

## Evaluation of Air Pollutants Concentrations Status through Passive Tube Sampling method in Albania

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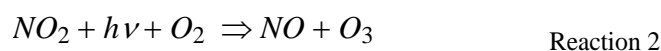
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**Abstract:-** Improving understanding of air pollution and implementing effective observational methods to evaluate their concentration and to reduce it remains a challenge and a priority. This paper presents the results of a passive tubes experimental campaign for primary air pollutants as nitrogen dioxide (NO<sub>2</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), sulfur dioxide, (SO<sub>2</sub>) and ozone (O<sub>3</sub>).

**Keywords:-** primary air pollutant, source evaluation

### I. INTRODUCTION

Through legislative and administrative action, health-protective and cost-effective risk-management decisions can be made, and regulatory actions may be implemented, that directly affect the starting point of our atmospheric system, that is, the primary emissions and their sources [1,2]. From the Directive 2008/50/EC of the European parliament of the council of 21 may 2008 on ambient air quality and cleaner air for Europe, Albania is required to assess air quality throughout the territory. The requirements depend on the nature of the area and the levels of air pollution, in relation to limit values, as defined in the Directive [3]. A variety of air pollution sources in Albania have been associated with different types of health effects. Most evidence is accumulated so far for an effect of carbonaceous material from traffic. More limited number of studies show that also traffic-generated dust contributes to the health effects. Exhaust emissions are an important source of traffic related pollution and several epidemiological and toxicological studies have linked such emissions to adverse health effects. Road abrasion, tire wear and brake wear are non-exhaust traffic emissions which become relatively more important with progressive reductions in exhaust emissions. Toxicological research increasingly indicates that such non-exhaust pollutants could be responsible for some of the observed health effects. Passive sampling technique was used to measure the primary pollutant concentrations collected in three main periods during June 2012 and January 2008 and January 2012. The pollutants measured consist of primary pollutants: nitrogen dioxide (NO<sub>2</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), sulfur dioxide, (SO<sub>2</sub>) and ozone (O<sub>3</sub>). Measurements of total accumulated pollutant, are made monthly at each site using diffusion tubes. Nitric oxide (NO) is short lived because it oxidized to produce nitrogen dioxide (NO<sub>2</sub>) which plays a major role in O<sub>3</sub> production. NO<sub>x</sub> comprise a mixture mainly of NO and NO<sub>2</sub>, prominent in air quality studies. As a precursor pollutant of O<sub>3</sub>, NO<sub>2</sub> poses a threat to public health. Previous studies have shown, however, that NO<sub>x</sub> emissions from anthropogenic sources exceed natural sources. Vehicular traffic emissions are the main sources of NO<sub>x</sub> [4]. High temperature causes the oxidation of atmospheric N<sub>2</sub>, first to NO and then to NO<sub>2</sub>, which plays a major role in the formation of ground-level O<sub>3</sub>. In urban areas, and downwind areas influenced by urban air masses, photochemically produced ground level O<sub>3</sub> and other oxidants form by atmospheric reactions involving oxides of nitrogen (NO<sub>x</sub>).



NO can be oxidized by hydro-peroxy (HO<sub>2</sub>) and organo-peroxy (RO<sub>2</sub>) in further reactions. VOCs refer to all carbon containing gas-phase compounds in the atmosphere, both biogenic (emitted from vegetation) and anthropogenic (man-made) in origin [5, 6]. Photochemically-produced O<sub>3</sub> takes some time to occur. Maximum O<sub>3</sub> concentrations from photochemical reactions usually occur 4 to 6 hours after maximum emissions of chemical precursors, and under conditions of light winds, usually downwind of urban areas.

