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THE MEASUREMENT OF BENZEN, ETHYLBENZEN, TOLUENE AND XYLENE IN INDOOR AIR IN SCHOOLS IN KARDZHALI

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Abstract: *Concentrations of BTEX (benzene, toluene, ethylbenzene and xylenes) were monitored at schools in Kardzhali town in Bulgaria, during the July and October 2015. The concentrations of all species during the investigation period were below guideline value Studies have shown that pollutants concentrations in indoor environments are always greater than in outdoor environments. Significant seasonal cycles with high values in winter and lower values in summer months could be modelled for indoor concentrations of BTEX. This is in accordance with findings with completely different climate and building characteristics*

ИЗМЕРВАНЕ НА БЕНЗЕН, ЕТИЛБЕНЗЕН,ТОЛУЕН И КСИЛЕН ВЪВ ВЪТРЕШЕН ВЪЗДУХ В УЧИЛИЩА НА ТЕРИТОРИЯТА НА ГРАД КЪРДЖАЛИ

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Ключови думи: *BTEX, замърсяване на вътрешен въздух, сезонност*

Резюме: *Концентрациите на BTEX (бензен, толуен, етилбензен и ксилен) бяха наблюдавани в училища в град Кърджали в България, през юли и октомври 2015 г. Концентрациите през периода на изследването са били в ниски стойности Изследванията са показали, че концентрациите на замърсители в закрита среда винаги са по-големи, отколкото в открити среди. Значителни са разликите при сезонносттаи са измерени по- високи стойности през зимата и по-ниски стойности в летните месеци.Това е в съответствие с констатациите за различен климат и характеристиките на строителните материали.*

Introduction

People generally spend more than 80% of their time in indoor environment [1]. The anthropogenic activities have caused degradation of air quality, both in open and in confined environments. With the current urban centres lifestyle, the man has spent more time indoors than in open spaces [2]. In closed environments, the emission sources can be diverse, such as construction material (in particular finishing materials), air conditioning systems, cleaning procedures, the low exchange between the indoor air with the outside air, among others [2].

Among numerous compounds which belong to VOCs, benzene, toluene, ethylbenzene and o-xylene (BTEX) are chosen for this study. The reason is that BTEX is the major VOCs found inindoor environments in different countries [3]

Volatile organic compounds (VOCs) are important outdoor air toxins suspected to increase chronic health problems in exposed populations [1, 2]. BTEX (benzene, toluene, ethylbenzene, (m+p) xylene and o-xylene) are some of the common VOCs found in urban and industrial areas and are classified as "hazardous air pollutants" (HAPs) because of their potential health impacts [3]. low levels of VOCs might have no significant health impacts, the interactionbetween VOC species and other criteria pollutants mightcause adverse health outcomes. Some researcheres studied the linkages between domestic exposure to VOCs andasthma in young children in Perth, Western Australia, and found that exposure to VOCs increased the risk of childhood asthma [4].

Among indoor volatile organic compounds (VOCs), the chemical families of carbonyls and BTEX are of interests [5,6]. The Environmental Protection Agency of USA has listed carbonyls and BTEX as hazardous air pollutants to human [7]. BTEX have been found to affect the immune,and central nervous system (brain), liver and kidneys [8,9]. Some studies have suggested associations between ambient carbonyls and adverse health outcomes [10]. Numerous indoor sources of BTEX and carbonyls have been well documented, including off-gassing from furniture made of wood-pressed products, paints, floor varnishes glues, smoking, cooking andconsumer products for cleaning, pest management, deodorizing, and personalcare, etc. [11,12].

In industrialised countries at moderate climate (e.g. Germany) pollutants in indoor air are accumulated due to central heating and low air exchangerates, especially in winter months. As a consequence, in regions of moderate climate indoor concentrations of VOCs can exceed the outdoor burden [13-15]. A typical seasonal cycle of the indoor total VOCs was found in German apartments [16,17]. These findings are presumably not necessarily valid for the Northern Egypt which is characterised by subtropical climate and a different lifestyle [18 - 21]**.** On this base of information about the indoor VOC exposure we made aur investigation in Kardzhali town in Bulgaria and the influence of the high outdoor BTEX concentrations.

