KAUNAS UNIVERSITY OF TECHNOLOGY

FACULTY OF CHEMICAL TECHNOLOGY

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ESTIMATION OF UNCERTAINTIES IN THE PROCESS OF THE DETERMINATION OF AIRBORNE POLYCYCLIC AROMATIC HYDROCARBONS

Final project for Master degree

Supervisor
Assoc. Prof. Dr. Dainius Martuzevičius

KAUNAS, 2015

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Environmental Engineering (code 621H17001)

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Final project "Estimation of uncertainties in the process of the determination of airborne polycyclic aromatic hydrocarbons"

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2015 June 12
Kaunas

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SUMMARY

The earth's atmosphere we live and into which chemical compounds are generally emitted as a result of human activities. Emission of nitrogen oxides Polycyclic Aromatic Hydrocarbons (PAH) sulphur compound and particulate matter lead to acid deposition , generation of ozone ,and finally affect human health however the effect of PAH in humans are well known this thesis is the study to minimize the PAH content in air

The main objective of this thesis is to find the methodology for calculating the uncertainty of the in-house validation data has been applied to multiple methods uncertainty sources have been identified and standard uncertainty established. The methods for finding the various PAH particles present in the air sample .The recommendation for reducing the PAH content in air particles

The project includes analysis of literatures and methodology for calculation of uncertainties and tabulation of results which includes estimation of uncertainties in ambient as well as combustion PAH concentration and sensitivity analysis

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1. Review of literature:

1.1 Air Pollution:

It is the introduction of particulates and other harmful materials in earth's atmosphere which causes disease to humans and damage to other living organisms .it is basically biological or chemical change in air in the environment .Air pollution they come from anthropogenic sources or by natural sources

Sources of air pollution:

Mobile sources

It includes the emission from trucks, buses, air planes, and other vehicles driven by emission of burning fossil fuels. The pollution emitted from these sources causes immense amount of air pollution in the environment. And smoke from industries which contains high amount of sulfur content in their smoke emitted. Carbon mono oxide is also generally emitted from automobiles another major pollutant is nitrogen oxides which are produced from both natural as well as manmade sources. Reference (32,31)

Evaporative sources

They are sources which are enclosed in a container which evaporate and releases vapors over time for example liquids such as paints hair spray ,gasoline ,pesticide, insecticide , perfumes etc

Waste disposal

The waste which are disposed or dumped in the incineration plant and they are heated at a very high temperature and release large amount of nitrogen and sulfur compounds in to atmosphere. Microbes and chemical reaction occurs on the waste and releases methane and carbon dioxide as well as small amounts of ammonia and nitrogen and other sulfides. Reference (32,31)

Military sources

Resources such as toxic weapons, gases missile testing and manufacture of explosives have considerable part in air pollution

Natural Sources of Air Pollution:

Volcanoes

It is a rupture on the crust of planetary mass object such as earth which allows hot lava, volcanic ashes which escapes from a magma chamber situated below the earth's surface volcanic activity which produces carbon dioxide sulfur dioxides and other carcinogenic gases in to atmosphere

Oceans and rivers

Methane emission caused by the digestive system of marine life methano genesis in sediments and drainage and areas along coastal regions possibly from methane hydrates on the ocean floors

Radioactive decay

Radioactive gases which are emitted by radioactive elements in to earth's atmosphere causes air pollution

Plants and trees

Biogenic sources from pine trees and other plants emit volatile organic compounds which also causes considerable amount of change in atmospheric air

Air pollutant

It is a substance were air can have effects on humans and the surrounding atmosphere .a pollution can be of manmade or of natural origin .they are classified as primary or secondary primary pollutant are from volcanic eruption ash etc.Some examples were carbon monoxide released from motor vehicles, sulfur dioxide released from large scale industries. Secondary pollutants form in primary pollutants and react in atmosphere ground level is ozone is an example for secondary pollutant; some pollutants are primary as well as secondary because they are emitted from primary pollutant .reference (32,31)

Primary pollutants

Some of the important primary pollutant causing gases and other compounds are listed as follows

- Sulfur oxides
- Nitrogen oxides
- Carbon monoxide
- Volatile organic compounds
- Particulates
- Persistent free radical
- Toxic metals
- Chlorofluorocarbons
- Ammonia
- Odors
- Radioactive pollutants

Secondary pollutants

Secondary pollutants are not directly emitted like primary pollutants but it combines with other natural pollutants and reacts in atmosphere. Some of the important secondary pollutants were listed they are as follows reference (31,32)

- Particulate matter
  Which are created from other gaseous primary pollutants and forms a photochemical smog .they usually comes from industrial pollution and are acted in the atmosphere by UV light from the sun to form secondary pollutants
- Ozone
  Ozone is the important component in the troposphere known as ozone layer it is formed due to human activities mainly by burning down of fossil fuels
- Peroxyacetyl nitrate which are formed from VOC
- A large amount of persistent organic pollutants which are attached to particulates

Exposure to Air Pollution and its Health Effects

It is a risk is a function of the hazard of the pollutant and the exposure to that pollutant. Air pollution exposure can be expressed for certain groups, for an individual, (e.g. neighborhoods or children living in a county), or for entire populations. For example, one may want to calculate the exposure to a hazardous air pollutant for a geographic area, which includes the various microenvironments and age groups. This can be calculated as an inhalation exposure. This would account for daily exposure in various settings (e.g. different indoor micro-environments and outdoor locations). The exposure needs to include different age and other demographic groups, especially infants, children, pregnant women and other sensitive subpopulations. The exposure to an air pollutant must integrate the concentrations of the air pollutant with respect to the time spent in each setting and the respective inhalation rates for each subgroup for each specific time that the subgroup is in the setting and engaged in particular activities (playing, cooking, reading, working, etc.). For example, a small child's inhalation rate will be less than that of an adult. A child engaged in vigorous exercise will have a higher respiration rate than the same child in a sedentary activity. The daily exposure, then, needs to reflect the time spent in each micro-environmental setting and the type of activities in these settings. The air pollutant concentration in each micro-activity/micro-environmental setting is summed to indicate the exposure. Reference (32,31)

Air pollution is a significant risk factor for a number of health conditions including respiratory infections, heart disease, , stroke and lung cancer. The health effects caused by air pollution may include difficulty in breathing, wheezing, coughing, and worsening of existing respiratory and cardiac conditions. These effects can result in increased medication use, increased doctor or emergency room visits, more hospital admissions and premature death. The human health effects of poor air quality are far reaching, but principally affect the body's respiratory system and the cardiovascular system. Individual reactions to air pollutants depend on the type of pollutant a person is exposed to, the degree of exposure, and the individual's health status and genetics. The most common sources of air pollution include particulates, ozone, nitrogen dioxide, and sulfur dioxide. Children aged less than five years that live in developing countries are the most vulnerable population in terms of total deaths attributable to indoor and outdoor air pollution. Reference (32,31)

Mortality

it was estimated that some 7 million premature death may be attributed to air pollution .In India the highest death rate is due to air pollution asthma is the one of the main disease caused due to air pollution according to united nations organization. In December 2020 air pollution was estimated to kill 500,000 people all over the world each year

Air pollution is estimated to reduce life expectancy by almost nine months across the European Union. Causes of deaths include, COPD, lung cancer, and lung infections.

The US EPA estimates that a proposed set of changes in diesel engine technology could result in 12,000 less premature mortality, 15,000 fewer heart attacks, 6,000 fewer emergency room visits by children with asthma, and 8,900 fewer respiratory-related hospital admissions each year in the United States. Reference (http://en.wikipedia.org/wiki/Air_pollution)

The US EPA estimates allowing a ground-level ozone concentration of 65 parts per billion would avert 1,700 to 5,100 premature deaths nationwide in 2020 compared with the current 75-ppb standard. The agency projects the stricter standard would also prevent an additional 26,000 cases of aggravated asthma and more than a million cases of missed work or school.

