Profiling of volatile organic compounds for environment discrimination in Vilnius City

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The aim of this study was to show how volatile organic compounds (VOCs) profiling can be used as a method to identify different environments across a city. To achieve that, we employed several methods. First, we carried out the profiling of VOCs in several different locations. Then we identified the marker compounds and their sources. Air samples were collected from 6 different locations within the Vilnius City centre using thermal desorption (TD) tubes. Samples were analysed using thermal desorption coupled with gas chromatography mass spectrometry (TD/GC-MS) methodology. Compound identification was performed by the library match using the NIST MS Search 2.0 (2005) mass spectral library. The results show how variation in the levels of different VOCs can distinguish between locations within a relatively small area of 2 km² depending on different emission sources.

Keywords: VOC, thermal desorption, chromatography, anthropogenic, biogenic

INTRODUCTION

Volatile organic compounds (VOCs) are compounds with a high vapour pressure and a low solubility in water. Any organic compound having an initial boiling point less than or equal to 250°C measured at a standard atmospheric pressure of 101.3 kPa is considered a VOC [1]. Thousands of VOCs have been identified from a wide range of sources [2, 3]. VOCs are precursors of O₃ and secondary organic aerosols (SOAs). Therefore, those compounds significantly contribute to the formation of photochemical smog, atmospheric oxidative capacity, visibility degradation and global climate changes [4–6].

VOCs can be biogenic and anthropogenic. Terrestrial vegetation is the dominant source of atmospheric VOCs accounting for about 90% of the total emission globally [7]. Isoprene and monoterpenes are the most abundant species among the biogenic VOCs [8]. Both isoprene and monoterpenes are mainly emitted in the tropical region (88 and 83% of the global total, resp.). Nevertheless, aromatic hydrocarbons are the most common VOCs to which we are exposed everyday in urban locations. Those VOCs are produced in human activities (anthropogenic source), mainly from fossil fuel emissions and they are considered cancerogenic [9]. As those compounds are a concern for human health their levels are one of the main parameters when considering environmental contamination, together with particle matter, CO₂, ozone and nitrogen oxide [10].

Both types of VOCs contribute to causing climate change and can be cancerogenic. Therefore, in recent years, much research has focused on the impacts of VOCs due to their influence on atmospheric chemistry and impacts on human health [11–13]. Consequently, VOCs profiling is widely used in many environments as an indicator...
for air quality. Most of the studies that analyse the VOCs levels in highly polluted cities show how different environments at different times of the day have varying levels of different VOCs [14].

Since 2010, Lithuania has been ranked among the fastest growing economies in the European Union [15], and therefore has seen an augment in the traffic. As it is common for all major cities around the world, the increase in traffic has boosted the environmental contamination, and therefore, the levels of VOCs. Several studies show how Vilnius had problems with atmospheric contamination [16, 17]. Especially in neighbourhoods like Žvėrynas [18], where many houses still use coal as a way of heating, the levels of VOC emissions were higher than the limits established by the Lithuanian Ministry of Environment.

In our study, we aim to collect the VOC pattern from several locations in the city centre and identify different emission sources influencing the air composition in Vilnius.

**EXPERIMENTAL**

**Locations**

We have checked the volatiles from 6 different locations in Vilnius, Lithuania. All the locations are in a 2 km² area within the Vilnius City center (Fig. 1). The locations were chosen with the criteria to have different traffic and greenery conditions with a variety of VOCs sources.

**Equipment**

Thermal desorption (TD) tubes were employed for the collection of samples. TD tubes with a Tenax® TA sorbent were purchased from Markes International (UK). The air samples were pumped through the sorbent by using an air sampler.
Aircheck Sampler model 224–44XRM from SKC Inc.