This investigation was designed to determine annual average concentrations of benzene, toluene, ethylbenzene, and xylene (BTEX) at a wide range of sites throughout in Kardzhali, understand seasonal variations and identify temporal trends of BTEX concentrations.

Methods

Field studies

Kardzhali municipality is situated in the northern part of the Eastern Rhodopes occupies an area of 624 km². Administrative municipality is part of the South-Central region and the town of Kardzhali is the administrative center of the district of Kardzhali. Northeast and east Kardzhali municipality borders the municipalities of Haskovo and Stambolovo. South borders Momchilgrad and Djebel, and in a very small area of Krumovgrad Municipality (near dam "Studen Well"). West the municipality borders with the municipality of Ardino and to the north and northwest with the municipality Municipality.

The geological structure of the municipality is characterized by a wide variety of rock formations and geological structures. The largest share of the territory is covered by volcano-sedimentary rocks of the Paleogene complex composed of rhyolites, andesites, tuffs and tuff mixed with various marine sediments. In the southwestern part of the municipality of large areas revealed metamorphic rocks represented by gneisses, amphibolites, mica schists and others. The municipality has considerable size deposits of non-metallic minerals: bentonite, zeolite, perlite track, feldspar, mica, limestone, sand, gravel and more. In the town had built the only side plant for the production of bentonite, perlite and zeolite. Still untapped deposits of quality marble and stone materials, such as gneiss, tuffs and limestone. This is very important for investigation, because this building materials are used in present and now for construction.

Climate characteristics

The climate of the municipality is continental Mediterranean, conditioned in the nature of atmospheric transport and transformation of air masses on the surface of the relief. The average annual temperature is 12.5 ^{o}C. On average, about 216 days a year, from early April to early November saw sustained retention temperature above 10^{o}C. Winters are relatively mild, the days of stay of snow about 39 days. The summer is long and hot, maximum temperatures reach 39-40^{o}C. The average winter temperature is about 0^{o}C and in the summer - about 24^{o}C. The relative humidity is lowest in the summer months from 57 to 67%, and highest in winter 78-83%. In the analysis and study of volatile organic compounds temperature differences have a particular important role of periodical concetration of emissions, as well as temperature and humidity during the periods.

Quality of atmospheric air

The condition of the air in the municipality of Kardzhali traces of AIS "Cold well" - situated in built-up part of town. Kardzhali reflecting the impact of emissions from production activities and emissions from the residential sector. The sampling results (automatically) are displayed every hour. The municipality has developed a program for air quality (AAQ) .Potential air pollutants are large industrial enterprises located in the town of Kardzhali and in some other places, but under strict control and effective management of many of the harmful emissions can be reduced to values tailored to the requirements of current legislation.

Of importance for the distribution and dispersion of air pollutants are the characteristics of the terrain and altitude, slope and orientation of rays that determine the distribution of heat, light, precipitation and humidity, wind picture. The persence of local ground transport of air masses along the Arda River in east-west direction also contributes to the accumulation of pollutants into the pool at certain times of the year.

An additional factor to air quality in urban areas are emissions from transport, local fuel sources, domestic heating and secondary air pollution with dust due to improper cleaning and washing of the street network.

The monitoring of indoor air pollution in classrooms

Air quality in the room or acquired universal significance term "Indoor air guality" (IAG) for the quality of the indoor air around the building and in particular the case of the building which is workplace.

Air quality in the room is part of the internal environment which includes physical factors and psychological aspects such as lighting, acoustics, thermal comfort.

The quality of indoor air can be exacerbated by the content of the gases generated inside the room (as a result of combustion, migrating from building materials and furnishings chemicals from cigarette smoke), microbial contamination. These pollutants come from activity in the premises of daily used items and products. Air in homes, schools, kindergartens, offices and other institutes can be 2 to 5 times more polluted than the air in the environment, in some cases up to 100 times

Report of the World Health Organization [22] points out that 30 percent axis new or renovated buildings in the world can be the subject of complaints related to poor air quality.

Measurements of volatile organic compounds (VOCs) were carried out in a field study in Kardzhali town in the period of January –August 2015. Four reconstructed and repaired schools were chosen as sites for passive sampling of VOCs in different parts of the Municipality, taking into consideration the traffic volume profile across the city and the suburbs.

