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ASSESSING LEVELS OF CO_2, CO, NO_X AND SO_2 IN INDOOR AIR USING DRÄGER SENSORS: A CASE STADY IN PRISHTINA, KOSOVO

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Abstract. Studies in large cities revealed that indoor air pollution concentrations are at such levels where it can cause serious health impacts. The main source of the release of substances in the environment is the emission of gases (produced during the combustion process) such as carbon dioxide, carbon monoxide, sulphur oxides, nitrogen oxides, ammonia and others. In this study the assessment of indoor air quality in 26 places in Prishtina city were investigated and the main objective of this study was monitoring of the air quality through the determination of gases concentration of $C0_2$, C0, $N0_x$ and $S0_2$. Also the ratio of CO_2/CO_2+CO was calculated. Concentrations of CO_2, CO, SO_2 and NO_x were determined using "Dräger" instrument, model "X-am 7000 digital gas monitor". Environmental risk assessment of air quality was done by comparing the obtained results with air WHO standards. During that period were found a permanent presence of some toxic gases in high concentrations in indoor areas. Results show that CO_2 levels were ranged 300-4000 ppmv. The concentration of CO was ranged 0.6-17 ppmv and was reported to be under limits value in all locations. Also concentrations of SO_2 and NO_x (except air sample S_6) were reported to be under WHO air limits value. According to gases concentration, many locations show values characteristic for highly and extremely contaminated indoor places.

Keywords: indoor air pollution, assessment, combustion process, sensors, biomass fuel

Introduction

Air quality is a very important for human health and the environment generally surrounding us, which is constantly under the influence of pollution. Buildings and other anthropogenic activities release heat and moisture that can increase the rate of reaction of pollutants, and buildings also act as surfaces for pollutants deposition. An increase in energy consumption may lead to more pollution generation as well (Rosenfeld et al., 1995; Chen & Kan, 2008). Well into the 21st century, 2.8 billion people still rely on solid fuels (wood, dung, crop wastes, charcoal, coal, etc.) and simple stoves for cooking and heating and 1.2 billion light their homes with simple kerosene lamps. Many studies show that these household energy practices result in very high levels of household air pollution. Global burden of disease estimates has found that exposure to household air pollution from cooking results in around 4 million premature deaths, with the most recent estimates from WHO reporting 4.3 million deaths for 2012. Indoor levels of many pollutants are often higher than those typically encountered outside, which would cause significant harmful health effects due to a long time period that people staying indoor. Klepeis et al. (2001) reported that people (in USA) may spend an average of 87 % of their time in enclosed buildings and approximately 6% of their time in enclosed vehicles. Tightly sealed buildings are an additional concern for the health of those who live and work inside. Skolnick (1989) reported that a population living in the tight energy efficient buildings contracted upper respiratory diseases at rates 46 to 50% higher than a compared group living in better ventilated houses. Indoor air pollution concentrations depend on a large number of factors such as indoor sources and the emission rates, air exchange rate, the penetration of outdoor pollutants into the indoor environment, and the pollutant sink or removal rate on indoor surfaces (Kamens et al., 1999; Thatcher & Layton, 1995; Beak et al., 1997). There are many types of household stoves for cooking and heating across the world. The major health impacts from household cook stoves, however, are experienced disproportionately in the developing world from solid fuel stoves, mainly biomass and coal, often in remote rural areas or urban slums. There is also increasing concern about the pollution from solid fuels, particularly wood, in household space-heating stoves and fireplaces in industrialized nations (WHO, 2014).

