VOLATILE ORGANIC COMPOUNDS IN INDOOR AIR: SCIENTIFIC, MEDICAL AND INSTRUMENTAL ASPECTS[*]

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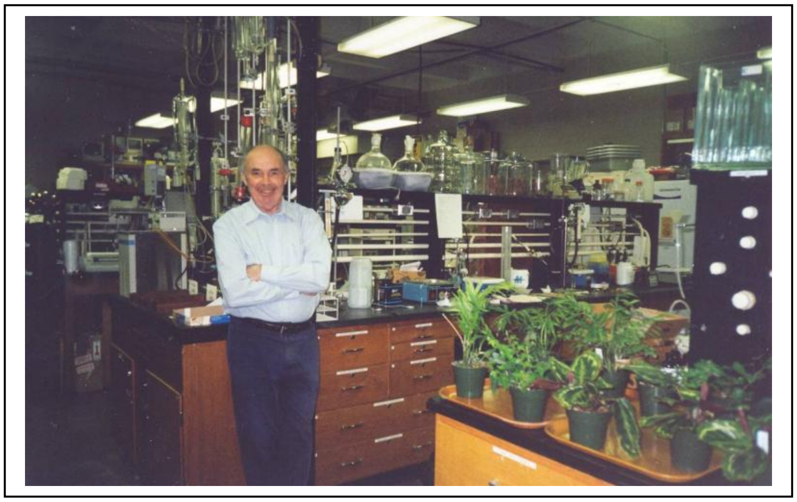

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SUMMARY

The focus of this review is on examination of sources of volatile organic compounds (VOCs) in indoor air, their concentration, rate of emission and effects of external factors on them, fate and interaction of VOCs with indoor surfaces, materials and products, health effects and toxicity of VOCs, methods of sampling, preconcentration and analysis of VOCs, technology of sick building syndrome prevention and control, investigation of main problems of phytoremediation of indoor air, particularly substantial variation among plant species in the rate and type of VOCs that can be removed, uptake and transport VOCs in phytoremediation systems, principal mechanisms of detoxification of VOCs in ornamental plants.

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INTRODUCTION

Indoor air quality means the content and nature of interior air that affects the health and well-being of building occupants.

The problem of indoor air quality and pollution has attracted the attention of investigators who published during last years a number of the books where the list of potential sources of indoor pollution, typical pollutants of indoor air, just as methodology of sampling and extraction of air samples, and analysis of indoor air quality are presented (Kay, 1991; Leslie, 1994; Indoor air quality…, 1995; Miller et al., 1998; Hansen, 1997; Godish, 2001; Hess-Kosa, 2002; Pluschke, 2004; Zhang, 2005).

The fact is that humans are spending almost all the time of their life activity in the closed spaces − at home and nonresidential buildings (offices, commercial establishments, universities, schools, hospitals, enterprises), or inside motor vehicles, trains, ships, airplanes. According to the investigations in the USA and Europe, the population of industrialized countries spend more than 90 percent of their time indoors and air quality is often inferior to that outside (Snyder, 1990; Jenkins et al., 1992; Indoor Air Pollution,…, 1994). This indoor environment is often contaminated with various air pollutants; the concentration of these pollutants may reach high levels due to the small spatial volume. Indoor air in cities has been reported to be as much as 100 times more polluted than that outdoors (Brown, 1997; Brown et al., 1994; Godish, 1995; Ingrosso, 2002; Yang et al., 2004).

According to the World Health Organization (WHO's Programme on Indoor Air Pollution. 2002) every year, indoor air pollution is responsible for more than 1.6 million annual deaths and 2.7 % of the global burden of disease.

The main pollutants of indoor air include inorganic pollutants (carbon dioxide, carbon monoxide, nitrogen dioxide, sulphur dioxide, ozone), organic pollutants (volatile organic compounds, formaldehyde, pesticides, polynuclear aromatic hydrocarbons, polychlorinated biphenyls), physical pollutants (particulate matter, asbestos, man-made mineral fibers, radon), environmental tobacco smoke, combustion-generated, microbial and biological contaminants, radioactive pollutants (Indoor air quality…, 1995; Godish, 2001).