A new economic study of the health impacts and associated costs of air pollution in the Los Angeles basin and San Joaquin valley of Southern California shows that more than 3,800 people die prematurely (approximately 14 years earlier than normal) each year because air pollution levels violate federal standards. The number of annual premature deaths is considerably higher than the fatalities related to auto collisions in the same area, which average fewer than 2,000 per year.

Diesel exhaust (DE) is a major contributor to combustion-derived particulate matter air pollution. In several human experimental studies, using a well-validated exposure chamber setup, DE has been linked to acute vascular dysfunction and increased thrombus formation. This serves as a plausible mechanistic link between the previously described association between particulates air pollution and increased cardiovascular morbidity and mortality. reference (32,31)

Cardiovascular disease

A 2007 review of evidence found ambient air pollution exposure is a risk factor correlating with increased total mortality from cardiovascular events (range: 12% to 14% per 10 mg/m^3 increase).

Air pollution is also emerging as a risk factor for stroke, particularly in developing countries where pollutant levels are highest. A 2007 study found that in women, air pollution is associated not with hemorrhagic but with ischemic stroke. Air pollution was also found to be associated with increased incidence and mortality from coronary stroke in a cohort study in 2011. Associations are believed to be causal and effects may be mediated by vasoconstriction, low-grade inflammation or autonomic nervous system imbalance or other mechanisms. reference (32,31)

Lung disease

Chronic obstructive pulmonary disease includes diseases such as chronic bronchitis and emphysema.

The research has shown that increases in asthma due and COPD from increased exposure to vehicle related air pollution reference (31,32)

A study conducted in 1960-1961 in the wake of the great smog of 1952 compared 293 London residents with 477 residents of Gloucester, Peterborough, and Norwich, three towns with low reported death rates from chronic bronchitis. All subjects were male postal truck drivers aged 40 to 59. Compared to the subjects from the outlying towns, the London subjects exhibited more severe respiratory symptoms (including cough, phlegm, and dyspnea), reduced lung function , and increased sputum production and purulence. The differences were more pronounced for subjects aged 50 to 59. The study controlled for age and smoking habits, so concluded that air pollution was the most likely cause of the observed differences.

It is believed that much like cystic fibrosis, by living in a more urban environment serious health hazards become more apparent. Studies have shown that in urban areas patients suffer mucus hyper secretion, lower levels of lung function, and more self-diagnosis of chronic bronchitis and emphysema. Reference (32,31)

Most Polluted cities in the World by Particulate Matter (PM)	
Particulate Matter ($\mu g/m^3$)	**City**
168	Cairo, Egypt
150	New Delhi, India
128	Kolkata, India
125	Tianjin, China
123	Chongqing, China
109	Kanpur, India
109	Lucknow, India
104	Jakarta, Indonesia
101	Shenyang, China

1.2. State of art on Polycyclic Aromatic Hydrocarbons (PAHs): policy and regulations

Polycyclic Aromatic Hydrocarbons (PAHs are carcinogenic and mutagenic pollutants, typically affecting urban areas, produced by incomplete combustion of organic substances (Kameda et al., 2005). PAH heavy congeners are air contaminants bond to fine particulate matter for their prevailing mass fraction. The national policies concerning PAHs are regulated by the Directive 50 released in 2008 (Directive 2008/50/EC of the European Council and Parliament of 21 May 2008 on Ambient Air Quality and Cleaner Air for Europe. Official Journal of the European Union L152/1, 11.6.2008). In particular, Italy adopted the Directive in 2010, through the Legislative Decree no. 155 (DecretoLegislativo 13 agosto 2010, n. 155. Attuazionedelladirettiva 2008/50/CE relative allaqualitàdell'ariaambiente e per un'ariapiùpulita in Europa.GazzettaUfficialedellaRepubblicaItaliana, 15 September 2010, Suppl. no. 217L). For PAHs, the air quality must be estimated through benzo[a]pyrene, which is overall associated to fine and ultrafine particles and is recognized as certain carcinogen (it is listed in Group 1 according to IARC classification). This approach, although affected by some uncertainty, is commonly accepted because B[a]P is the most potent carcinogenic component of the group (except for dibenz[a,h]anthacene and dibenzopyrenes that occur at much lower extents), and the percentage distribution of PAHs is expected fairly constant with time and space. The concentration limit is equal to 1.0 ng/m3 of B[a]P, calculated as mean annual concentration at a set of sites representing as a whole the real exposure experienced by population. The sites and time schedule of PAH measurements are established by European Countries according to distribution of population over the territory, and taking in account the influence of weather and seasonality. In Italy, ten sites have been chosen in nine cities (two in Milan), where the measurements will cover at least 126 days per year, and three sites in rural areas (51 days); there, six other "carcinogenic" PAHs must be investigated, to check for possible modulations of the PAH signature in the airborne particulates, regulated by year time. In highly urbanized areas, mobile sources and domestic heating are usually regarded as the largest contributors of

PAHs, with diesel fuelled vehicles emitting much more particulate than gasoline fuelled cars (Zhang et al., 2009; Ravindra et al., 2008).

At this regard, according to monitoring campaigns performed in many European countries including Italy, the PAH concentrations show a negative trend over the last decades, due to availability of new technologies that have abated the emissions from industries, power and heating plants and vehicles; moreover, new regulations have promoted the recycling of materials and the heat recovery. Nonetheless, nowadays this trend seems to show a reverse direction as a consequence of the increase of emissions released by burning devices fuelled with biogenic or low-cost matter (wood and its derivatives). B[a]P is still considered a problem in Europe, even increasing nowadays in areas where wood or coal are used for house heating (EEA, 2013). This trend has been further emphasized by the effects of the ongoing economy crisis. The impact of the increased non-industrial emission sources turned out to have major relevance and their impact is far to be reliably accounted for. As regards the assessment of PAH toxicity on the basis of the sole B[a]P, it must underlined that: i) different PAH emissions show different fingerprints all comprising B[a]P, thus this latter as alone is insufficient recognize the pollution source nature ; ii) the choice of the only B[a]P to index the PAH-associated toxicity highlights the carcinogenicity, but omits other adverse effects are associated with PAHs overall, e.g. mutagenicity; and iii) synergistic or antagonistic effects of the individual PAHs and the particulate substrate are neglected. Reference (24,25,26)

PAHs concentration results Indoor and outdoor

Citizens are exposed to PAHs during the whole day. PAHs are released both indoors and outdoors by a list of sources. They penetrate indoors due to air exchange. Exogenous PAHs are driven inside by fine airborne particles and add to those generated by indoor activities. Living environment such as houses, schools, offices and public and private transportation vehicles are affected by an indoor air contamination of PAHs, like benz(a)anthracene (BaA); benzo(b)fluoranthene (BbF), benzo(j)fluoranthene (BjF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (B[a]P), indeno(1,2,3-cd)pyrene (IP); dibenz(a,h)anthracene (DBahA), benzo(g,h,i)perylene (BPE), the magnitude of which depends mainly on outdoor pollution, but also by indoor resuspension and generation by fireplace, cooking and smoking. The heating sources, in general, are also responsible of a seasonal variation of PAHs environmental pollution. Other variables affect the entity of PAHs indoor contamination: indoor temperature, pressure, air exchange capacity. The presence of cooking sources and/or smokers contributes to the indoor emission of PAHs. The EXPAH results show that the indoor PAHs levels are about one order of magnitude higher in winter than in spring/summer period; but indoor levels were lower than the outdoor ones in all seasons, as showed in Figure 1. Reference (23)