Wood fuel that is not properly burned to carbon dioxide is diverted into products of incomplete combustion – primarily carbon monoxide, but also benzene, butadiene, formaldehyde, poly aromatic hydrocarbons and many other compounds posing health hazards. The best single indicator of the health hazard of combustion smoke is thought to be small particles, which contain many chemicals (Smith, 1993). Cooking and heating with solid fuels (wood, charcoal, crop waste, dung, and coal) produces high levels of smoke in and around the home that contains a variety of health-damaging pollutants. There is strong evidence that exposure to household air pollution can lead to a wide range of child and adult disease outcomes, including acute and chronic respiratory conditions (e.g. pneumonia, chronic obstructive pulmonary disease), lung cancer, ischemic heart disease, stroke and cataract (WHO, 2016). There is also supporting evidence suggesting exposure to household air pollution is linked with adverse pregnancy outcomes, tuberculosis, upper aero-digestive tract, cervical and other cancers. An analysis of the pollutants originating from anthropogenic activities is crucial for formulating effective policies to reduce pollution and protect human health (Mavroidis & Ilia, 2012). Household use of solid fuels is thus estimated to be the largest single environmental risk factor and ranks sixth among all risk factors examined for ill-health (Smith et al., 2005). Burning biomass emits large amounts of pollutants, just like burning other solid fuels such as coal. Burning organic material emits particulate matter (PM), nitrogen oxides (NO_x), carbon monoxide (CO), sulfur dioxide (SO_2), lead, mercury, and other hazardous air pollutants (HAPs). Hazardous air pollutants (HAP) are a group of 187 toxics that according to EPA are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects (Air pollution/Partnership for Policy Integrity). Therefore, a series of guidelines relevant to typical indoor exposures is recommended as follows: 100 mgm^{-3} for 15 minutes and 35 mgm^{-3} for 1 hour (assuming light exercise and that such exposure levels do not occur more often than one per day); 10 mgm^{-3} for 8 hours (arithmetic mean concentration, light to moderate exercise); and 7 mgm^{-3} for 24 hours (WHO, 2010). Carbon monoxide is produced indoors by combustion sources (cooking and heating) and is also introduced through the infiltration of carbon monoxide from outdoor air into the indoor environment (WHU, 1999). In developed countries, the most important source of exposure to carbon monoxide in indoor air is emissions from faulty, incorrectly installed, poorly maintained or poorly ventilated cooking or heating appliances that burn fossil fuels. In homes in developing countries, the burning of biomass fuels and tobacco smoke are the most important sources of exposure to carbon monoxide. Combustion of low-grade solid fuel and biofuels in a small stove or fireplace can generate high carbon monoxide emissions, which may become lethal to occupants unless the flue gases are vented outdoors via a chimney throughout the entire combustion process. Carbon monoxide enters the body via inhalation and is diffused across the alveolar membrane with nearly the same ease as oxygen (O_2). Carbon monoxide is first dissolved in blood, but is quickly bound to hemoglobin (Hb) to form COHb, which is measured as the percentage of hemoglobin so bound. The binding of carbon monoxide to hemoglobin occurs with nearly the same speed and ease as with which oxygen binds to hemoglobin, although the bond for carbon monoxide is about 245 times as strong as that for oxygen (Longo, 1970; Roughton, 1970). The previous WHO guidelines were established for 15 minutes to protect against short-term peak exposures that might occur from, for example, an unvented stove; for 1 hour to protect against excess exposure from, for example, faulty appliances; and for 8 hours (which is relevant to occupational exposures and has been used as an averaging time for ambient exposures).

Sulfur dioxide (SO_2) exposure causes breathing difficulty for people with asthma, and is also implicated in regional haze and acid rain formation. A recent EPA risk assessment for SO_2 concludes that definite health risks to asthmatics occur at concentrations significantly lower than the current 24-hour health standard for SO_2. The document further notes that over 20 million people in the USA have asthma and therefore, exposure to SO_2 likely represents a significant health issue. The main sources of SO_2 are fossil fuel combustion at power plants and industrial facilities. Along with its direct effects, SO_2 also contributes to the formation of fine particulate matter. Controlled studies involving exercising asthmatics indicate that a proportion experience changes in pulmonary function and respiratory symptoms after periods of exposure to SO_2 as short as 10 minutes. Based on this evidence, it is recommended that a SO_2 concentration of 500 µgm^{-3} (0.176 ppmv) should not be exceeded over averaging periods of 10 minutes duration. Because short-term SO_2 exposure depends very much on the nature of local sources and the prevailing meteorological conditions, it is not possible to apply a simple factor to this value in order to estimate corresponding guideline values over longer time periods, such as one hour (WHO, 2006).

Nitrogen dioxide (NO_2) is the indicator species for the NO_x group of gases, It primarily forms when fuels are burned at high temperatures. These acidic gases directly impact respiratory health, and also contribute to formation of ozone and condensable particulate matter. NO_x reacts with ammonia, moisture, and other compounds to form nitric acid vapor and related particles. Small particles can penetrate deeply into sensitive lung tissue and damage it, causing premature death in extreme cases. Inhalation of such particles may cause or worsen respiratory diseases, such as emphysema or bronchitis, or may also aggravate existing heart disease. An one hour indoor nitrogen dioxide guideline of 200 µgm^{-3} (0.105ppmv), consistent with the existing WHO (2006) air quality guideline, is recommended.