VOLATILE ORGANIC COMPOUNDS

One of the hazardous pollutants of the indoor air are volatile organic compounds (VOCs) (Koppmann, 2007). The National Institute for Occupational Safety and Health (NIOSH) reported in 2007 that average concentration of total volatile organic compounds from area air samples can reach 2.90 mg/m^3.

Volatile Organic Compounds mean the gases that are emitted from certain solids or liquids and include a variety of chemicals hazardous for human health (An

Introduction to Indoor Air Quality. http://www.epa.gov/iaq/voc.html). These compounds have enough vapor pressures under normal conditions to significantly vaporize and enter the atmosphere. The term “volatile” related to the tendency of these compounds to vaporize at normal temperature and pressure because of their low boiling points. It is possible to distinguish (Volatile Organic Compound. Wikipedia. http://en.wikipedia.org/wiki/Volatile_organic_compound):

very volatile (gaseous) organic compounds (VVPC) which have boiling points ranging from < 0 ^{0}C to 50-100 ^{0}C;

volatile organic compounds (VOC) ranging from 50-100 ^{0}C to 240-260 ^{0}C;

semivolatile organic compounds (SVOC) ranging from 240-260 ^{0}C to 380-400 ^{0}C;

organic compounds, associated with particulate matter or particulate organic matter (POM) with boiling point range > 380 ^{0}C.

Nomenclature of VOCs

The number of identified VOCs has increased progressively from more than 300 in 1986 to over 900 in 1989 (Indoor air quality…, 1995); nowdays, according to the information of Minnesota Department of Health (Volatile Organic Compounds (VOCs) in Your Home. http://www.health.state.mn.us/divs/eh/indoorair/voc/vocfactsheet.pdf), “there are thousands of different VOCs produced and used in our daily lives” due to increased analytical precision and the number of new sources each year.

A list of common volatile compounds includes: aromatic hydrocarbons, aliphatic and alicyclic hydrocarbons, ketones, alcohols, glycol ethers, esters, phenolics, chlorinated hydrocarbons, terpenes, aldehydes, acetates and miscellaneous other compounds (Hess-Kosa, 2002). A detailed list of types, concentrations and distributions of VOCs in indoor air can be found in “Indoor Air Quality. A comprehensive reference book.” (Eds. Maroni et al., 1995).

Volatile organic pollutants emanate from carpet, wood panels, paint, occupants, pets and other sources. Benzene and toluene, for example, are emitted from household and consumer products such as newspapers, scientific journals, schoolbooks, electric shavers, portable CD players, liquid waxes, and certain adhesives (Salthammer, 1999). Toluene and benzene derivatives are also found during cooking (Yang et al., 2007*a*).

The results of analysis of the volatile organic compounds in the air of a relatively well aerated residence (ca. 1927, without carpet and drapes) made it possible to find the following compounds in descending concentration (Yang et al., 2004): butyl butyrate, d-limonene, nonanal, toluene, benzaldehyde, eucalyptol, α-pinene, mono(2-ethylhexyl) phthalate, decanal, p-xylene, nonane, 1-butoxy-2-propanol, 1,2,4-trimethylbenzene, 2-butoxyethanol, 2-(hexyloxy)-ethanol, undecane, 1-methyl-2-(1-methylethyl)-benzene, β-pinene, decane, o-xylene, heptanal, tetradecane, acetic acid, 3-carene, 1-ethyl-4-methylbenzene, pentadecane, 3-furaldehyde, dodecane, menthol, ethylbenzene, 2,6-di-tert-butyl-1,4-benzoquinone, styrene, tridecane, 1,3,5-trimethylbenzene, benzyl alcohol, propylcyclohexane, camphene, methyl salicylate, 1-ethyl-2-methylbenzene, naphthalene, 3-methylbutyl acetate, aromadendrene, 1,2,4,5-tetramethylbenzene, 1-ethyl-4-methylcyclohexane, 1-ethyl-3-methylcyclohexane, 1-methyl-4-(1-methylethenyl)-benzene, 2-methylnaphthalene. Newer, more tightly constructed homes and those with carpet and drapes generally have a far greater number, variety and concentration of volatiles in the air. Collectively pollutants result in a significant reduction in indoor air quality that can affect the health and well-being of those exposed (Assimakoppoulos, 2004; Jones, 1999; Wolverton, 1986; Wood et al., 2002; Yang et al., 2004).