### II. SAMPLING

The decisions around where to locate a monitoring site are based on the objectives of monitoring. The siting of an air quality monitor has a profound effect on the resulting measurements of contaminant levels and on achieving monitoring objectives. Locations have been selected based on a number of considerations as the number of monitoring sites chosen within each zone reflects the risk of being exposed to elevated levels of air pollution. Also to understand the contribution of different sources, like vehicle traffic, to air quality. It is important also to take into consideration the population of urban areas in each zone, including urban, suburban,

rural and background areas. Diffusion tubes for NO<sub>2</sub>, O<sub>3</sub> and benzene have been installed in 59 sites in January 2008 while during January 2012 diffusion tubes for SO<sub>2</sub>, NO<sub>2</sub> and benzene have been installed in respectively 39 sites. Measurements were conducted also during June 2012 for SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub> and benzene. For each pollutant, “BLANK” tubes (not exposed) have also been included in the campaign. Duplicates and triplicates were systematically positioned for all pollutants. Because of the long sampling period of diffusion tubes, it is only possible to compare the results from the diffusion tube sites in this study against to the Upper Assessment Threshold, Lower Assessment Threshold as described in the results below.

### III. RESULTS AND DISCUSSIONS

Weather patterns and meteorological conditions play a major role in establishing conditions conducive to photochemical O<sub>3</sub> formation and accumulation, and in terminating episodes of high O<sub>3</sub> concentrations. Episodes of high O<sub>3</sub> concentrations from photochemical production are associated with slow-moving, high-pressure weather systems. Away from areas affected by urban emissions, ground level O<sub>3</sub> is driven by the atmospheric boundary layer mixing effect in the spring and early summer period. In the summer period, ozone levels can be enhanced by photochemical reactions. Biogenic VOCs can contribute to summertime photochemical O<sub>3</sub> production close to urban areas in the presence of anthropogenic NO<sub>x</sub> and under favourable meteorological conditions.

Seasonal variations in pollutant concentrations are associated with the changes in meteorological parameters (temperature, relative humidity, wind speed and solar radiations). The changes in meteorological parameters reflect the changes in solar radiation and boundary layer stability, which have significant influence on air pollutant dispersion. During the winter season, the pollutants emitted from various anthropogenic and natural sources, are trapped in the boundary layer due to frequent temperature inversions, while in summer; this polluted air mixes well with the free tropospheric air causing dilution of the pollutants and the greater photochemical reactions due to the higher solar radiation, which leads to high ozone concentrations in polluted NO<sub>x</sub> and VOC<sub>s</sub> areas (fig. 1, 2, 3 and 4 ).

Incomplete combustion of fuels is the largest source of C<sub>6</sub>H<sub>6</sub>. Benzene is an additive to petrol and most of C<sub>6</sub>H<sub>6</sub> emissions are due to vehicle traffic in Albania. This is shown in the graphs below where the maximum value in January is measured in Urban areas (Traffic) with a concentration of 12.73 µg/m<sup>3</sup>, which is 2.5 times higher than the EU limit value (fig. 1).

Other sources, mainly in sub-urban areas, are domestic heating, oil refining and petrol handling, distribution and storage. In general the contributions from domestic heating are small. Wood combustion can be an important local source of C<sub>6</sub>H<sub>6</sub> where wood burning can account for more than half of the domestic energy needs in rural areas where average benzene concentration is 1.23 µg/m<sup>3</sup>.