Carbon dioxide is an asphyxiant gas and not classified as toxic or harmful in accordance with globally harmonized system of classification and labeling of chemicals standards of united nations economic commission for Europe by using the OECD guidelines for the testing of chemicals. In concentrations up to 1 % (10,000 ppm), it will make some people feel drowsy and give the lungs a stuffy feeling.1) Concentrations of 7-10 % (70,000-100,000 ppm) may cause suffocation, even in the presence of sufficient oxygen, manifesting as dizziness, headache, visual and hearing dysfunction, and unconsciousness within a few minutes to an hour. NO_x is a generic term for the mono-nitrogen oxides NO and NO_2.

The air quality monitoring network in Kosovo is being upgraded. The most part of the data from the monitoring of air quality are calculated by classical methods. An automatic station for air quality monitoring is located in the yard of the Hydro-meteorological Institute of Kosovo in Prishtina. In this station are monitored: particulate matter (PM_{10}), SO_2, NO_2, NO_x, CO and O_3. Energy supply systems and fossil-fuel systems in particular, are dominant contributors to the emission of these gases. Data on air quality in Kosovo remains weak due to the lack of air quality monitoring network. Also still does not exist the inventory of polluters and is not designed the cadastre of air pollutants. As a result of this situation it cannot be talked authoritatively for the current level of air pollution and its quality. As the main sources of air pollution in Kosovo is considered the energy sector, traffic and heavy industry (State of envirinment in Kosovo 2008-2010 report, 2011). The aim of the current work was to assess indoor air pollution from burning of natural gas, coal and biomass fuels in Prishtina city.

Study area and sampling

Prishtina city has acquired pace in commercial and industrial activities and with the dense population load the city has been under stress due to increasing urbanization. According to the data given by the census of Kosovo (2011), the population of Prishtina was 198.214 and the area of Prishtina envisaged to be 572 sq. km. The city is situated between 42° 40′ 0″ N latitude and 21° 10′ 0″ E longitude at an average altitude of 652 meters above mean sea level.2) Measurement of emitted gasses in current concentration are included in stations (residential spaces and work spaces). Sampling instruments were placed in the main living/work area at a floor height 1.0-1.5 m Where possible, devices were placed at a distance of at least 1.0 m from windows, doors and the heating/cooking sources. The sampling was performed during May, 2012. We measured the indoor concentrations of CO_2, CO, SO_2 and NO_x in 26 stations (household and business offices) in the city of Prishtina (south-western). We carried out the sampling was done once in the morning at each location for 1 hour (CO and NO_x), 45 minutes (CO_2) and 10 minutes (SO_2). The purpose of our study was to estimate the personal exposure of residents to the indoor concentrations of CO_2, CO, SO_2 and NO_x and to identify the indoor sources of these pollutants that affect their indoor levels. All indoor spaces were naturally ventilated without any air conditioning. The sampling location is shown in Fig. 1.

Concentrations of CO_2, CO, SO_2 and NO_x were determined using “Dräger” instrument, model “X-am 7000 digital gas monitor” (Fig. 2). Dräger “X-am 7000” is the solution for the simultaneous and continuous measurement of up to five gases. It is the ideal companion in a variety of applications where the reliable detection of oxygen, toxic and combustible gases and vapors are necessary. The extensive portfolio of over 25 different Dräger sensors enables the detection of more than 100 gases and vapors. The Dräger “X-am 7000” can be equipped with three electrochemical, and two catalytic bead, infrared or photo ionization sensors. During operation, it is also possible with the catalytic-ex sensor to change the gas being measuring or the measurement range of the sensor. In this way, the instrument can be easily adapted to various applications. Dräger sensors are renowned for their fast response time, minor cross sensitivities, high level of accuracy and long lifetimes. In addition to the electrochemical sensors, the catalytic, infrared and photo ionization sensors are automatically recognized by the instrument upon insertion. All sensors are pre-calibrated and therefore a reconfiguration of the Dräger X-am 7000 can be done by simply changing the sensor. Measurment ranges of CO_2 were up to 5.0 % (vol.), of CO 500 ppmv, NO_x 20 ppmv and SO_2 20 ppmv. Program Statistica 6.03) was used for the statistical calculations in this work, such as descriptive statistics