**Sample collection**
TD tubes were conditioned following manufacturers’ instructions. Air samples were collected at the specific locations (Fig. 1) by applying a flow of 1000 ml/min for 10 min. All the samples were collected the same day, in a range of 2 h to have similar weather conditions in all the locations (Table 1). The samples were analysed within 3 h from their collection time. The samples from the same

### Table 1. Weather conditions

| Time       | Temperature | Humidity | Wind | Wind speed | Precip. | Condition      |
|------------|-------------|----------|------|------------|---------|----------------|
| **Day 1 (3 August 2021)** |             |          |      |            |         |                |
| 10:20 AM   | 17°C        | 77%      | WSW  | 17 km/h    | 0.0 mm  | Mostly cloudy  |
| 10:50 AM   | 16°C        | 88%      | WSW  | 15 km/h    | 0.0 mm  | Light rain shower |
| 11:20 AM   | 18°C        | 83%      | WSW  | 19 km/h    | 0.0 mm  | Mostly cloudy  |
| 11:50 AM   | 18°C        | 73%      | W    | 17 km/h    | 0.0 mm  | Mostly cloudy  |
| **Day 2 (20 August 2021)** |             |          |      |            |         |                |
| 10:20 AM   | 19°C        | 60%      | WSW  | 17 km/h    | 0.0 mm  | Fair           |
| 10:50 AM   | 20°C        | 56%      | WSW  | 19 km/h    | 0.0 mm  | Mostly cloudy  |
| 11:20 AM   | 20°C        | 60%      | SW   | 20 km/h    | 0.0 mm  | Mostly cloudy  |
| 11:50 AM   | 20°C        | 60%      | WSW  | 19 km/h    | 0.0 mm  | Mostly cloudy  |
| **Day 3 (23 August 2021)** |             |          |      |            |         |                |
| 10:20 AM   | 19°C        | 56%      | SSW  | 7 km/h     | 0.0 mm  | Fair           |
| 10:50 AM   | 20°C        | 52%      | VAR  | 7 km/h     | 0.0 mm  | Partly cloudy  |
| 11:20 AM   | 18°C        | 56%      | W    | 6 km/h     | 0.0 mm  | Mostly cloudy  |
| 11:50 AM   | 19°C        | 56%      | VAR  | 6 km/h     | 0.0 mm  | Mostly cloudy  |
| **Day 4 (24 August 2021)** |             |          |      |            |         |                |
| 10:20 AM   | 15°C        | 63%      | NNE  | 17 km/h    | 0.0 mm  | Partly cloudy  |
| 10:50 AM   | 15°C        | 63%      | NNE  | 19 km/h    | 0.0 mm  | Mostly cloudy  |
| 11:20 AM   | 15°C        | 59%      | N    | 22 km/h    | 0.0 mm  | Partly cloudy  |
| 11:50 AM   | 16°C        | 55%      | NNE  | 20 km/h    | 0.0 mm  | Partly cloudy  |
| **Day 5 (25 August 2021)** |             |          |      |            |         |                |
| 2:50 PM    | 17°C        | 52%      | N    | 17 km/h    | 0.0 mm  | Mostly cloudy  |
| 3:20 PM    | 17°C        | 52%      | SW   | 19 km/h    | 0.0 mm  | Mostly cloudy  |
| 3:50 PM    | 16°C        | 55%      | WSW  | 15 km/h    | 0.0 mm  | Mostly cloudy  |
| 4:20 PM    | 17°C        | 52%      | WSW  | 13 km/h    | 0.0 mm  | Mostly cloudy  |
| **Day 6 (7 September 2021)** |             |          |      |            |         |                |
| 10:20 AM   | 15°C        | 55%      | SW   | 13 km/h    | 0.0 mm  | Fair           |
| 10:50 AM   | 15°C        | 55%      | SSW  | 15 km/h    | 0.0 mm  | Fair           |
| 11:20 AM   | 16°C        | 48%      | SW   | 15 km/h    | 0.0 mm  | Fair           |
| 11:50 AM   | 16°C        | 45%      | WSW  | 15 km/h    | 0.0 mm  | Fair           |

Source: www.wunderground.com. The Weather Company, an IBM business.
exact locations were collected during 6 different days to compare the variations of the VOC profile.