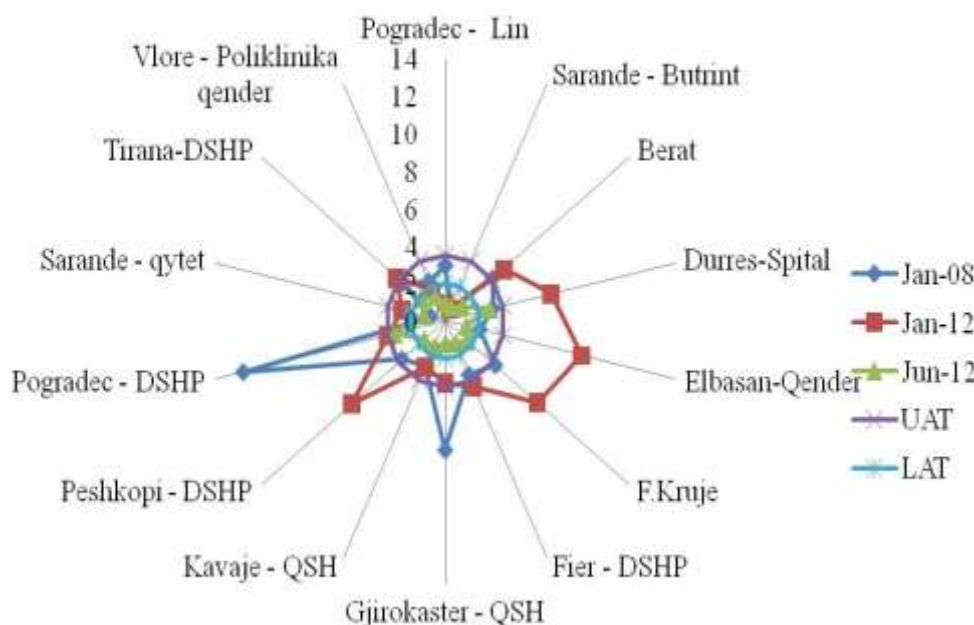
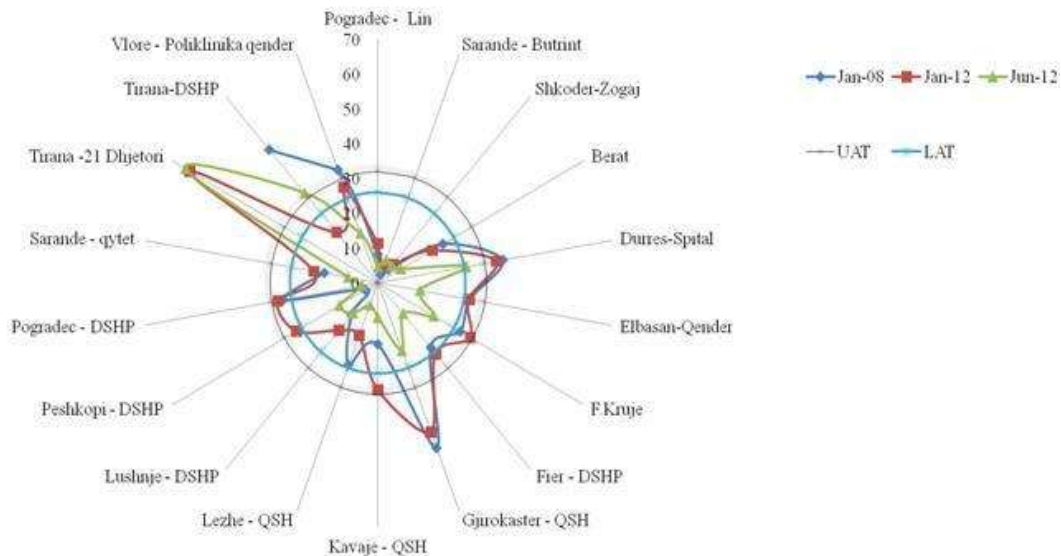


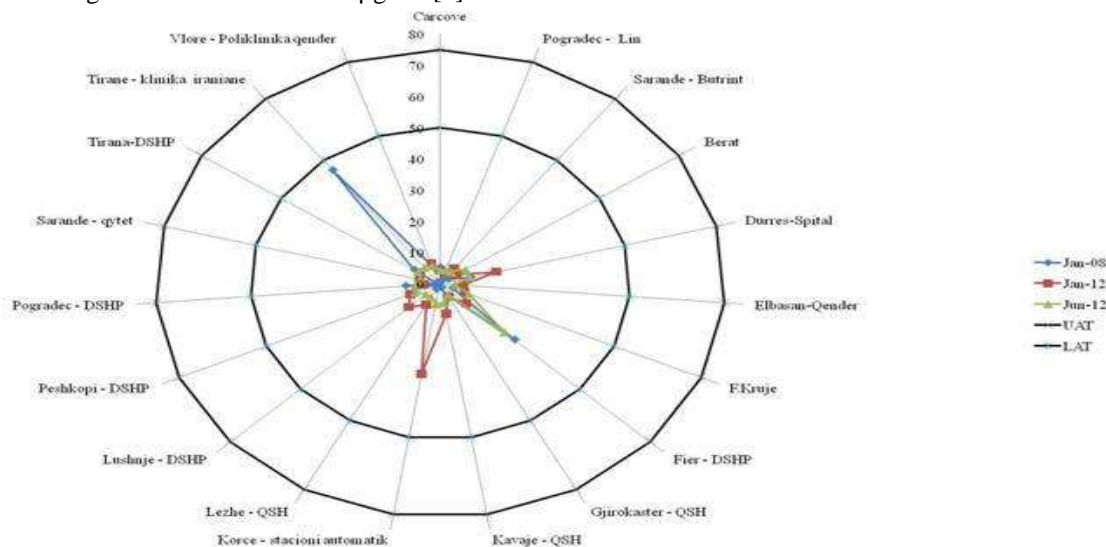
Fig. 1. Concentration trends for benzene concentration in main sites, during January 2008, January 2012 and June 2012, UAT-Upper Assessment Threshold, LAT- Lower Assessment Threshold (µg/m<sup>3</sup>).