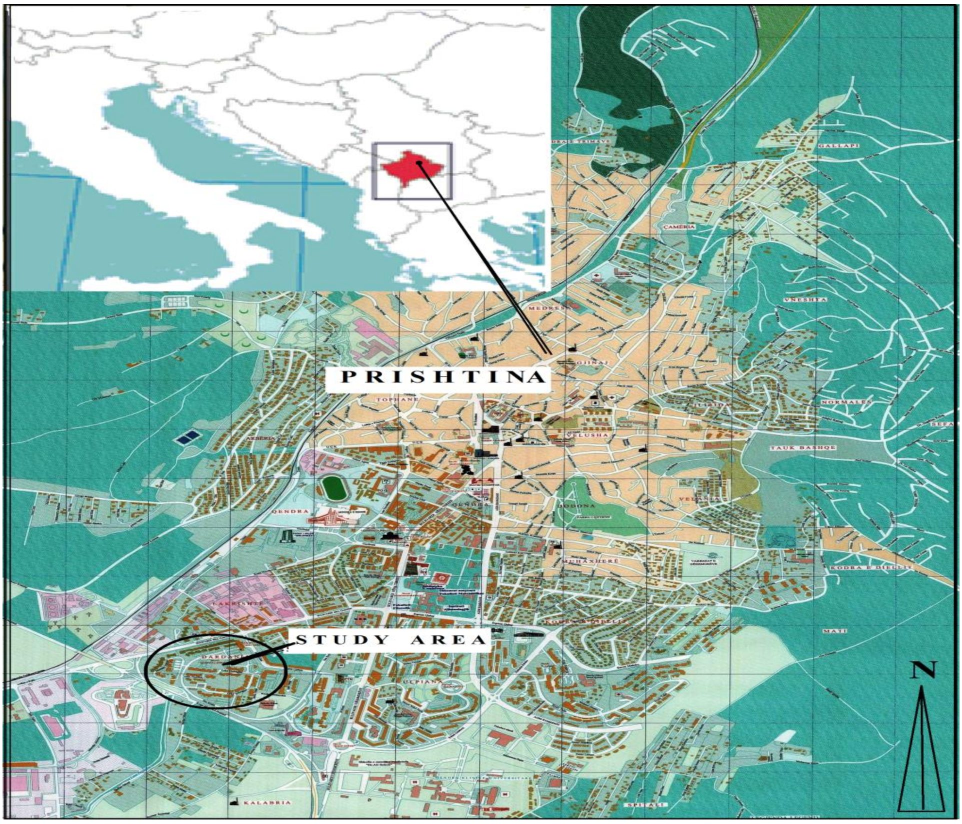

Fig. 1. Sampling location in Prishtina

and two dimensional box plot diagrams for determination of anomalies (extremes and outliers) for solution data.

Fig. 2. Dräger gas detector, model “X-am 7000 digital gas monitor”

Results and discussion

Air pollution status

Mean values of gases concentrations (CO_2, CO, SO_2 and NO_x and ratio of CO_2/CO_2+CO) in 26 air samples is presented in Table 1 and the distribution of CO_2, CO, SO_2 and NO_x and ratio of CO_2/CO_2+CO is presented in Figs. 3 and 4. The Descriptive statistics summary of the selected variables are presented in Table 2. For each variable, the values are given as arithmetic mean, geometric mean, median, minimum and maximum concentration, variance and standard deviation. Frequency distributions and box-whiskers plot of 3 measured variables are presented in Fig. 3. Using experimental data (Table 1) and box plot approach of Tukey (1977), anomalous values (extremes and outliers) of 5 variables were determinate (Table 3).