Indoor air quality improvement and prevention of hazardous effects of VOCs can be resolved through the thorough control of indoor air quality, application of systems of ventilation of indoor air and its cleaning (Dyer et al., 1996; Leovic et al., 1999; Inoue, 1999; Torii, 2000; Ro, 2002; Kadosaki, 2003; Gao et al., 2006; Liu et al., 2003, 2005; Cooper, 2007).

In the following review, we address:

1. Sources of VOCs in indoor (home and office) air; the type, concentration, rate of emission of VOCs that are responsible for contamination of indoor air; and factors that lead to the elimination of the hazardous effects of VOCs;
2. The fate and transport of VOCs within the room/house/office;
3. The principal methods of sampling of indoor air and analysis of VOCs in indoor space;
4. Sick building syndrome prevention and control;
5. The species of plants that are best for removing a particular VOC or mixture of VOCs from the indoor air;
6. Processes and mechanisms by which plants modify and transform VOCs, with special emphasis on ornamental plants.

SOURCES OF VOLATILE ORGANIC COMPOUNDS

The primary classification of VOCs in the indoor air gets into account such principal components of the indoor environment as household and consumer products, new constructions or renovation, building occupant emissions, biological and microbial sources, automobile exhausts and products (Indoor air quality…, 1995; Organic Indoor Air Pollutants…, 1999; Godish, 2001; Hess-Kosa, 2002).

HOMEHOLD MATERIALS

These sources include furnishings, floor covering, carpets, curtains, draperies and clothing, books, newspapers and journals.

Furnishing

Production and manufacture of wood furniture is accompanied with the technology of elaboration of wood surfaces with various chemicals that perform the protective or decorative functions. These chemicals (paints, lacquers, varnishes and other coatings) can emit hazardous VOCs and present certain health risk (Organic Indoor Air Pollutants…, 1999).

The emissions of VOCs from different types of furniture coatings usually was investigated by test chamber and a total of 150 VOCs were identified (Salthammer, 1997).

Compounds groups occurring most often were aliphatic and aromatic aldehydes, ketones, aromatic hydrocarbons, glycols and esters. Special attention was paid to the detection of typical components of coating materials such as acrylic monomers, photoinitiators and other additives.

A group of investigators **(**Huang et al., 1996) proposed to use water-based products that can be introduced to the wood coating industry to replace the high VOCs and high hazardous air pollutant materials previously used on wood products. The problems concerning the application of water-based products are mentioned: hardness, toughness, adhesion, and stain resistance.

Different coated wood based products and furniture have been studied on their emission behavior of VOCs by means of different emission test chambers combined with an appropriate sampling and analyzing procedure (Jann and Wilke, 1999). The effect of various parameters such as temperature, relative humidity, air exchange rate, loading rate, air velocity and clean air supply have been studied. The large influence of most of these parameters on the emission behavior of the materials and thus on the materials aging has been shown.

The paper of Stachowiak-Wencek and Pradzynski (2005) presents results of investigations on the emission levels of VOCs from surfaces of furniture elements, which were carried out on articles manufactured from particleboards finished with natural oak veneer and treated with nitrocellulose wood stain, nitrocellulose primer and acrylic finishing lacquer.

Ecological properties of lacquers designed for furniture finishing and problems related to emission of VOCs from top coatings applied on furniture are discussed by Tesarova and Muzikar (2005). Special emphasis has made on the interior atmospheric and ecological standards and requirements in Europe. Results of detection of VOCs emitted from freshly painted furniture, as well as from fiberboard-based furniture after prolonged time are presented.

All these results have shown that furniture may contribute significantly to indoor air pollution.

Flooring

These sources of VOCs emission include wood covering and parquets, synthetic materials, linoleum and flooring components such as paints, additives, colorants, solvents, plasticizers (Organic Indoor Air Pollutants,…1999).