**Weather conditions**
The weather conditions for the 6 days when the samples were collected are presented in Table 1.

**Sample analysis**
TD tubes were loaded into the TD system (ATD 400, Perkin Elmer) where the tubes were heated, releasing the trapped compounds into the system using the parameters from Table 2. The compounds were then separated and identified using a GC-MS system (Agilent 6890N coupled to a mass spectrometer AutoSpec Premier, Waters/Micromass). The DB-5MS, 30 m, 0.25 mm ID, 0.25 mm (Agilent Technologies) column temperature was held at 40°C for 3 min and was then increased by 5°C/min to 120°C, followed by ramping at 10°C/min to 220°C. The MS analyses were performed in the full-scan mode, using a scanning range m/z 50–200. The ion source was maintained at 250°C, and ionization energy (EI+) of 70 eV was used for each measurement. Compound identification was performed by the library match using the NIST MS Search 2.0 (2005) mass spectral library. Data statistical analysis was performed using the R Core Team, the jamovi project and OriginLab software [19, 20].

**RESULTS AND DISCUSSION**
The compounds from all the locations were identified and their relative concentration was obtained by collecting the areas from the chromatograms (Table 3). In an area of two square kilometers we found different sources of VOCs; each area gave a distinctive pattern of compounds (Fig. 2).

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**Table 3. Main compounds identified in the locations studied and their average relative concentration for each location**

| Ret. time | Compound                  | Possible sources                     | Loc. 1 Rel. % | Loc. 2 Rel. % | Loc. 3 Rel. % | Loc. 4 Rel. % | Loc. 5 Rel. % | Loc. 6 Rel. % |
|----------|---------------------------|--------------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 1.00     | Acetone                   | Petrol/car exhaust/human breath      | 6.24          | 8.08          | 9.95          | 6.73          | 5.57          | 5.79          |
| 1.13     | tert-Butyl methyl ether   | Fuel additive                        | 5.67          | 2.42          | 2.75          | 2.32          | 2.48          | 2.67          |
| 1.40     | *Benzene                  | Petrol/car exhaust                   | 4.68          | 5.77          | 3.83          | 4.79          | 4.92          | 5.24          |
| 1.59     | Heptane                   | Fuel additive                        | 1.93          | 2.47          | 2.90          | 3.05          | 3.01          | 3.05          |
| 1.81     | Butyl octanol             | Petrol/car exhaust                   | 0.51          | 0.87          | 0.70          | 0.89          | 0.76          | 0.83          |
| 1.98     | Hexone                    | Other                                 | 0.45          | 0.59          | 0.64          | 0.80          | 0.55          | 0.55          |
| 2.24     | *Toluene                  | Petrol/car exhaust                   | 20.65         | 18.12         | 12.65         | 15.03         | 17.78         | 17.42         |
| 2.72     | Octane                    | Petrol/car exhaust                   | 0.93          | 0.53          | 0.70          | 0.50          | 0.79          | 3.29          |
| 3.05     | Butyl acetate             | Fragrances                            | 1.02          | 2.92          | 2.97          | 1.70          | 1.56          | 1.31          |
| 3.97     | *Ethyl benzene            | Petrol/car exhaust                   | 3.83          | 3.94          | 2.94          | 3.07          | 3.73          | 4.07          |
| 4.22     | *m, p xylene              | Petrol/car exhaust                   | 12.99         | 11.66         | 8.85          | 9.55          | 12.69         | 13.12         |
| 4.77     | *o xylene                 | Petrol/car exhaust                   | 4.57          | 5.22          | 3.58          | 4.30          | 5.01          | 5.41          |
| 5.84     | #a-pinene                 | Vegetation/fragrances                 | 2.90          | 4.46          | 6.79          | 5.35          | 3.03          | 3.01          |
| 6.31     | #Camphene                 | Vegetation/fragrances                 | 1.05          | 0.67          | 1.06          | 0.56          | 0.80          | <LOD          |
| 6.41     | Dimethylolpropane         | Other                                 | 8.46          | <LOD          | <LOD          | <LOD          | <LOD          | <LOD          |
| 6.54     | *Propyl benzene           | Petrol/car exhaust                   | 1.10          | 1.13          | 1.19          | 0.59          | 0.93          | 0.96          |
| 6.74     | *1,2,4-Trimethylbenzene   | Petrol/car exhaust                   | 2.37          | 1.87          | 2.74          | 1.28          | 2.43          | 2.33          |
| 6.85     | *m-Ethyltoluene           | Other                                 | 1.29          | 0.78          | 2.57          | 1.00          | 0.92          | 1.04          |
Table 3. (continued)