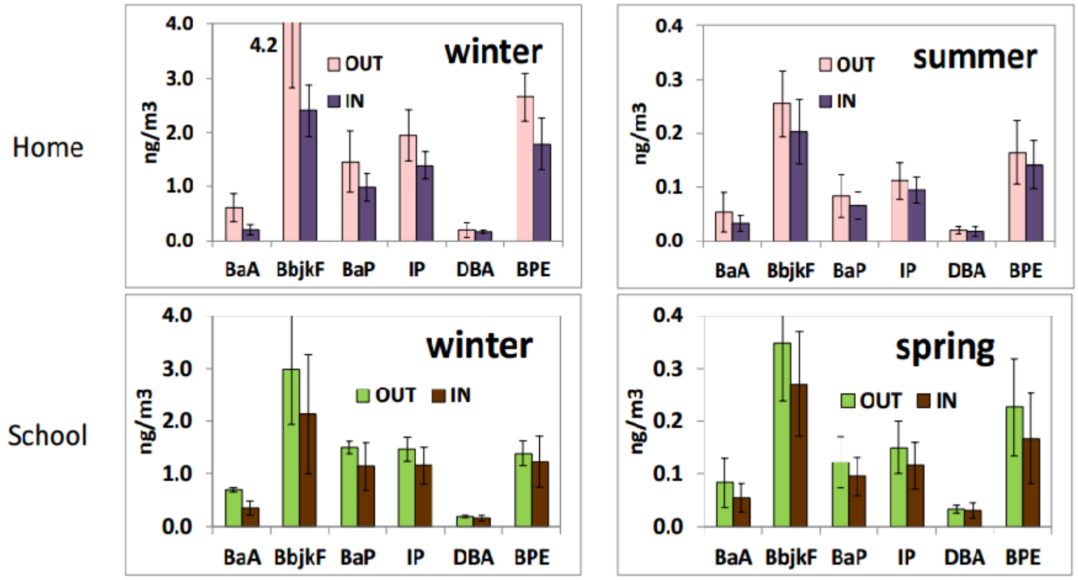


Figure 1. Average airborne PAHs observed at homes and schools.

1.3.Uncertainties in Environmental Measurements

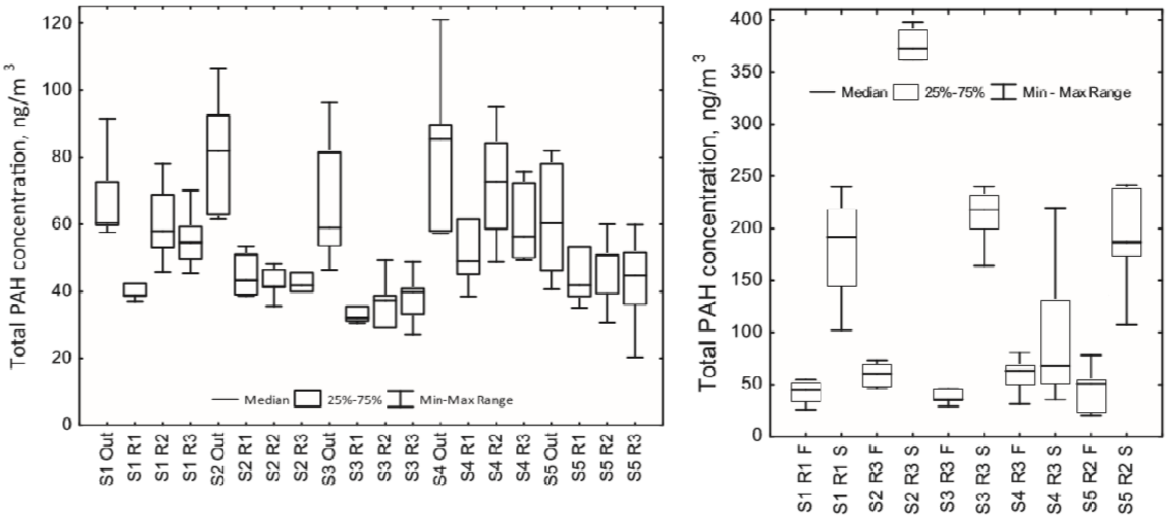
Uncertainty

It is a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand . The measured result may vary with each repetition of the measurement and should therefore be considered a random variable.

Uncertainty and measurement error are quite often taken as synonymous. The difference between the measured result and the actual value of the measurand is the error of the measurement, which is also a random variable. Measurement error may be caused by random effects or systematic effects in the measurement process. Random effects cause the measured result to vary randomly when the measurement is repeated. Systematic effects cause the result to tend to differ from the value of the measurand by a constant absolute or relative amount, or to vary in a non random manner. Generally, both random and systematic effects are present in a measurement process.

The error of a measurement is primarily a theoretical concept, because its value is unknowable. The uncertainty of a measurement, however, is a concept with practical uses. According to the definition of uncertainty, it is a parameter that characterizes the dispersion of the values that could reasonably be attributed to the measured; thus gives a bound for the likely size of the measurement error. In practice, there is seldom a need to refer to the error of a measurement, but an estimate of the uncertainty is required for every measured result.

Also existing is a certain confusion involving the related concepts of accuracy and precision. Accuracy is the closeness of the agreement between the result of a measurement and a true value of the measurand. A measurement is accurate if its error is small. In this document we take the definition as “A quantitative indication of the variability of a series or repeatable measurement results”. Measurement of the sample with a large standard deviation are not very precise thus causing the lack of precision to be caused by random errors.



The above mentioned figure shows the concentration in various sampling sites and to the left the concentration of PAHs particle phase and indoors and outdoors (ref.20,26)

1.3.1Sources of Uncertainty

The uncertainty on the result of a measurement or determination may arise from many possible sources, some of them are common to any analytical determinations such as: incomplete definition of the measurand, sampling, sub-sampling, storage conditions, matrix effects and interferences, environmental conditions, uncertainties of masses and volumetric equipment, reference values, approximations incorporated in the measurement method, digital displays and rounding

In the case of radioactive determinations, many analytical techniques are to be used before measuring and the measurement involves sophisticated instrumentation. Besides some specific sources have to be considered due to the random nature of radioactive decay and radiation counting.

The predominant source of uncertainty is the counting uncertainty, particularly at the low activity levels encountered in environmental samples, other possible causes of uncertainty include: radioactive standards, radionuclide half-life, counting efficiency, background, radioactive decay, source geometry and placement, variable instrument backgrounds and efficiencies, time measurements used in decay and in growth calculations, instrument dead -time corrections, approximation errors in simplified mathematical models, impurities in reagents, and uncertainties in the published values for half-lives and radiation emission probabilities. In particular for gamma spectrometry also should be considered the Compton baseline determination, background peak subtraction, multiples and interference corrections, peak-fitting model, efficiency calibration model, summing, density correction factors, etc.

After all conceivable sources of uncertainty are listed; they should be categorized as either potentially significant or negligible. Uncertainties potentially significant should be evaluated quantitatively. reference (33)

Uncertainty Components

In estimating the overall uncertainty, it may be necessary to take each source of uncertainty and treat it separately to obtain the contribution from that source. Each of the separate contributions to uncertainty and the input estimates is referred to as an uncertainty component. When expressed as a standard deviation, an uncertainty component is the standard uncertainty $u(x_i)$. These components are grouped into two categories according to the way in which their numerical value is estimated: Type A or Type B method of evaluation. Reference (33)

Type A

Uncertainty that is evaluated from the statistical distribution of the results of a series of measurements can be characterized by standard deviation s_i: $s_i = \left|\sqrt{s_i^2}\right|$

The associated number of degrees of freedom is v_i, being the standard uncertainty $u_i = s_i$

Type B

This is the uncertainty that is evaluated by means other than the statistical analysis of a series of observations. In this case, the standard uncertainty is evaluated by scientific judgment based on all available information on the possible variability of the input quantity; assumed probability distribution based on experience or other information, represented by a quantity u_j which can be characterized by a corresponding standard deviation: $u_j = \left|\sqrt{u_j^2}\right|$

Since the quantity u_j is like standard deviation, the standard uncertainty is u_j.