Effect of relative humidity on the emission of volatile organic substances from polyvinylchloride floorings was analyzed by Rittfeldt (1991).

Emission of volatile organic compounds from a vinyl floor covering was evaluated in two small climatic chambers and a microchamber using different air exchange rates and loading factors. Temporal dependence of concentration for cyclohexanone and PhOH was studied; a simplified model for internal diffusion-controlled emissions in the source was developed, applying a diffusion coefficient which depends exponentially on the concentration in the source (Clausen et al., 1993).

Analysis of the unoccupied test houses has shown that paints and flooring were the most important sources of indoor air pollution. Formaldehyde, benzene, toluene, xylenes, and undecane were found in high concentrations; these VOCs declined quickly during the first 6 months after construction (Crump et al., 1997).

In study of Wiglusz et al. (1998) 29 polyvinylchloride floor coverings were tested for emission of vinyl chloride and other volatile organic compounds (VOCs). The effect of higher temperature on emission of VOCs from newly manufactured PVC flooring was also carried out. The increase of temperature caused increase of total volatile organic compounds (TVOC) emission during 24 hours of experiment. Then the emission was comparable for both temperatures. The study conducted showed that PVC floorings after 10 days of installation in the room should not be source of indoor air contamination.

It is known that latex paints are used widely and surface area covered by these paints is relatively large. Investigation of latex paint emission were provided due to stainless steel painted with latex and unpainted gypsum board substrates to study latex paint emission characteristics. It was shown that emissions from stainless steel were relatively short lived (3-4 days), whereas emissions from gypsum board lasted more than 200 days (Sparks et al., 1999).

The principal sources of VOCs in new manufactured and site-built unoccupied houses were plywood flooring, latex paint, and sheet vinyl flooring (Hodgson et al., 2000).

The complex investigation of the emission from various adhesives and floor coverings (different floor covering adhesives, a primer, a filler material, carpets, PVC coverings, linoleum coverings, a rubber covering and a polyolefin covering was realized by Wilke et al.(2003). It was shown that the emissions from floor coverings were influenced by sorption effects and different permeabilities of the floor materials. Emissions from the complete structures were smaller than the sum of emissions from the individual materials.

VOC- and SVOC-emissions from materials for flooring installation (primer, screed, adhesive, floor covering) were measured by emission test chambers and cells over a time period of at least 28 days (Wilke et al., 2003). Single components were tested in comparison to 3 complete structures (same concrete, primer, screed, adhesive) with different types of floor covering (PVC, carpet, linoleum).

The relationship between a high incidence of bronchial asthma among employees working in an office building and an indoor air problem related to the degradation of polyvinyl chloride (PVC) floor coverings in the building was studied by Tuomainen et al. (2004). In an office with about 150 employees, 8 new cases of asthma were found in 4 years. In addition, the workers complained of respiratory, conjunctival, and nasal symptoms. Emissions indicating the degradation of plastic floor coverings (e.g. 2-ethyl-1-hexanol, 1-butanol) were found in the indoor air and floor material samples. The plastic floor coverings, adhesives, and the leveling layers were carefully removed from 12 rooms.

Analysis and VOCs detection from latex paints was described by Lorenz et al. (2005). The comparison of a PVC adhesive was detected by infrared spectroscopy, pyrolysis gas chromatography and flame ionization detector. A test chamber was used to detect exhalations from a floor covering, where volatiles were captured in an adsorber tube and then detected by thermodesorption and gas chromatography.

The emission of VOCs from 20 species of composite flooring materials has been measured using a small chamber technique (Ookoshi, 2006). The concentration of toluene, xylene and styrene were very low after one day of emission test, but total VOC concentration exceeded provisional guideline concentrations for most of the flooring samples. It was shown that the VOC emissions inside house depend strongly on the materials that are used for floor covering such as the wood, solvents, adhesives, coloring and coating (Ookoshi, 2006).

A method for preparing multilayer flooring material for reducing sick house syndrome was proposed by Hong et al (2006).