A small part of  $\text{NO}_x$  emissions is directly emitted as  $\text{NO}_2$ , typically 5–10% for most combustion sources, with the exception of diesel vehicles. There are clear indications that for traffic emissions the direct  $\text{NO}_2$  fraction is increasing significantly due to increased usage of diesel vehicles, especially newer diesel vehicles. Such vehicles can emit up to 70 % of their  $\text{NO}_x$  as  $\text{NO}_2$  because their exhaust after-treatment systems increase the direct  $\text{NO}_2$  emissions. This may lead to more frequent breaching of the  $\text{NO}_2$  limit values in traffic hotspots (fig. 2). Nitrogen dioxide concentrations are higher close to the sources, urban stations and at traffic stations where they pass the limit value of  $40 \mu\text{g}/\text{m}^3$  (WHO 2006) and reach a maximum value of  $66 \mu\text{g}/\text{m}^3$ . We can see that there is a decreasing in quantity in sub-urban and background areas. The lowest concentrations are found in rural areas the average measured value is  $7 \mu\text{g}/\text{m}^3$ , as we can see below.

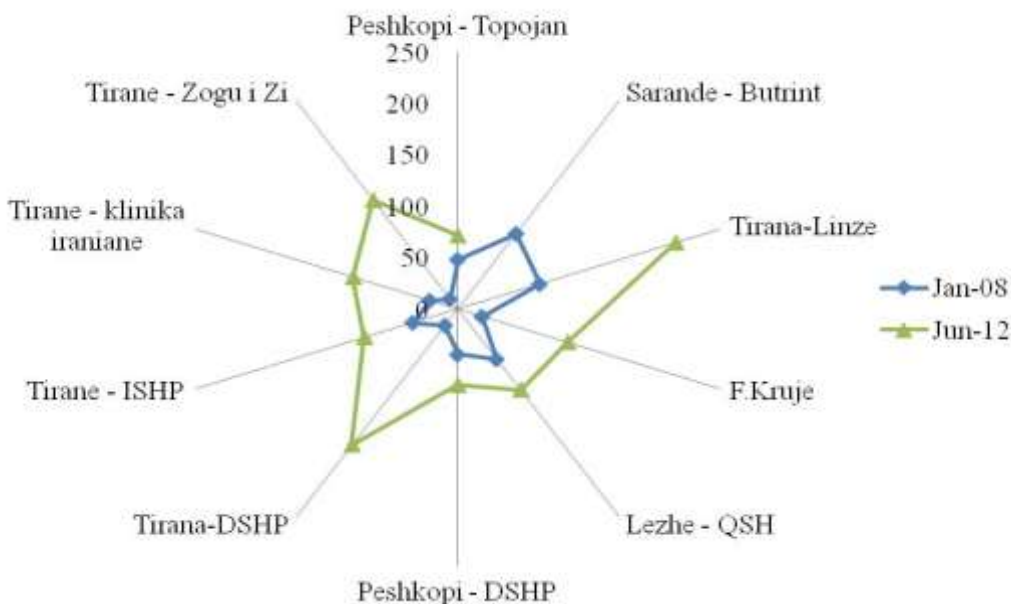


**Fig 2. Concentration trends for nitrogen dioxide concentration in main sites, during January 2008, January 2012 and June 2012, UAT-Upper Assessment Threshold, LAT- Lower Assessment Threshold ( $\mu\text{g}/\text{m}^3$ ).**