Table 1. Average value of CO_2, CO, ratio of CO_2/CO_2+CO, SO_2 and NO_x

Sample	Fuel type	CO_2 /ppmv	CO /ppmv	Ratio CO_2/CO_2+CO	SO^2 /ppmv	NO_x /ppmv
WHO standard		1000 (in 45 min.)	30.03 (in 1 hour)		0.176 (in 10 min.)	0.105 (in 1 hour)
S_1	Natural gas	2400	17	0.993	<0.1	<0.1
S_2	Natural	1400	5	0.9965	<0.1	<0.1
S_3	Natural gas	800	4	0.995	<0.1	<0.1
S_4	Natural gas	1000	5	0.995	<0.1	<0.1
S_5	Natural gas	1700	3	0.998	<0.1	<0.1
S_6	Natural gas	4000	12	0.997	0.7	0.8
S_7	Natural gas	1200	5	0.9958	<0.1	<0.1
S_8	Natural gas, wood and coal (business locations, grill)	1800	17	0.9906	<0.1	<0.1
S_9	Natural gas	2200	7	0.9968	<0.1	<0.1
S_{10}	Natural gas	1200	4	0.9968	<0.1	<0.1
S_{11}	Wood and coal	1100	3	0.9973	<0.1	<0.1
S_{12}	Wood and coal	1200	2	0.9983	<0.1	<0.1
S_{13}	Wood	1110	0.6	0.9994	<0.1	<0.1
S_{14}	Wood	1100	3	0.9946	<0.1	<0.1
S_{15}	Wood	800	3	0.9963	<0.1	<0.1
S_{16}	Wood	2300	2	0.9991	<0.1	<0.1
S_{17}	Wood and coal	500	2	0.996	<0.1	<0.1
S_{18}	Electrical power heating	1500	0	-	<0.1	<0.1
S_{19}	Electrical power heating (business locations, grill)	300	2	0.9934	<0.1	<0.1

S_{20}	Electrical power heating (business locations)	1200	3	0.9975	<0.1	<0.1
S_{21}	Electrical power heating	700	2	0.9971	<0.1	<0.1
S_{22}	Electrical power heating	700	3	0.9957	<0.1	<0.1
S_{23}	Electrical power heating	800	2	0.9975	<0.1	<0.1
S_{24}	Electrical power heating	1400	7	0.995	<0.1	<0.1
S_{25}	Electrical power heating	600	2	0.9967	<0.1	<0.1
S_{26}	Natural gas, wood and coal, oil.	700	2	0.99715	<0.1	<0.1

Table 2. Basic statistical parameters of 5 variables at 26 air stations

Variable	Unit	Descriptive statistics						
		Mean	Geo. Mean	Median	Minimum	Maximum	Variance	Std. Dev.
CO_2	ppmv	1296.538	1120.443	1155.000	300.0000	4000.000	599431.5	774.2296
CO	ppmv	4.704000	3.493148	3.000000	0.600000	17.00000	19.17373	4.378782
Ratio, CO_2/ CO_2+CO	-	0.996222	0.996220	0.996700	0.990600	0.999400	0.000004	0.001948
SO_2	ppmv	0.700000	0.700000	0.700000	0.700000	0.7000	-	-
NO_x	ppmv	0.800000	0.800000	0.800000	0.800000	0.8000	-	-