Aldehyde and volatile organic compound emissions from laminated veneer lumber were detected by Miyamoto et al. (2006). The samples were made from three different veneer species, namely larch (*Larix* species), radiata pine (*Pinus radiata* D. Don) and sugi (*Cryptomeria japonica* D. Don), and were bonded with phenol-formaldehyde resins for structural use and melamine-urea-formaldehyde resins for nonstructural use. The effects of veneer species, adhesive type, and formaldehyde scavenger on aldehyde and VOC emissions from the samples were investigated. It was concluded that the predominant VOCs derived from the veneer. All the laminated veneer lumber samples used in this study had very low emissions of VOCs according to the indoor air quality guidelines of the Japanese Ministry of Labor, Health and Welfare.

The emission of formaldehyde, volatile organic compounds (toluene, styrene, 4-PC), and total volatile organic compounds from new textile floor coverings was measured with the use of environmental chamber (Igielska et al., 2002). Formaldehyde was detected by colorimetric method, VOCs by gas chromatography. The tested carpets did not emit formaldehyde. The emission of other VOCs was very low and fulfill known requirements.

Carpets

Carpets are the potential sources of VOCs due to the materials that these carpets include: synthetic fibers, latex components and adhesives (Indoor Air Quality…, 1995). A list of volatile organic chemical emissions from carpets are reflected in articles of Gammage and Matthews (1988), Weschler et al. (1992).

Group of researchers provided an experiment the primary objective of which was to measure the emission rates of selected individual VOC from carpets (Hodgson et al., 1992). The carpet samples were collected directly from the manufacturers and packaged to preserve their chemical integrity. The measurements of the concentrations. and emission rates of these compounds were made under simulated indoor conditions in a 20-m^3 environmental chamber for one week. The four carpets emitted a variety of VOC, forty of which were identified. Eight of these were considered to be dominant. They were (in order of chromatography retention time) HCHO, vinyl acetate 2,2,4-trimethylpentane, 1,2-propanediol, styrene, 2-ethyl-l-hexanol, 4-phenylcyclohexene, and 2,6 di-tert-butyl-4-methylphenol.

The effect of ozone on the VOCs emission was measured by Weschler et al. (1992) in a freshly carpeted 20-m^3 stainless-steel room (ozone concentration was ranging from 30 to 50 ppb). It was demonstrated that the gas-phase concentrations of selected carpet emissions (e.g., 4-phenylcyclohexene, 4-vinylcyclohexene, and styrene) significantly decreased in the presence of ozone while the concentrations of other compounds such as HCHO, AcH, and aldehydes with 5-10 C significantly increased. Furthermore, the total concentrations of VOCs increased markedly in the presence of ozone. The additional appearance of VOCs can be explained by reactions between ozone and relatively nonvolatile compounds associated with the carpets. These studies suggest that VOCs measured within a building at elevated ozone levels (>30 ppb) may differ from those measured at lower ozone levels (>10 ppb).

A series of experiments with several carpet systems, various VOCs and environmental conditions (relative humidity, air exchange rate) were performed by Won et al. (1999).

Carpet is recognized not only as a potential source of VOCs in indoor air but can also serve as adsorptive sinks that provide re-emission of VOCs over prolonged periods of time (Won et al., 1999)

The study of Black and Worthan (1999) evaluated the impact of soiled carpet on the indoor environment and detected the effectiveness of carpet cleaning removing biological contaminants. Soiled carpet was removed from two buildings, one where environmental conditions were well maintained at normal conditions (70-75 ^{0}F and 40-60% relative humidity) and one where environmental conditions were been controlled with resulting extreme conditions elevated temperature and high humidity (80-90 ^{0}F, 85-95% relative humidity). Carpets were removed from buildings and installed in controlled environmental chambers where original building temperature and relative humidity conditions were replicated.

Results of experiments of Elkilani et al. (2003) showed the carpet fibers acted as a significant sink causing a prolonged elevation of VOC concentrations in the air within the chamber.

A review of Smith and Bristow (1994) proposes an information about specifications, test methods, low emitting materials, and infinite sinks for textile products which can be considered as sources of VOCs emission.

HOMEHOLD MACHINES AND DEVICES

These potential sources of VOCs include electronic devices such as copy machines, toners and printers, and heating, ventilating, and air-conditioning systems.