High temperature combustion of hydrocarbon fuel sources, such as oil, can produce sulfur dioxide ( $\text{SO}_2$ ) from the oxidation of any sulfur in these fuels. This is the reason that maximum concentration on  $\text{SO}_2$ , located in urban and background areas (fig. 3), reach  $53.81 \mu\text{g}/\text{m}^3$  which is 37 % higher than the limit value defined by European air quality limit for  $\text{SO}_2$  (EU, 2008c) [7]. Emissions of sulfur dioxide are associated also with industrial operations (e.g., combustion processes associated with the extraction, upgrading, and refining of bitumen, electricity etc.) and contribute to the majority of  $\text{SO}_2$  emissions from man's activities, reaching the higher average measured value  $19.34 \mu\text{g}/\text{m}^3$  [8].



**Fig 3. Concentration trends for sulfur dioxide concentration in main sites, during January 2008, January 2012 and June 2012, UAT-Upper Assessment Threshold, LAT- Lower Assessment Threshold ( $\mu\text{g}/\text{m}^3$ ).**



**Fig 4. Concentration trends for Ozone concentration in main sites, during January 2008 and June 2012 ( $\mu\text{g}/\text{m}^3$ ).**

The highest concentrations of  $\text{NO}_2$  and  $\text{SO}_2$  is expected during winter, due to poor winter atmospheric dispersion conditions with relative low wind speed, and to a lower atmospheric oxidation and conversion of these pollutants due to lower photochemical reactions. In urban areas concentration of ozone varies from  $111 \mu\text{g}/\text{m}^3$  to  $136 \mu\text{g}/\text{m}^3$  during June 2012 influenced by high level of traffic vehicles, largest population number, including here many construction sites. Also in other urban areas ozone levels are higher due to the industrial activity which is higher during summer and lead to increased ozone production. During January 2008 ozone levels are below  $100 \mu\text{g}/\text{m}^3$ , due to lower photochemical activity, which is related with meteorological conditions and sunlight availability. In rural areas (background type) like Peshkopi-Topojan, Lezhe-autostrade, Shkoder-Zogaj and Carcove concentration levels vary from  $71 \mu\text{g}/\text{m}^3$  to  $100 \mu\text{g}/\text{m}^3$  (fig. 4). These levels may be associated with biogenic or anthropogenic levels of VOCs.

#### IV. CONCLUSIONS

On the results themselves, the concentrations recorded brings new light on the pollution levels existing in Albania Nitrogen dioxide concentrations are higher close to the sources, urban stations and at traffic stations. High temperature combustion of hydrocarbon fuel sources, such as oil, produce sulfur dioxide. This is the reason that maximum concentration on  $\text{SO}_2$ , located in urban and background areas, reach maximum value of  $53.81 \mu\text{g}/\text{m}^3$  which is 37 % higher than the limit value defined by European air quality limit for  $\text{SO}_2$  (EU, 2008c). Maximum and average concentration values of ozone were high, in Urban, Sub-Urban, Rural, Traffic and Background areas during June 2012 which is associated with high concentration of primary pollutants like  $\text{NO}_2$  which form  $\text{O}_3$ . In urban areas with high level of traffic vehicles, largest population number, including here many construction sites as in Tirane- center (other main cross-roads), concentration of ozone varies from  $111 \mu\text{g}/\text{m}^3$  to  $136 \mu\text{g}/\text{m}^3$  during June 2012. During January 2008 ozone levels are below  $100 \mu\text{g}/\text{m}^3$ , due to lower photochemical activity, which is related with meteorological conditions and sunlight availability. These levels may be associated with biogenic or anthropogenic levels of VOCs. It is clear that passive samplers can be used with some success to monitor ambient levels of primary pollutants, but that there are also a number of uncertainties and pitfalls which need to be considered. With regard to the application of passive samplers for ambient monitoring on a monthly timescales, the following recommendations can be made. Replicate samplers should be exposed in parallel to provide estimates of precision of the method and to identify contamination artefacts. Procedures should be established giving clear guidelines on how to prepare, handle, expose, and analyse the passive samplers. Knowing the interaction between urban, sub-urban zones with industrial, traffic and background areas, it is very important to increase the number of monitored areas.

#### ACKNOWLEDGEMENTS

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