The levels of indoor air pollutants measured in the investigated classrooms in the selected schools in area of Kardzhali (Fig 1). The same environmental monitoring methodology was used in all the classrooms. According to the project Cherrie, the same equipment was used during the january-march 2015 and july-august 2015 environmental monitoring to discover some seasonal dependency

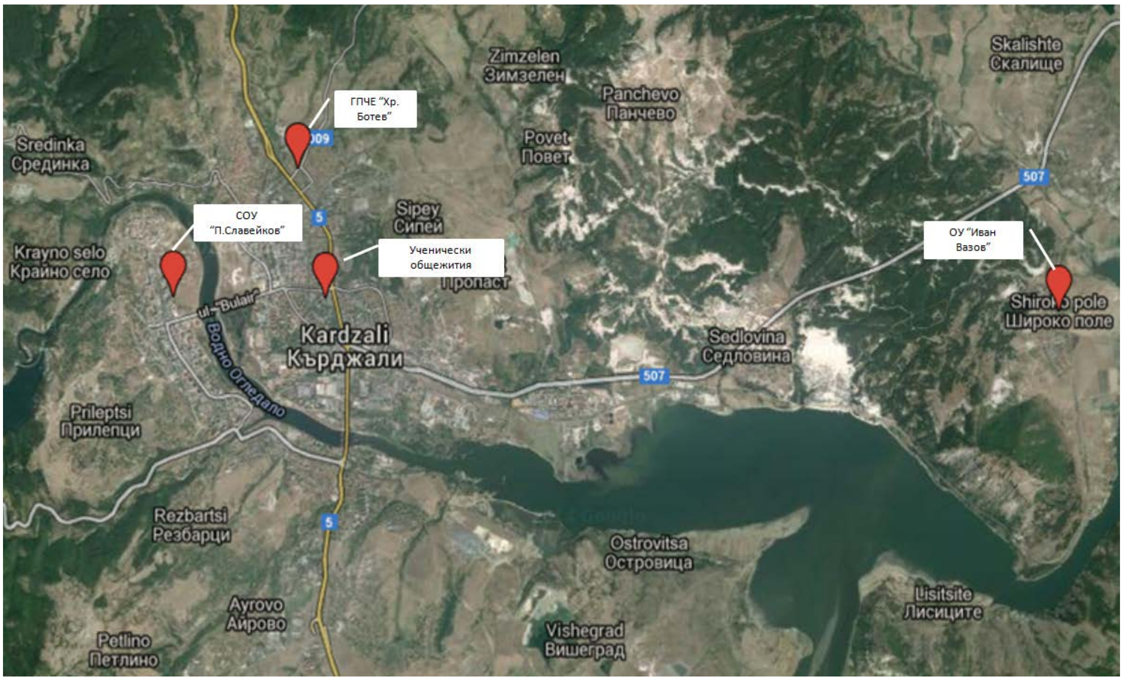

Fig. 1. Selected schools in Kardzhali area

Sampling and analysis

The selected pollutants were measured inside schools in the area during the heating and cooling season. The concentrations of BTEX (benzene, toluene, ethylbenzene and xylenes), were examined using a passive sampling method (Radiello-type samplers-Fig.2.).

The sampling for BTEX was conducted using passive samplers incorporated with activated charcoal absorption element.Passive samplers offer a cost–effective method for screening concentrations over alarge spatial distribution. Sampling using Radiello monitors begins with a quick assembly of the support plate. The adsorbent cartridges used to collect samples are housed in a sealed glass tube that is used to store the cartridge before and after sampling. Prior to sampling, the adsorbent cartridge needs to be transferred to the appropriate diffusive body, which is then screwed onto the triangular support plate horizontally for stationary sampling, or vertically (with adapter) for personal sampling. The overall design of the Radiello sampler allows users to easily transfer the adsorbent cartridges from the diffusive body without touching the adsorbent itself. Protective outdoor shelters are recommended for environmental/ ambient air sampling. Uptake rates are dependent on temperature; therefore, concentration values obtained during sampling will be more accurate if precise temperature values are recorded during sampling. For all 7 day period of sampling was recorded a temperature in every 15 min. One sampling point per classroom was designated for indoor measurements. Samples were collected in classrooms where the children spent most of their time. The passive samplers were placed at a height of 1.5 to 2 m in the classrooms. Exposed BTEX samples were analysed using the "PerkinElmer" model of GC-FIDmethod (Fig 3) and standards ISO 16200-2:2002 and ENISO 16017.