Photocopiers and Printers

The tests concerning the determination of emission rates of VOCs that are related to the function of the offset printing are reported by Wadden et al. (1995). Tests were conducted at three offset printing shops that varied in size and by process. Main VOCs included benzene, toluene, xylenes, ethylbenzene, and hexane.

Photocopiers are sources of office indoor air pollution. A photocopier's toner and dispersant contain heavy-treated naphtha, a mixture consisting primarily of decane, which is known to be toxic to humans.

Experimental study of VOC emissions from a photocopier located at the University of Texas, USA, made it possible to establish the air turnover rate in the room, the VOC concentration in the room during photocopier operation, and a typical daily concentration profile (Shepherd et al., 1997)

Gehr et al. (2004) investigated indoor air pollution caused by recycling papers during printing or copying with respect to their causes and health risk. The air pollution potential was in essential caused by the offset printing colors. It was shown that the choice of an appropriate printing apparatus may change the sum of VOCs by a factor of 25 and the sum of less VOCs by the factor 7.

Investigations for determining VOCs emissions from printers and copiers (Jann et a., 2003) have shown higher VOC emissions from recycling paper in comparison with paper produced from primary fibers. As the result a test method for the detection of emissions from hardcopy devices was developed.

Emission of ozone and VOCs from laser printers and photocopiers was studied by Tuomi et al. (2000). It was shown that laser printers emitted significant amounts of ozone and formaldehyde, while the photocopier emitted mainly ozone. In a well-ventilated office environment, concentrations of individual VOCs were within recommended maximal exposure limits. It is recommended that laser printers equipped with traditional corona rods not be placed near office personnel working sites.

Tsuchiya et al. (1988) demonstrated that wet process copying machines are the major sources of VOC emissions in buildings and libraries.

The study of Lee et al. (2006) investigates the indoor air quality of typical photocopy centers in Taiwan to evaluate the human health risk following inhalation exposure. The benzene, toluene, ethylbenzene, xylenes, and styrene measurements indicated no difference between personal and area samplings and found that air conditioning improves indoor air quality. However, the mean benzene and styrene levels in the current study were 138 and 18 times, respectively, higher than those in another study conducted in the United States. It was shown that the photocopier is not the only VOCs source in photocopy centers. The lifetime cancer and non-cancer risks for workers exposed to VOCs were also assessed. All seven centers in this study had a lifetime cancer risk exceeding $1 \cdot 10^{-6}$ (ranging from $2.5 \cdot 10^{-3}$ to $8.5 \cdot 10^{-5}$). Regarding non-cancer risk, levels of toluene, ethylbenzene, xylenes, and styrene were below the reference levels in all photocopy centers; however, the hazard indexes for all still exceeded 1.0 (range 26.2-1.8) because of the high level of benzene in the photocopy centers.

HOMEHOLD CHEMICALS AND MATERIALS

Nomenclature of these sources of VOCs includes cleaners, waxes, room fresheners, deodorants, furniture polishes, paints, lacquers, adhesives, insecticides, cosmetics.

Homehold Chemicals

Solvent- and H_2O-based adhesion contained MePh [Chemical Abstracts Service Registry Number108-88-3], styrene [100-42-5], and a variety of normal, branched, and cyclic alkanes were studied as potential sources of indoor air pollution (Girman et al., 1984).

Study of 35 houses in West Virginia, USA, showed that the source of VOCs in the indoor air was generally inside the house. Houses with moth balls and/or air fresheners contained increased indoor air concentrations of p-dichlorobenzene, decane, $MeCCl_3$, and C_2HCl_3, while houses with attached garages had increased concentrations of C_6H_6, PhEt, m-xylene, o-xylene, trimethylbenzene, CCl_4, CH_2Cl_2, $MeCCl_3$ C_2HCl_3, PhCl, p-dichlorobenzene, and decane (Cohen et al., 1988).