Process of evaluating uncertainty

The steps for evaluating and reporting the uncertainty of a radioactive determination may be summarized as follows (adapted from [5] and [6], additional description on each step can be found in these references:

Step 1. Specify measurand. Identify the measurand Y and all the input quantities $X_i$for the mathematical model. Include all quantities whose variability or uncertainty could have a potentially significant effect on the result. Express the mathematical relationship $Y = f(X_1,X_2,\ldots,X_N)$ between the measurand and the input quantities.

Step 2. Identify uncertainty sources. List the possible sources of uncertainty; determine an estimate$x_i$of the value of each input quantity X_i

Step 3. Quantify uncertainty components. Measure or estimate the size of the uncertainty component associated with each potential source of uncertainty identified. Evaluate the standard uncertainty $u(x_i)$ for each input estimate x_i, using either a Type A or Type B method of evaluation

Step 4. Calculate combined uncertainty. The information obtained in step 3 will consist of a number of quantified contributions to overall uncertainty, whether associated with individual sources or with the combined effects of several sources. The contributions have to be combined according to the appropriate rules, to give a combined standard uncertainty, $u_c(y)$ of the estimate, y.

Step 5. Determine expanded uncertainty. Multiply(y)by a coverage factor obtain the expanded uncertainty U such that the interval [y±U] can be expected to contain the value of the measurand with a specified probability.

Step 6. Expression of the result. Report the result asy ± U with the unit of measure, and, at a minimum, state the coverage factor used to compute **U** and the estimated coverage probability reference (33)

1.4. Uncertaintes in PAH Measurement

Polycyclic aromatic hydrocarbons (PAHs) are a group of pollutants composed of carbon and hydrogen atoms with a fused ring structure. Airborne PAHs are mainly formed as a result of incomplete combustion processes (Poly nuclear aromatic hydrocarbons, 1987). The most common sources of PAHs in an urban environment are the fuel combustion for heating (biomass, coal, natural gas) and the propulsion of vehicles with an internal combustion engine (gasoline, diesel, LPG), as well as food cooking, candle burning, aerosolized street dust particles and long-distance transport (Callén et al., 2008; Martuzevicius et al., 2011; Mostert et al., 2010). PAHs are broadly distributed in every air-based environment, even in the cleanest one (Vestenius et al., 2011), and were proved to be cancer-causing air pollutants (Ravindra et al., 2008). Because of their carcinogenic, mutagenic and toxic properties 16 PAHs are included in European Commission and USA EPA priority pollutant list (IARC, 2010; European Commission, 2001). Benzo(a) pyrene is the most investigated PAH, characterized as highly carcinogenic compound. It should be noted that European annual limit value for benzo(a)pyrene in PM10 fraction is 1 ng m_3 (Directive 2004/107/EC, 2005).

PAHs are distributed between vapor and particulate phases. Most of the low molecule mass and high vapor pressure (2e3 rings) PAHs are present in the vapor phase. On the contrary, 4-ring PAHs having low vapor pressure commonly are present in the particulate phase. The phase distribution comprehensively depends on environmental conditions. During summertime more PAHs get transferred to the vapor phase. In winter, the reverse processes were observed (Zhu et al., 2009).

The human exposure to PAHs mostly occurs via complex mixtures of individual PAHs. The Toxic Equivalency Factor (TEF) is used to estimate carcinogenic effect of complex PAHs mixtures (USEPA, 2005; WHO, 2000). The half-lives of PAH are long enough that these pollutants can be transported from the sources to living and working environments (Fromme et al., 2004). The fuel burning in residential heating boilers, emissions from vehicles and weather conditions unfavorable for pollution dispersion cause the increase of PAH concentration several times during cold seasons in Nordic countries (Ravindra et al., 2008; Bari et al., 2009). The penetration of particulate and vapor phase PAHs into buildings through windows, doors, cracks and ventilation system is a significant source of indoor PAHs (Shi and Zhao, 2012; Chen et al., 2012). The sources of PAHs may also be indoors (Fromme et al., 2004; Orecchio, 2011).

Possible indoor sources of PAHs at schools are food cooking (Shen et al., 2012), domestic heating (fuel burning) (Bari et al., 2009), and burning of candles (Orecchio, 2011).

Sabin et al. (2005) investigated exposure of children to PAHs during trips in school buses. Fan et al. (2012) determined PAH concentrations in urine of children from elementary schools. Exposure of children to particulate matter, volatile organic compounds as well as various organic and inorganic substances was studied by Almeida et al. (2011). Despite of the fact that levels of most of the air pollutants at schools are regulated, there is lack of complex studies on indoor and outdoor PAHs in schools, which in turn may lead to reviewing of air quality standards and support recommendations for air quality improvement.

Environmental pollution by persistent organic pollution is the focus of attention worldwide of which polycyclic aromatic hydrocarbons have been widely studied. (Zhou et. al. 2001; Zhang et. al. 2002; Maskaoui et. al. 2005; Jian et. al. 2011; Cachada et. al. 2012) PAHs are composed of two or more fused benzene rings that have been found to be ubiquitous contaminants in the natural environment. PAHs are mainly derived from incomplete combustion of organic material .due to their chemical stability they are highly persistent and have become global environmental problem.

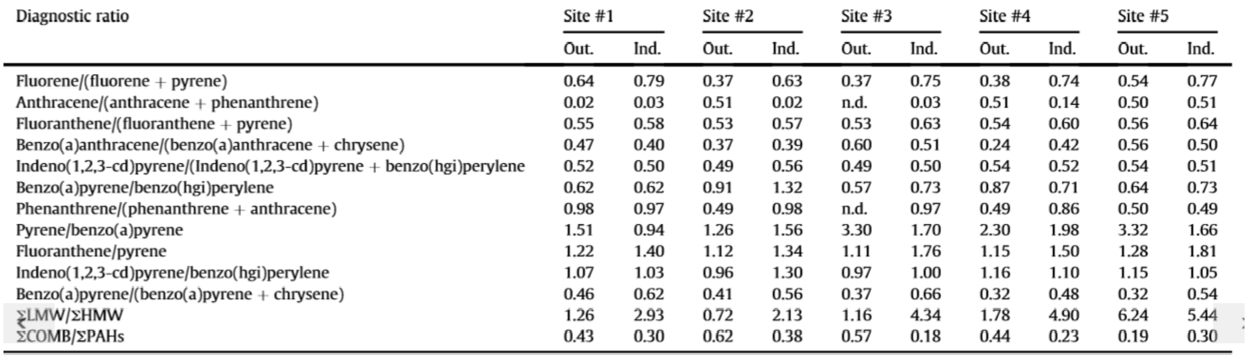
In addition to their persistence PAHs are known to be carcinogenic in animals when they are given in high doses and are suspected of being carcinogenic to human as well. This is manifested by the induction of DNA adduct formation and P450 in human, rat and avian liver cells following exposure to PAH. The US Environmental protection agency and department of Health and Human services have classified PAHs as probable human carcinogens in addition to their known adverse effects on the human immune, reproductive, nervous and endocrine system.