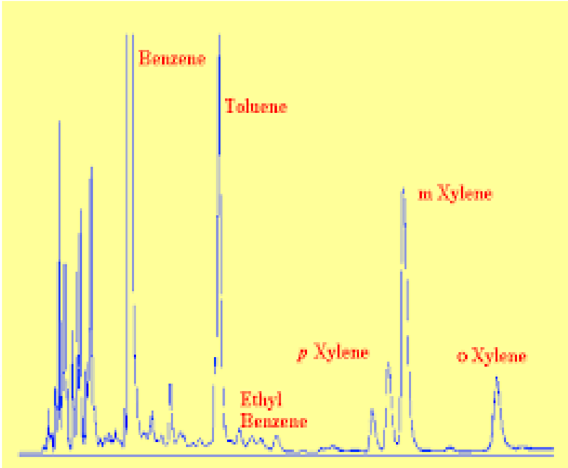

Fig. 2. Radiello samplers

Fig. 3. Result of GC-FID method

Sample preparation and gas chromatographic analysis

After exposure, the VOCs Caught from the cartridge with activated charcoal volatile organic compounds are extracted with carbon disulfide. Aliquots of this extract is injected into a gas chromatograph equipped with a capillary column and flame ionization detector. Quantification is done by absolute calibration.

Conditions for gas chromatography determination of benzene, toluene, xylene, ethylbenzene are as follows:

• Gas chromatograph: "PerkinElmer" model 8310 with FID detector
• Injection port: 250 ° C
• Column: DB-5MS, 30m, I.D.-0,25mm, film-0.25μm
• Detector FID: 300 ° C
• Column temperature: 32 ° C / 3 min, 8 ° C / min up to 100 ° C.

Results of air quality measurements

In practice, indoor exposure levels are assessed on the basis of existing guidelines and recommendations. Each EU member state sets limit values for workplace environments, but only some member states have guideline values for public places, and limit values for private spaces are very rare.

On the following figures (4-7) are represent the investigation in all 4 schools in Kardzhali town.