A total of 1159 consumer and commercial products were analyzed for 31 VOCs as potential indoor air pollutants. Among these products automotive products (14.4% of the products); household cleaners/polishes (9.2%); paint-related products (39.9%); fabric and leather treatments (7.9%); cleaners for electronic equipment (6.0%); oils, greases and lubricants (9.6%); adhesive-related products (6.6%); and misc. products (6.1%). These products emitted VOCs in relatively high concentrations such as CCl_4; Me_2CO, 2-butanone, hexane, methylene chloride, tetrachloroethylene, PhMe, 1,1,1-trichloroethane, trichloroethylene, 1,1,2-trichlorotrifluoroethane and the xylenes (Sack et al., 1992).

The emissions from adhesives for floor coverings in offices were analyzed in view of indoor air pollution and industrial hygiene measures (Augustin et al., 2002).

Polyurethane foam (PUF) as the source of indoor VOC was studied at first time (Zhao et al., 2004). This compound which is used widely in indoor consumer products was studied as a possible sorbent of eight aromatic VOCs ranging in molecular weight – from naphthalene to benzene. It was found that humidity reduces the extent of sorption and slows the sorption kinetics.

Group of investigators (Norback et al., 1995) shown that the application of water-based paints has improved the work environment for most house painters by reducing the total VOC exposure.

Homehold Materials

Sources of VOCs, such as open oil lakes, chemical and petrochemical industries and indoor pollution from household items, concentrations of aliphatic and aromatic VOCs, comprising n-hexane to n-hexadecane, benzene, toluene, xylene, ethyl benzene, methanol and o-dichlorobenzene, were measured in indoor air samples from seven different cities in Kuwait using a gas chromatography (Bouhamra, 1995).

The application of decorative materials in office buildings provokes the emission aromatic hydrocarbons (benzene, toluene, o-, m-, p-xylene, and ethylbenzene) in indoor air; it was shown that indoor pollution mainly resulted from wall paper, plastic floor board, paint, and glued wood (Zhang et al., 1998).

The emission of VOCs derived from wood-based materials, such as particleboards, flooring, panel wall, finishing, and furniture were studied in a small stainless steel chambers (Shen et al., 2005).

Indoor air quality at nine locations such as food courts, restaurant, bar, conference room, office and theater in West Bengal, India, have been monitored for VOCs content. Forty VOCs have been identified and one fourth of these are classified as hazardous air pollutants (Srivastava and Devotta, 2007).

Various VOCs emitted from paint, wallpaper glue, multicolor paint, floor wax, floor covering glue, air freshener, etc, were analyzed by headspace GC-FID and GC-MS. The emitted compounds such as paraffin, olefin, alcohol, aldehyde, ether, ester and aromatic compounds just as emission rate from different materials were studied (Han and Jing, 2008).

The results of GC-MS analysis of organic vapors emitted from polyurethane foam insulation (Krzymien, 1989) made it possible to identify over 70 compounds as polyurethane foam off-gases. Among them the most numerous are hydrocarbons. The most abundant is the blowing agent, $CFCl_3$.

NEW CONSTRUCTION AND RENOVATION

The concentration of VOCs such as benzene, toluene, Bu acetate, ethylbenzene, m-xylene, styrene and m-dichlorobenzene were measured in three newly erected and remodelled dwellings (Zabiegata et al., 1999); the relationship between concentration of indoor air chemicals and the age of houses was studied by Saito et al. (2000).

The investigation of the indoor air in newly built houses of Tsukuba, Japan, have shown that high concentration of VOCs such as toluene and xylenes originated from interior materials that contained synthetic chemicals, and terpenes originated from woody materials (Zheng et al., 2000).

In Japan, over a million personal dwellings are newly constructed each year and the problems associated with indoor air pollution and dampness have become a very important environmental health issues (Saijo et al., 2004).