| Ret. time | Compound               | Possible sources         | Loc. 1 Rel. % | Loc. 2 Rel. % | Loc. 3 Rel. % | Loc. 4 Rel. % | Loc. 5 Rel. % | Loc. 6 Rel. % |
|-----------|------------------------|--------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 6.90      | Benzaldehyde           | Vegetation/fragrances    | 2.57          | 6.03          | 6.74          | 9.40          | 5.05          | 3.98          |
| 7.14      | #4-Carene              | Vegetation/fragrances    | 0.61          | 0.90          | 2.19          | 3.38          | <LOD          | <LOD          |
| 7.23      | *p-Ethyltoluene        | Petrol/car exhaust       | 0.83          | 0.97          | 2.06          | 0.58          | 0.90          | 1.13          |
| 7.72      | *1,2,3-Trimethylbenzene| Petrol/car exhaust       | 3.79          | 3.49          | 2.88          | 3.20          | 3.86          | 3.61          |
| 8.02      | 4-Ethylloctane         | Petrol/car exhaust       | 0.79          | 1.10          | 0.88          | 1.23          | 1.11          | 1.30          |
| 8.14      | #Terpinen              | Vegetation/fragrances    | 1.31          | 3.19          | 9.31          | 7.20          | 2.94          | 1.58          |
| 8.22      | Octanal                | Petrol/car exhaust       | 0.74          | 0.53          | 1.43          | 1.69          | 1.03          | 0.77          |
| 8.53      | *1,3,5-Trimethylbenzene| Petrol/car exhaust       | 0.76          | 0.94          | 1.29          | 0.73          | 0.87          | 1.12          |
| 8.85      | #D-Limonene            | Vegetation/fragrances    | 0.55          | 0.68          | 2.27          | 1.50          | 0.89          | 0.47          |
| 8.90      | p-Methylstyrene        | Other                    | 0.59          | 0.73          | 0.54          | 0.90          | 0.62          | 0.74          |
| 9.03      | 2-Ethyl-1-decanol      | Other                    | 0.55          | 0.63          | 1.03          | 1.16          | 0.96          | 1.00          |
| 9.42      | *1,3-Diethylbenzene    | Petrol/car exhaust       | 0.14          | 0.41          | <LOD          | <LOD          | 0.28          | <LOD          |
| 9.51      | *1-Methyl-3-propylbenzene| Petrol/car exhaust       | 0.58          | 0.83          | <LOD          | <LOD          | 0.64          | 0.80          |
| 9.68      | *1-Methyl-2-propylbenzene| Petrol/car exhaust       | 0.43          | 1.07          | <LOD          | <LOD          | 0.71          | 1.05          |
| 9.72      | *2-Ethyl-1,4-dimethylbenzene| Petrol/car exhaust  | 0.83          | 1.02          | <LOD          | <LOD          | 1.46          | 1.10          |
| 9.90      | 2-indanol              | Other                    | 0.51          | 0.43          | 0.65          | <LOD          | 0.37          | 0.32          |
| 10.11     | Acetophenone           | Vegetation/fragrances    | 1.89          | 3.80          | 4.35          | 4.57          | 2.62          | 2.29          |
| 10.28     | *1,2-Dimethyl-4-ethylbenzene| Petrol/car exhaust   | 0.38          | 1.93          | <LOD          | <LOD          | 1.08          | 1.52          |
| 10.36     | *1-Ethyl-2,4-dimethylbenzene| Petrol/car exhaust       | 0.68          | 0.78          | <LOD          | 1.19          | 0.72          | 0.56          |
| 10.53     | *1,2,4,5-Tetramethylbenzene| Petrol/car exhaust       | 0.60          | 1.30          | <LOD          | 0.67          | 0.93          | 0.77          |
| 11.13     | Undecane               | Other                    | 1.27          | 1.37          | 1.08          | 1.15          | 1.27          | 1.90          |
| 11.38     | Nonanal                | Fragrances/human breath  | 5.80          | 2.51          | 4.84          | 3.28          | 4.73          | 3.08          |
| 11.52     | *1,2,3,4-Tetramethylbenzene| Petrol/car exhaust       | 0.17          | 0.66          | <LOD          | <LOD          | 0.22          | 0.58          |
| 11.59     | *1,2,3,5-Tetramethylbenzene| Petrol/car exhaust       | 0.48          | 0.66          | <LOD          | <LOD          | 0.65          | 0.70          |
| 12.42     | 4-Methylindane         | Other                    | 0.52          | 0.38          | <LOD          | <LOD          | 0.67          | 0.77          |
| 12.51     | *1,2-Dimethyl-3-ethylbenzene| Petrol/car exhaust       | 0.29          | 0.76          | <LOD          | <LOD          | 0.31          | 0.47          |
| 13.53     | 1-Methylene-1H-indene  | Other                    | 0.65          | 1.41          | 1.23          | 1.13          | 0.96          | 1.53          |
| 14.18     | 6-Methyltridecane      | Other                    | 1.01          | 2.00          | 1.21          | 1.79          | 1.16          | 1.80          |
| 14.44     | Decanal                | Vegetation/fragrances    | 0.98          | 1.88          | 2.71          | 3.34          | 2.98          | 1.42          |
| 14.89     | Benzothiazole          | Fragrances               | 0.56          | 1.45          | 0.83          | 1.19          | 1.26          | 1.40          |
| 15.03     | Cyclohexyl isothiocyanate| Other                    | 0.66          | 1.19          | 1.39          | 1.41          | 1.90          | 1.12          |
| 16.58     | #Isobornyl acetate     | Vegetation               | 0.97          | 0.81          | 3.75          | 1.33          | 0.30          | 0.42          |
| 17.06     | Tridecane              | Petrol/car exhaust       | 1.05          | 1.25          | 1.19          | 1.25          | 1.16          | 1.50          |
| *Total benzene derivates |                        |                           | 58.88         | 55.97         | 37.05         | 41.93         | 54.76         | 57.41         |
| #Total terpenes |                        |                           | 4.71          | 8.10          | 22.11         | 14.43         | 6.75          | 4.97          |