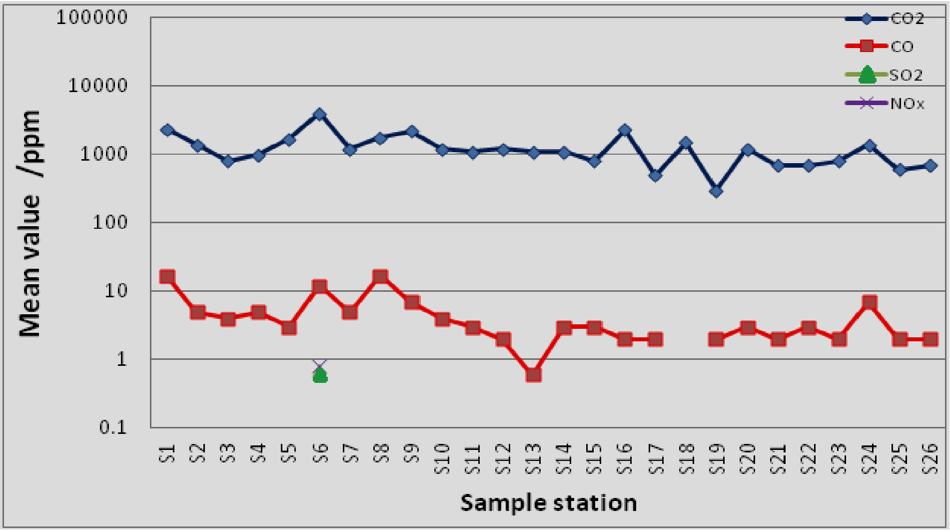

Fig. 3. Mean values of gases (CO_2, CO, SO_2 and NO_x) at 26 indoor air stations

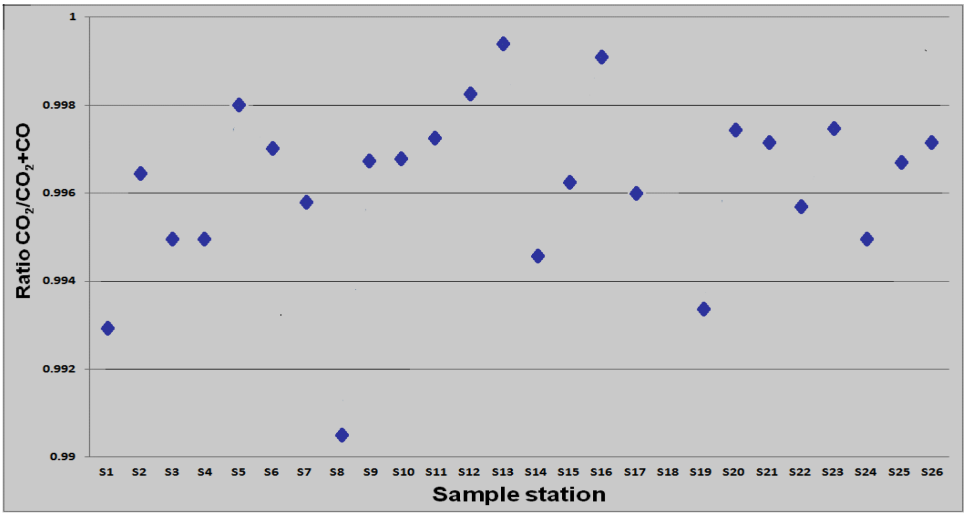

Fig. 4. Ratio of CO_2/CO_2+CO in 26 indoor air samples

The results revealed the 45 minutes concentration of CO_2 at 20° C were found to be in the range of 300-4000 ppmv with an average of 1296.54 ppmv. Our results show that significantly high values of CO_2 in most indoor air samples exceed allowable WHO limit value, as higher influence of the indoor pollution sources from burned of soil gas, coal and biomass fuels. 1 hour concentration of CO at 20° C does not exceed WHO permissible limits of 30.03 ppmv. CO concentrations found to be in the range of 0.6-17 ppmv and with an average concentration of 4.704 ppmv. 10 minutes concentrations of SO_2 at 20° C were registered and only air sample station S_6 found to be 0.7 ppmv and exceed 0.176 ppmv of WHO permissible limit, as higher influence of the indoor pollution sources from (haushold) heating with burning of natural gas. Also, 1 hour concentrations of NO_x at 20° C were registered and only air sample station S_6 found to be 0.8 ppmv (produced during combustion from the reaction among nitrogen, oxygen and even hydrocarbons, especially at high temperatures) and exceed 0.105 ppmv WHO air permissible limit. The results for ratio of CO_2/CO_2+CO in 26 indoor air samples were found to be in the range of 0.9906-0.9994. The highest value of ratio was registered in the air sample station $S_{13.}$ The lowest value of ratio was registered in the air sample station $S_{8,}$ as higher influence of the indoor pollution sources from incomplete combustion of biomass fuels.

Based on the frequency histograms and the two dimensional scatter box plot diagrams (Fig. 5) anomalous values (extremes and outliers) were registered in Table 3. In samples S_1 and S_8 extreme value of carbon monoxide was registered. In the sample S_6 extreme value of carbon dioxide was registered. In the S_8 outlier value of the ratio of CO_2/CO_2+CO was registered. The present study suggests that it is necessary to monitor the air quality as well as the health effects at regular intervals and at strategic locations and that there is a need for better space ventilation.

Table 3. Anomalous values (extremes and outliers) determined in air samples

Air sample	Extremes of parameters (¤)	Outliers of parameters (o)
S_1	CO (17 ppmv)	No reg.
S_6	CO_2 (4000 ppmv)	CO (12 ppmv)
S_8	CO (17ppmv)	The ratio of CO_2/CO_2+CO

Conclusions

Unprocessed coal that has not been treated by chemical, physical, or thermal means to reduce contaminants should not be used as a household fuel. Three reasons guide this recommendation, over and above the documented health risks from products of incomplete combustion of solid fuels: the International Agency for Research on Cancer has concluded that indoor emissions from household combustion of coal are carcinogenic; in those parts of the world where it is most extensively used as a household fuel and the evidence base is strongest, coal contains toxic elements, such as arsenic, lead and mercury, which are not destroyed by combustion and technical constraints make it difficult to burn coal cleanly in households. Regarding to concentrations of CO_2, especially in station S_6, values are characteristic for highly and extremely contaminated indoor spaces as in most stations the WHO permissible limits are exceeded. Station S_6 has also higher concentration of SO_2 and NO_X that are exceeding the WHO permissible limit. We recommend better indoor air ventilation and using of the central heating system for heating purpose in cases where this is possible. Also, to obtain a better information regarding indoor air quality in Prishtina, it is necessary to conduct a more extensive research that include more compounds, and to assess the risks for human health, primarily those carcinogens.