In addition, in any environmental measurement there is always an element of uncertainty due to systematic and random errors, which should be fully considered. Uncertainty may be defined as a non-negative parameter characterizing the dispersion of the quantity values being attributed a measurand based on the information used. (BIPM 2012) Uncertainty may be estimated from calculation of precision and bias. Precision is defined as the closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions. Bias may be defined as the estimate of systematic measurement error. (BIPM 2012)

In addition to analytical components sampling procedure and sample preparation can also contribute to overall uncertainty due to inherent heterogeneity of most environmental media. As a consequence environmental measurement for quality assessment often has a degree of uncertainty, which leads to false negative or false positive classification. (Taylor et. al. 2005; Boon and Ramsey, 2012) To estimate the measurement uncertainty caused by sampling, the Eurachem guide introduced two approaches, empirical and modeling methods; these approaches can also be used in combination if desired. In the modeling method the estimation of uncertainty involves the identification, quantification and summation of each potential source of uncertainty. However, this approach can become increasingly problematic in identifying all of such sources when it is applied to primary sampling.

The objective of this work were therefore to determine the contamination, intensity, spatial variation and sources of PAHs; to compare the concentration of PAHs found in air sample with relevant air guideline values and to assess the uncertainty generated by sampling and analytical procedures and its impact on risk assessment reference (23,24,28)

1.4.1. Health risk assessment



Diagnostic ratio	Site #1		Site #2		Site #3		Site #4		Site #5	
	Out.	Ind.	Out.	Ind.	Out.	Ind.	Out.	Ind.	Out.	Ind.
Fluorene/(fluorene + pyrene)	0.64	0.79	0.37	0.63	0.37	0.75	0.38	0.74	0.54	0.77
Anthracene/(anthracene + phenanthrene)	0.02	0.03	0.51	0.02	n.d.	0.03	0.51	0.14	0.50	0.51
Fluoranthene/(fluoranthene + pyrene)	0.55	0.58	0.53	0.57	0.53	0.63	0.54	0.60	0.56	0.64
Benzo(a)anthracene/(benzo(a)anthracene + chrysene)	0.47	0.40	0.37	0.39	0.60	0.51	0.24	0.42	0.56	0.50
Indeno(1,2,3-cd)pyrene/(Indeno(1,2,3-cd)pyrene + benzo(hgi)perylene	0.52	0.50	0.49	0.56	0.49	0.50	0.54	0.52	0.54	0.51
Benzo(a)pyrene/benzo(hgi)perylene	0.62	0.62	0.91	1.32	0.57	0.73	0.87	0.71	0.64	0.73
Phenanthrene/(phenanthrene + anthracene)	0.98	0.97	0.49	0.98	n.d.	0.97	0.49	0.86	0.50	0.49
Pyrene/benzo(a)pyrene	1.51	0.94	1.26	1.56	3.30	1.70	2.30	1.98	3.32	1.66
Fluoranthene/pyrene	1.22	1.40	1.12	1.34	1.11	1.76	1.15	1.50	1.28	1.81
Indeno(1,2,3-cd)pyrene/benzo(hgi)perylene	1.07	1.03	0.96	1.30	0.97	1.00	1.16	1.10	1.15	1.05
Benzo(a)pyrene/(benzo(a)pyrene + chrysene)	0.46	0.62	0.41	0.56	0.37	0.66	0.32	0.48	0.32	0.54
ΣLMW/ΣHMW	1.26	2.93	0.72	2.13	1.16	4.34	1.78	4.90	6.24	5.44
ΣCOMB/ΣPAHs	0.43	0.30	0.62	0.38	0.57	0.18	0.44	0.23	0.19	0.30

The table was taken for reference from (reference 5,30)

In the above mentioned table the various types of PAH particles present in air were listed and their amount present in the 5 sampling location across Kaunas city .The samples were taken in a period of 24 hours periodically for 5 working days .The outdoor concentration was higher than the indoor concentration in all sites .

The lowest concentration was observed in site 3. Due to usage of fuels for heating inside the house and lack of ventilation system it increase the level of PAH indoor which causes various carcinogenic diseases and other respiratory problems

The issues of pollutant penetration should be addressed by the installation of mechanical ventilation with treatment of the incoming air. This would allow efficient removal of co_2 from the indoors but at the same time providing higher quality air to the indoors.

2. Methodology

2.1. Analytical procedure for Quantification Of Standard Uncertainties

The particulate matter was extracted from filters by means of an ultrasonic extractor (Emmi-30HC, EMAG GmgH, Germany) in 10ml of dichloromethane (GC, Sigma-Aldrich, USA) for 10min. The extraction procedure was repeated 3 times with a final volume of the extract of 30ml. Before the extraction an internal standard was added to the samples.

Prior to the analysis a recovery estimation standard was added, and the volume of a sample was further reduced to 0.5ml. A silica gel and anhydrous sodium sulfate were employed for the sample cleaning and moisture removal. A mixture of hexane and dichloromethane was used for the elution of samples.

After a cleaning procedure, the sample was concentrated to 0,1ml and the recovery standard was added. The prepared samples were stored in a refrigerator at 4^oC. The GC/MS system (GCMS-QP2010 Ultra, Shimadzu, Japan) with capillary column Rxi-5ms (Restek, USA) was used for the quantitative analysis of the extractor of injector 250^oC, column flow 0.58ml. The temperature program was set from 50^oC (3min), $10^oC\ min^{-1}$ to 300^oC (10min).

The MS scanning was performed from 30 to 450 m/z. The following target compounds were analyzed: naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, flouranthene, pyrene, benz(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and denzo(ghi)perylene. reference (30,29)

2.2. Methodology for Ambient and combustion PAH Measurement

Ambient air sample for PAHs were collected using several standard semi volatile sampling trains .from the sampling location the samples were collected in thin quartz filter after the ultrasonic extraction process the samples were analyzed for the presence of PAH amount present in the sample and then to GC/MC system where the mass (M in ng) of PAH were found. The flow rate and time taken were calculated and the percentage of PAH present in the samples are determined reference (29,28)