<LOD: below the limit of detection.

As we collected the volatiles from those locations during several days, we could identify the punctual events happening in each location: re-fuelling the petrol station (Fig. 3), cutting the grass and installation of new benches (newly painted). Meteorological events also affected the results; during a windy day, the composition of VOCs was diluted, obtaining a decrease in the levels of compounds (Fig. 4).
Fig. 2. Chromatogram from the 6 locations (same day)

Fig. 3. Increase of VOC levels when re-fuelling petrol. Green: re-fuelling event, Location 1 (Day 2); red: usual day, Location 1 (Day 6)

Fig. 4. Decrease of VOC levels on a windy day. Green: wind speed 7 km/h, Location 1 (Day 3); red: wind speed 17 km/h, Location 1 (Day 1)
Even though the levels of VOCs might differ depending on various factors and weather conditions, we studied the full profile for each location. We calculated the average relative concentration of VOCs for the 6 different locations during all the sampling days (Table 3).

Principal component analysis (PCA) was performed to decrease the amount of variables (Fig. 5). The data showed that the main difference across the locations was the presence of benzene derivates and terpene compounds. The park locations have a higher concentration of biogenic VOCs (terpenes), while the locations with intense traffic have a higher concentration of anthropogenic VOCs (benzene derivates). Therefore, we decided to group those variables to perform ANOVA analysis (Fig. 6).

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**Fig. 5.** PCA analysis. Clusters: red: Locations 1, 2 and 6; blue: Location 3; green: Location 4; black: Location 5

**Fig. 6.** Relative concentration of total benzene derivates (a) and total terpenes (b) for each location. Column graph: total average; scatter graph: daily value
However, a big variance of the results might be a problem to get statistically significant differences. We firstly performed the Levene’s test (Table 4) for the analysis of variance homogeneity and the Shapiro–Wilk test (Table 5) for the study of the normal distribution of the results. Looking at the test results we cannot assume a normal distribution of the results for the total terpene concentration nor assume equal variances. Because of that, we performed Welch’s One-way ANOVA for total terpenes, and Fisher’s One-way ANOVA for total benzene derivates (Table 6).

The analysis shows a non-statistically significant result for total terpene concentration for the 6 locations \( (p = 0.180) \), but a statistically significant result for total benzene derivates concentration \( (p = 0.008) \). We finally performed a Tukey (equal variances) Post-Hoc Test (Table 7) to identify in which locations the results were statistically significantly different. Only the locations 4 and 6 show a statistically different result.