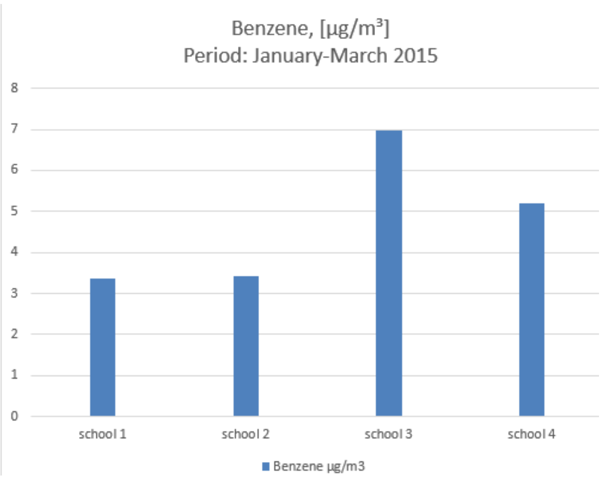

Fig. 4a. Result of benzene concentration in winter period

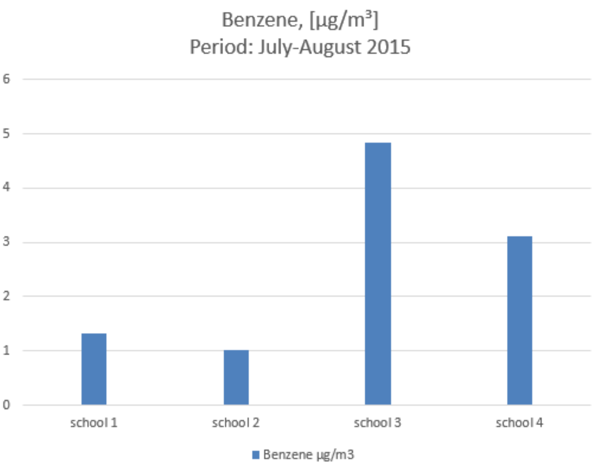

Fig. 4b. Result of benzene concentration in summer period

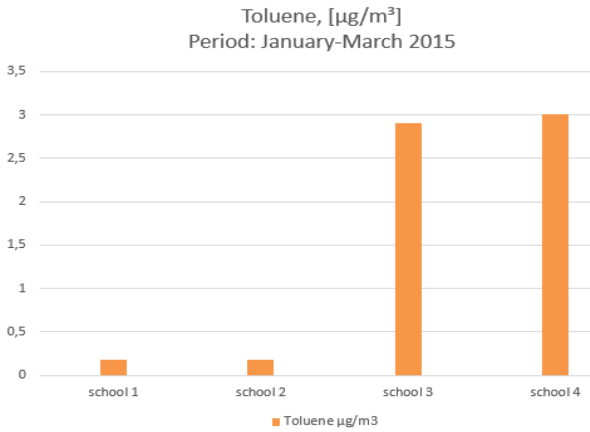

Fig. 5a. Result of toluene concentration in winter period

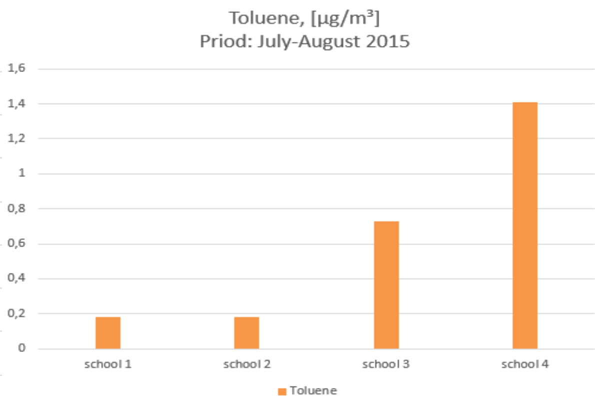

Fig. 5b. Result of toluene concentration summer period

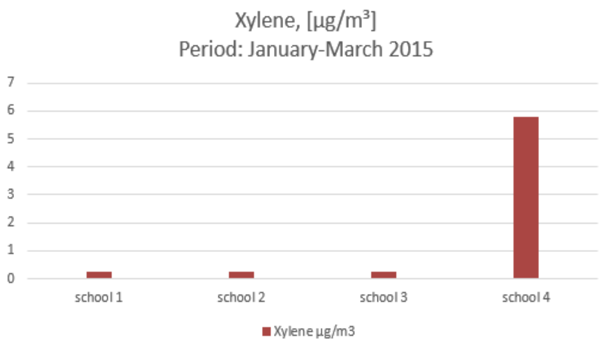

Fig. 6a. Result of toluene concentration in winter period

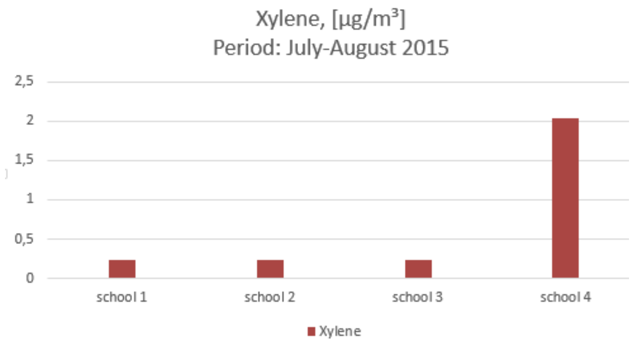

Fig. 6b. Result of toluene concentration in summer period

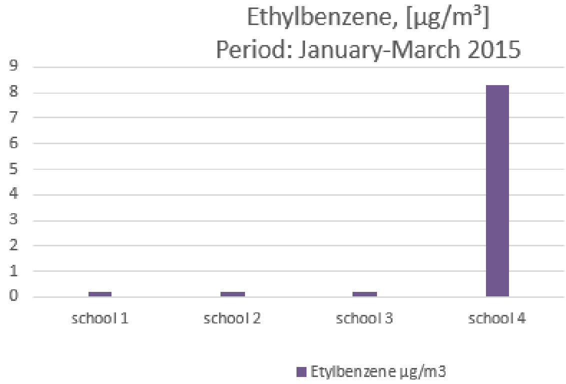

Fig. 8a. Result of toluene concentration in summer period

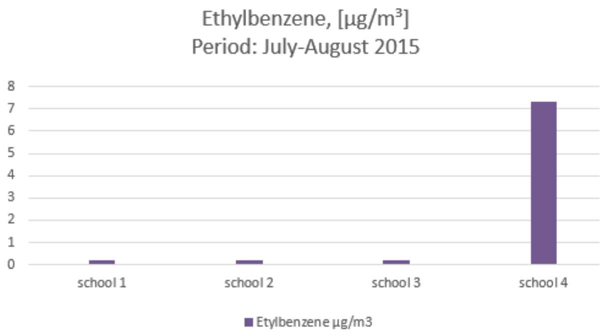

Fig. 8b. Result of toluene concentration in summer period

Assessment of the possibilities for the conduct of secondary degradation, which could lead to the generation of secondary emissions of pollutants into the environment has different physicochemical basis for volatile organic pollutants in the premises. The very nature of building materials is also different and that even determines the opportunities to generate one or another type of contaminants in the environment. All this imposes specific consideration. The emergence of organic pollutants in the premises is primarily related to the presence of organic components in the materials used. These may include:

- The majority of primary and secondary waterproofing and insulating materials are currently widely used in the renovation of old buildings and new construction but in which the main objective is to increase energy efficiency;

- Different connecting composites produced are often based on widely used traditional binders, such as lime, gypsum and cement, but with significant active organic additives;
- Various mixes with a high content of organic components frequently used in finishing to achieve certain objectives;
- Polymer plastic and rubber mixtures directly used for gaskets or manufacture of windows and seal in their homes;
- Coatings of various dyes, pigments and varnishes final coatings on the premises.

In furnishing and operation of housing require repair and bring many other products and techniques necessary for living, which further complicates the distribution of emitted organic pollutants in a dwelling. It is therefore possible in the same house in different rooms to establish different levels of emissions of volatile organic contaminants. This is determined by the availability of substantial difference mixtures with different content of organic chemical components. Another feature of composite materials is their gradual reduction over time due to their passage in the gas phase and spreading into the air. The manner of their distribution is carried out with a variety of software products that allow simulation and with different contents of organic substances in construction materials.