The general formula for calculation of ambient air

Flow rate ×time =volume

v- volume of the samplers and then the concentration is found by the formula

$c=m/v \times 1000\ ng/m^3$

2.3. Analytical Procedure for Sensitivity analysis

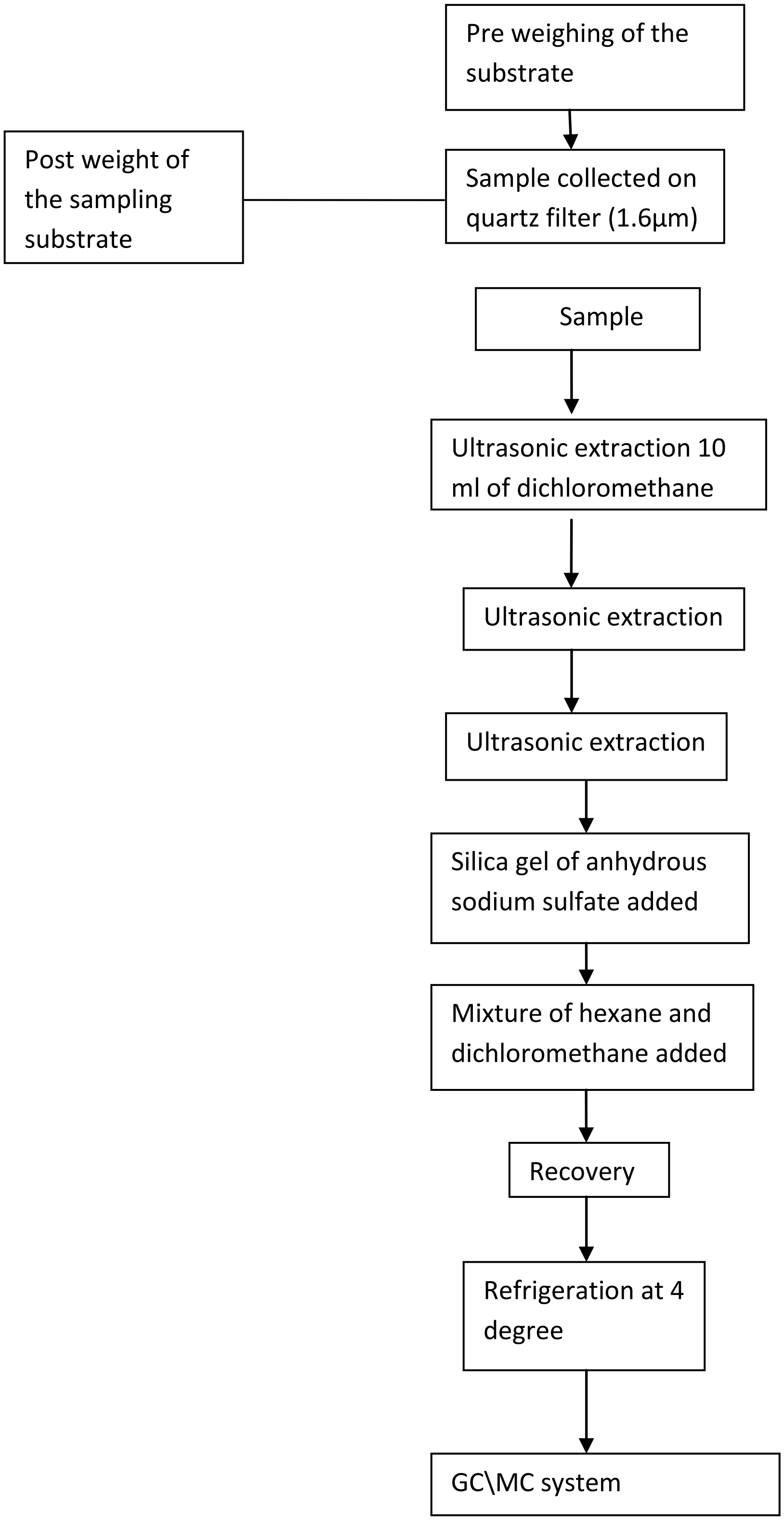
A deterministic analysis was performed to measure the sensitivity of the results. The sensitivity analysis for different time interval and input data's were performed was selected as a key parameter to measure by a sensitivity analysis in the PTW stage. The linear graphs illustrate how input data influence assessment results (see Fig. 3). Variation of input data increase/decrease the uncertainty; A 50% input data value change in uncertainty indicated the highest change in the result (sensitivity) (2.449), other input data indicated a lower result change. The lowest sensitivity was that for -50% in input data the other input % exhibited the highest sensitivity. The other values have moderate sensitivity to input data change. The sensitivity analysis showed that the greatest result change was for the 20% and 50% thus, the assessment of the sensitivity analysis remains the most contentious issue throughout the whole assessment. So this implies that the increase in input data with respect to time. reference (29 , 28)

3. Results

3.1. Quantification of standard uncertainties

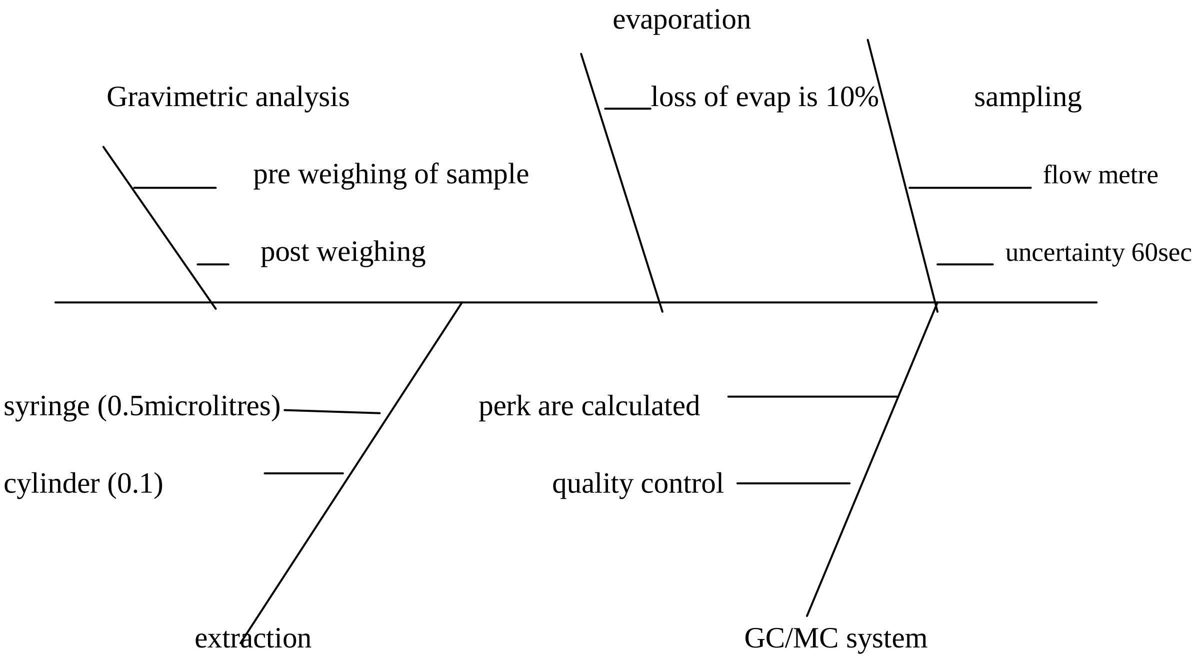
In order to make the process easier based on the procedure and methodology flow chart and cause and effect diagram were constructed. And the source of uncertainties for PAH analysis is found and their uncertainty ,tolerance level , and variation coefficient were listed and then the combined uncertainty is calculated reference (29,27)

Flowchart for the methodology



Cause and effect diagrams for the main source of uncertainties

For this diagram the uncertainties of the various instruments used for the experiment were listed and the gravimetric analysis uncertainties were also analyzed total uncertainty values for the experiment can be calculated using this method



Source of uncertainties for PAH analysis Table 1

Equipment	Tolerance(	Correcti	Variation coeffici	uncertainit
Samplers	±1	±1		
Measurement cylinder	±0.2	±0.2	±2%	±0.1
Syringe	±0.025	±1	±1.5%	±0.5 micro
Extraction				±1
Loss of substance in ev			10%	
Uncertainty of stopwat				±1
Flow rate		±1		±1

3.2. Calculation of standard uncertainties

The combined uncertainty can be calculated with the expression

$$U_{rel}(CON)=\sqrt{u_{rel}^2(CA)+u_{rel}^2(Fdil)+u_{rel}^2(CS)}$$

It is estimated for each analyte the combination of the uncertainty derived from the preparation of primary solutions u^2(primary solution) and from the preparation of calibration curve at concentration levels by diluting the standard solution u^2(dilute)

$$U_{rel}(std)=\sqrt{u_{rel}^2(primary)+u_{rel}^2(dil)}$$

The concentration of primary solution is given by mass (m) the volume (vf) of first dilution and volume (vp)taken with measuring cylinder tables shows the data used for calculation of this term of the uncertainty . so that standard uncertainty associated to these steps can be obtained as

$U_{rel}(\text{primary})=\sqrt{u_{rel}^2(m)+u_{rel}^2(vf)+u_{rel}^2(vp)}$

24 x 60 x 10/1000 = 14.41 (volume) m3.