**CONCLUSIONS**

We analysed the VOC content and their relative concentrations in 6 different locations in Vilnius within an area of 2 km\(^2\). The results show a tendency which areas with a higher traffic load (Locations 1, 2 and 6) have a higher concentration of anthropogenic VOCs. In addition to that, the levels of biogenic VOCs were higher in the locations dominated by greenery (Locations 3 and 4). Location 5 (a park with heavy traffic) has a mix of both conditions, therefore the weight of anthropogenic and biogenic VOCs is similar. We observe a very dispersive variation of the results for each location. This is due to a number of parameters that could affect the results: punctual events like re-fuelling in a petrol station, cutting the grass, fumigating plants, traffic conditions, installation or renewal of urban furniture, as well as weather conditions like air temperature, wind speed, wind direction or rain. Due to these variations and data that contain a large number of outliers, we could not establish

**Table 4. Homogeneity of Variances Test (Levene’s)**

|          | \( F \) | \( df_1 \) | \( df_2 \) | \( p \) |
|----------|---------|------------|------------|--------|
| Terpenes | 4.72    | 5          | 31         | 0.003  |
| Benzene derivates | 2.18  | 5          | 31         | 0.082  |

**Table 5. Normality Test (Shapiro–Wilk)**

|          | \( W \) | \( p \) |
|----------|---------|--------|
| Terpenes | 0.868   | <.001  |
| Benzene derivates | 0.949 | 0.087  |

Note. A low \( p \)-value suggests a violation of the assumption of normality.

**Table 6. One-way ANOVA**

|          | \( F \) | \( df_1 \) | \( df_2 \) | \( p \) |
|----------|---------|------------|------------|--------|
| Terpenes | Welch’s | 1.81      | 5          | 13.0   | 0.180  |
| Benzene derivates | Fisher’s | 3.82 | 5          | 31     | 0.008  |

**Table 7. Games–Howell Post-Hoc Test – benzene derivates**

|          | 1       | 2       | 3       | 4       | 5       | 6       |
|----------|---------|---------|---------|---------|---------|---------|
| Mean difference | –       | 2.91    | 21.8    | 16.95   | 4.12    | 1.47    |
| \( p \)-value  | –       | 0.998   | 0.224   | 0.338   | 0.996   | 1.000   |
| Mean difference | –       | 18.9    | 14.04   | 1.21    | –1.44   |         |
| \( p \)-value  | –       | 0.127   | 0.120   | 1.000   | 0.997   |         |
| Mean difference | –       | –4.89   | –17.72  | –20.36  |         |         |
| \( p \)-value  | –       | 0.976   | 0.293   | 0.080   |         |         |
| Mean difference | –       | –12.83  | –15.48  | *       |         |         |
| \( p \)-value  | –       | 0.431   | 0.050   |         |         |         |
| Mean difference | –       | –2.65   |         |         |         |         |
| \( p \)-value  | –       | 0.995   |         |         |         |         |

Note. * \( p < .05 \).
statistically significant results. We could not establish that the differences in VOCs compositions across locations were statistically significant. However, we still observed differences in VOCs compositions across the six locations. This shows that even though the area of sampling was rather small, the different sources of VOCs have a strong influence in the air composition. This difference in the air composition allows us to discriminate different environments in the city.

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LAKIŲJŲ ORGANINIŲ JUNGINIŲ PROFILIAVIMAS SKIRTINGAI APLINKAI IDENTIFIKUOTI VILNIAUS MIESTE

Santrauka
Šio tyrimo tikslas buvo parodyti, kad lakiųjų organinių junginių (LOJ) profiliavimas gali būti naudojamas kaip būdas identifikuoti skirtingas miesto aplinkas. Norėdami tai pasiekti, taikėme kelis metodus. Pirmiausia atlikome LOJ profilio matavimus keliose skirtingose vietose. Tada nustatėme potencialių žymenų junginius ir jų šaltinius. Rezultatai parodė skirtingus LOJ lygių rezultatus santykinai mažame 2 km² plote, priklausomai nuo skirtingų emisijų šaltinių, kuriuos galima naudoti skirtingų aplinkų identifikuoti.