where highly polluting electric arc furnace plants, integrated iron and steel plants, rolling mills, foundries are also located. Due to the presence of industrial establishments (iron and steel industry, fertilizer factory, arc furnaces...etc) and heavy traffic in L1 and L2, element concentrations were found to be higher in these regions. Some slags contain significant amounts of heavy metals and their release can cause some environmental problems. It is thought that slags are another reason for the EFc>10 in L1 and L2 regions for Mn. High enrichment factors for soil and marine elements such as Ca, Na, K and Mg were found in all locations. The fertilizer factory is also thought to have an effect. Within 10 years, EFc values have decreased in most of the metals. However, ion and element values in rainwater in the Iskenderun Gulf in 2009 are still high. So, in order to prepare a clean air plan in the region, it is suggested that the number of sampling sites where rainwater is taken should be increased, continuous measurements should be made with automatic devices and regular reports should be obtained on a yearly basis. On 6 February 2023, two earthquakes with magnitudes of 7.8 and 7.5 occurred in Türkiye and caused major damage in Iskenderun Gulf. This study provides valuable information on the use of post-earthquake rainwater analyses in Iskenderun Gulf.

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Data Availability: *The dataset analysed during the current study is not publicly available due to the corresponding author does not possess full rights to the entire dataset, but it may be available on a reasonable request.*

Conflict of Interest: *The authors declare no competing interests.*

Author contribution: *The authors contributed equally to the study.*

Ethics committee approval: *This study does not require ethics committee permission or any special permission.*

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