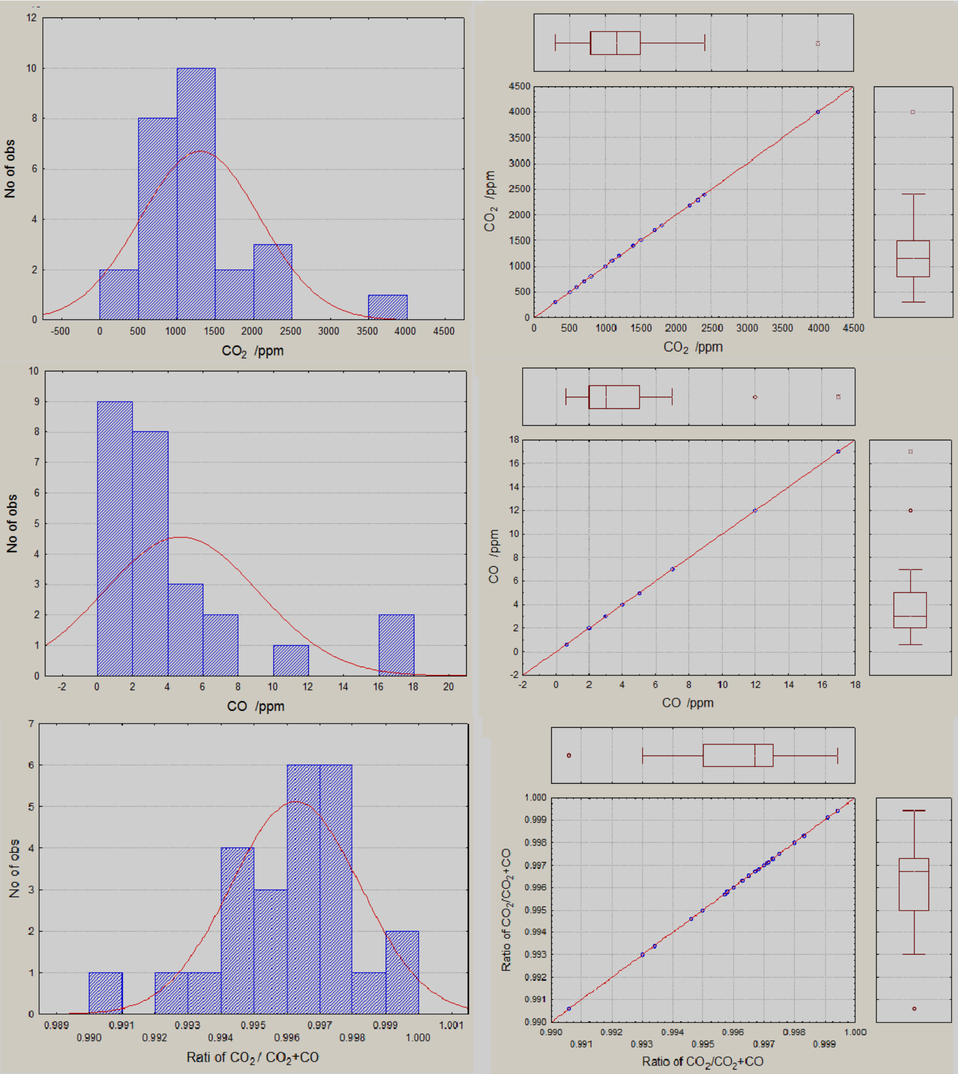

Fig. 5. Frequency histograms and scatter box plot diagrams of 2 measured variables and their ratio

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NOTES

1. http://copublications.greenfacts.org/en/indoor-air-pollution/l-2/1-risk-assessment.htm
2. https://en.wikipedia.org/wiki/Pristina
3. http://www.statsoft.com

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