Potential negative impact of construction materials on people during their life cycle from extraction to use in different sites can be substantially different depending on the type and capacity of the emissions generated by them during the entire period of use of homes and buildings . Logically and usually does in practice the emissions generated are the highest in the initial period after production and application and gradually decreased over time. Significant difference is that the generation of organic pollutants in some cases it may be meaningful only a few hours after manufacture and packaging. This is determined by the nature of the processes in time and technological characteristics of individual processes in production. It follows that the potential negative impacts and health risk is higher when the time of delivery of produced construction materials is shorter with limited storage in the warehouses after production. At the same time it must be considered that the negative impact is determined not only by specific levels of emissions of an organic pollutant, but also their number. With the increase in the number of chemical contaminants usually gets certain cumulative effect in which the negative effects increase. Based on the measured concentrations of volatile organic contaminants analyzed in the test subjects can be argued that the potential impacts on humans will be limited. It is limited and the potential for negative impacts as a result of a cumulative effect, because in most cases the majority content of volatile organic pollutants is too low or below the detection limit of the analytical techniques.

In accordance with the foregoing now expect higher potential negative impacts in the sites where it is carried out renovation postigane higher energy efficiency. In such cases are attached modern new building materials produced with a higher content of organic components in them.

Used traditional building materials such as cement, lime mortars for plasters and bricks that are placed in the test subjects more than 30 years is unlikely. Above all still in the process of their production is used high firing temperatures and remaining organic components in them is unlikely. It still in the early years is reached equilibrium with the surrounding environment and the generation of emissions of organic contaminants can not be expected.

Conclusion:

- Indoor air is very important issue – affects everyone almost all the time
- Better ventilation should be provided for the public buildings and air cleaners should be used, specifically for the department store, to reduce the indoor BETX levels.
- Chemicals in indoor environments change seasonly
- The long term effects of many chemicals are still inknown – more research is needed

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