Mass=$\frac{595.6}{15}$ =39.707×10^{-3}

Concentration=mass×volume

Conc. = 39.70710^{-3} x 14.4 = 0.572

The uncertainty associated to the equipment have been previously calibrated as correction /√3+u the volume (vp) is taken with measuring cylinder

U(vp)= Correction/√3 +cv nominal (from the table)

$U(VP_1)_{1000}$ = Correction/√3 + (0.002 x 1000) = 2.115

U(primary) = $\sqrt{}u^2_{rel}(m) + u^2rel(VF_1) + u^2(VP_1)$

$= \sqrt{}(39.707 \times 10^{-3})^2 + (2.115)^2 + [(0.03/\sqrt{3})/30]^2 = 2.1154$

In similar way the uncertainty associated to the preparation of the calibration curve is calculated for each concentration level as

u_{rel} (dil) $= \sqrt{}u^2_{rel}(VP) + u^2_{rel}(VF)$

$u^2_{rel}(vf)$ = 0.025/√3/0.5

u_{rel}(dil) $= \sqrt{}(2.115)^2 + [0.025/\sqrt{3}/0/5]^2 = 2.112$

in this case the correction and coefficient variation also the mean value of the interval to which they belong

finally the uncertainty associated to the preparation of the calibration standard solution is

$u_{rel}(std) = \sqrt{u^2_{rel}(primary)+u^2_{rel}(dil)}$

$u_{rel}(std) = \sqrt{(2.115)^2 + (2.115)^2} = 2.9889$

$u(std) = 0.5 \text{ mg/l} \times 2.112 = 1.045 \text{ mg/l}$

Estimation of u^2(rept)

In order to estimate the uncertainty associated to the precision 10 samples spiked at 0.5mg/l were analyzed in repeatability conditions this uncertainty is given by expression

$$u(repet) = S_{s/}\sqrt{r}$$

$$= 0.0194/\sqrt{1} = 0.0194 \text{ mg/l}$$

Where S_s is the standard deviation and r the number of replicates of each sample when analyzed from the table

The uncertainty derived from the estimation of the anlayte concentration from the calibration curve u(CA) is given by

$u(CA) = \sqrt{u^2(std) + u^2(cal) + u^2(repet)}$

$u(CA) = \sqrt{(1.045)^2 + (0.05)^2 + (0.0194)^2} = 1.064/0.5 = 2.12$

$u^2_{rel}(Fdil) = 0.005$ (from the table) the sample concentration in the final extract is given by the sample weight m_s and the volume of extract v_s and its uncertainty is calculated from the table

$u_{rel}(CS) = \sqrt{}u^2_{rel}(ms) + u^2_{rel}(Vs)$

$CS = ms/vs = 50g/5 = 10g/ml = 10kg/l$

$U_{rel}(CS) = [0.2/\sqrt{}3/20]^2 + [\ 0.025/\sqrt{}3/2.5]^2 = 0.003$

Combined uncertainty

Once the relative standard uncertainty of each uncertainty source were calculated the overall combined uncertainty of the analytical method can be estimated from the general expression mentioned above

$U_{rel}(con) = \sqrt{}u^2_{rel}(CA) +u^2_{rel}(Fdil) + u^2_{rel}(CS)$

$U_{rel}(con)=\sqrt{}(2.12)^2 + (0.005)^2 + (0.003)^2$

$u_{rel}(con) = 2.12$

3.3. Estimation of uncertainty in ambient and combustion PAH measurement

For the calculation of ambient and combustion PAH measurement the flow rate is kept constant and the time changes periodically and the volume of the substance were found and graph was plotted volume against concentration the table were listed below and graph was drawn based on the procedure . reference (3,4,28)

Table 2 :Ambient and combustion PAH measurement

Flow rate	Time(minutes)	Volume(liter)	Concentration(ng/m$^{3)}$
10	1	10	3.970
10	2	20	1.98
10	3	30	1.32
10	5	50	0.794
10	7	70	0.56
10	9	90	0.441
10	10	100	0.397

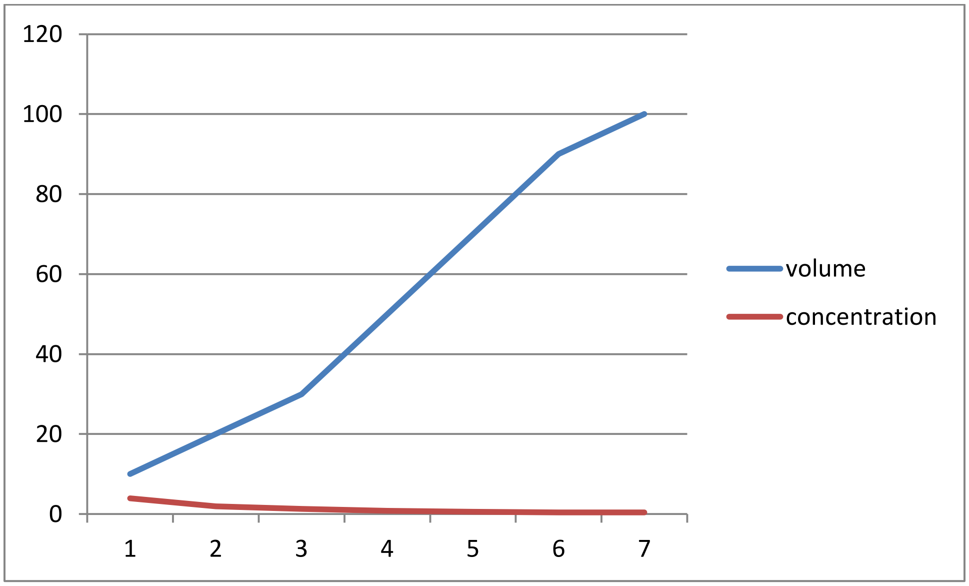
Model calculation

Volume=10×1=10

C=m/v ×1000ng/m^3

Concentration=0.0397×1000/10= 3.970

Graph 1



Concentration of the analyzed PAHs from the sampling location was represented in the above mentioned graphs .the highest concentration was recorded as 3.97ng/m^3. The lowest median concentration was recorded as 0.397ng/m^3. The indoor variation of PAH in $PM_{2.5}$ fraction was not statistically significant.

The analysis of PAH distributions between particulate and vapor phases revealed that the particulate phase (TSP) ∑PAHs ranged from 0.397ng/m^3 to 3.97ng/m$^{3.}$ Variation in PAH concentration were illustrated in fig 2

Individual PAHs have their own physical and toxicological properties .so important to analyze the concentration level of PAH compounds

3.4. Sensitivity analysis

The sensitivity analysis for different time interval and input data's were performed and percentage of uncertainty were predicted similar way the flow rate , time were changed and the uncertainty percentage were calculated

Table 3: sensitivity analysis

Input %	Time(minutes)	uncertainty	Percentage uncertainty
-50	30	1.244	
-20	45	1.322	0.059%
-10	54	1.378	0.040%
0	1	1.414	0.025%
10	2	1.732	0.0183%
20	4	2.236	0.225%
30	5	2.449	0.0869%

Model calculation :

Uncertainty of flow rate is =1 minutes

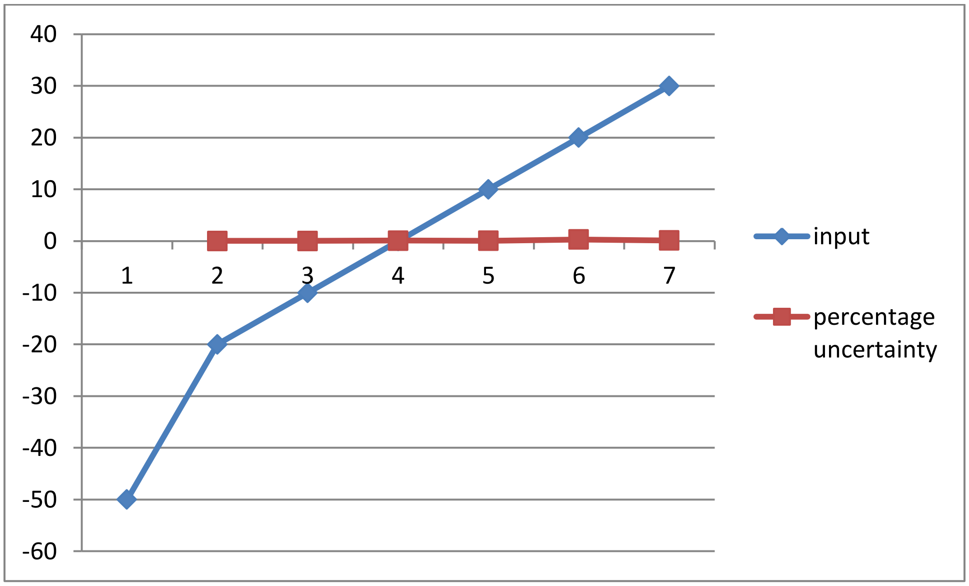
V=flow rate ×time

Uncertainty =$\sqrt{u^2(flowrate) + u^2(time)}$

=$\sqrt{1 + 0.5}$=1.224

Percentage uncertainty =1.322-1.244/1.322 = 0.059%

Graph 2



The time is changed with same flow rate and the process id repeated to see how much the uncertainty percentage changes with respect to time

Table4: sensitivity analysis time change

Input %	Time(minutes)	Uncertainty	Percentage uncertainty
-50	10 sec	1.079	
-20	20sec	1.153	0.0641%
-10	35sec	1.258	0.0834%
0	50sec	1.353	0.0702%
10	1	1.414	0.043%
20	3	2	0.2930%
30	4	2.236	0.1055%

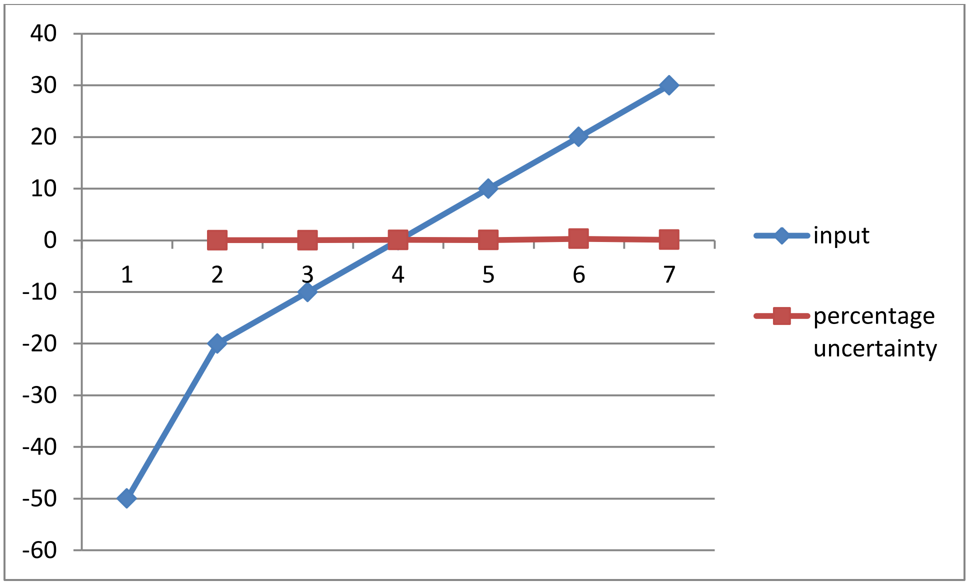
Uncertainty of flow rate is =1 minutes

V=flow rate ×time

Uncertainty =$\sqrt{u^2(flowrate) + u^2(time)}$

=$\sqrt{1 + 0.166}$=1.079

Percentage uncertainty =1.153-1.079/1.153 =0.0641%



Graph 3

In the next case both input s well as time has been changed and percentage of uncertainty is calculated

Table 5: sensitivity analysis change in both time and input data

Input %	Time(minutes)	Uncertainty	Percentage of uncertainty
-40	8 sec	1.06	
-25	18 sec	1.14	0.070%
-5	37 sec	1.27	0.10%
0	55 sec	1.38	0.079%
5	3	2	0.310%
25	4	2.23	0.103%
35	6	2.64	0.155%

Uncertainty of flow rate is =1 minutes

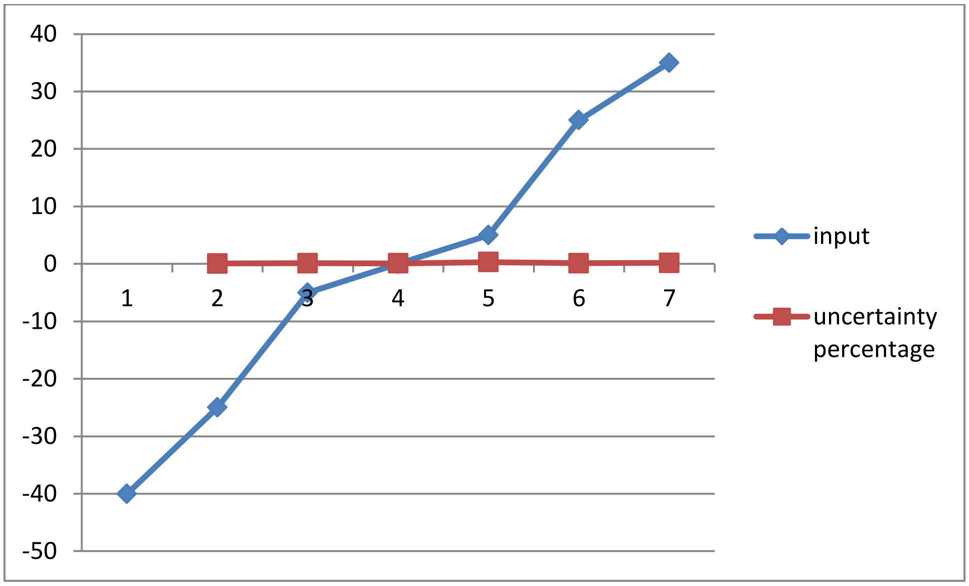
V=flow rate ×time

Uncertainty =$\sqrt{u^2(flowrate) + u^2(time)}$

$=\sqrt{1 + 0.133} = 1.06$

Percentage uncertainty =1.14-1.06/1.14 = 0.07%

Graph 4



4. Conclusion

The methodology for the calculation of uncertainty and in house validation data has been applied to multiple methods of uncertainty sources have been identified and standard uncertainty has been established

The quantification uncertainties have been estimated and the combined uncertainty has been calculated and the value is found to be 2.12 which is slightly higher compare to similar particles estimation. This can be overcome by increasing the uncertainty of measuring cylinder and syringe. Instead of 25 ml of measuring cylinder 25 ml pipette can be used because the loss due to measuring cylinder is more when compared to pipette

And in sensitivity analysis there were three cases in first two cases only time is changed so the uncertainty percentage do not show much variation when both time as well as input data's were changed the uncertainty percentage change to some extent

When the system error is present the bias is significant a correction of recovery factors would decrease the uncertainty results drastically it is difficult to establish whether the sample is positive or negative unless an uncertainty level be established by regulatory norms

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