The symptoms of 343 residents in 104 detached houses at Hokkaido region were surveyed (Takeda et al., 2009); a total of 429 dwellings in Sapporo and 135 in the environs of Sapporo were analysed (Saijo et al., 2004); the questionnaires were distributed to the occupants of 1,240 dwellings which were all detached houses that have been newly built within 7 years (Takeda et al., 2009). These questionnaires were used to investigate the relation of dampness to sick building syndrome: dampness indicators were as follows: condensation on the windowpanes and on the walls and/or closets, visible mold in the bathrooms and on the walls, window frames, moldy odor, slow drying of the wet towels in bathrooms, water leakage and bad drainage in bathrooms (Saijo et al., 2009). It was measured the concentrations of formaldehyde, acetaldehyde, VOCs, airborne fungi, and dust mite allergen in the living rooms (Takeda et al., 2009). Some VOCs such as toluene, butyl acetate, ethylbenzene, alpha-pinene, p-diclorobenzene, nonanal, and xylene were significantly related to the sic building syndrome (Saijo et al., 2004).

Newman (2007) has proposed a comparison of VOCs in new homes, older homes and their outside environment.

Researchers have found that pollutant levels in the air inside homes are two to five times higher than the air outside. The majority of the population suffers from asthma and other pollution-related health problems because of indoor VOC levels (Gao et al, 2006).

New and established buildings in Melbourne, Australia, have been analyzed from the point of view of VOCs in indoor air. It was established that the presence of attached garages, site contamination and 'faulty' wool carpet were associated with higher indoor pollution. Total VOC concentrations were low, but were approximately four times higher than in outdoor air. Building materials were found to be responsible for long-term emissions of VOCs (Brown, 2002).

One hundred twelve homes with 10 or more stories were studied from the point of view of quantitative estimation of VOCs. It was shown that both the outdoor and the indoor air concentrations of three VOCs such as methyl tert-butyl ether (MTBE), benzene, and toluene were significantly higher for the low-floor apartments than for the high-floor apartments (Jo et al., 2003)

Seven apartments were studied in three different apartment buildings, where the occupants had been suffering from different symptoms. The air exchange rates were as regulated. As a renovation procedure, the floor covering and adhesive (and smoothing material at one site) was removed and replaced with a new, low-emitting product. The concentration of indoor air pollutants (VOCs, formaldehyde, ammonia) was detected prior to the renovation. The TVOC and formaldehyde concentration was two times higher in the inhabited apartments compared to the emptied and cleaned apartments. The floor structure was detected to be the source of the pollutants at all sites. The results gained from a survey made among the inhabitants concluded that the symptoms had markedly decreased after the renovation (Jarnstrom, 2005).

AUTOMOBILE EXHAUSTS AND PRODUCTS

These sources of VOCs in indoor air are related to the garages which are either attached or located inside the building; automobile exhausts and a number of automobile products such as gasoline, oils, automobile fluids that are kept in these garages can be potential sources of VOCs (Gammage and Matthews, 1988; Kindzierski, 2000).

Protocol for determining the daily volatile organic compound emission rate of automobile and light-duty truck topcoat operations (EPA-450/3-88-018) was published in 1988 (Protocol…, 1988). Directions were given for determining the daily VOC emission rate (pounds of VOC's/gal of coating solids deposited) for a complete automobile and light-duty truck topcoat operation, including such factors as daily usage of each coating,

Automobile exhausts

A review dedicated to the VOCs emitted from automobiles and pollution from using MeOH as fuel was proposed by Ohi (1992).

Gasoline that is emitted from automobiles as uncombusted fuel and via evaporation is a source of VOCs which penetrate into automobile cabine from the roadway, thereby exposing commuters to higher levels than they would experience in other microenvironments. The levels of VOCs were related to traffic density and were inversely related to driving speed and wind speed (Weisel et al., 1992).

Nearby vehicle traffic provides also significant effect of the indoor airborne VOCs (aldehydes, ketones, and ethanol) in Toronto, Canada. It was shown that indoors concentrations were greater than outdoors for ethylacetate, tetrachloroethane, pinene, limonene, 1,4-dichlorobenzene, naphthalene, formaldehyde, acetaldehyde, and ethanol (Otson et al., 1998).

Schlapia and Morris (1998) investigated the effect of the presence of an attached garage on the in-home benzene. Elevated benzene was estimated in homes with garages to park vehicles or store fuel or small engines; with living space located over the garage; with forced air furnaces in comparison with those that was equipped with hot water boilers.

Concentrations of 15 VOCs including 1,3-butadiene, benzene, and styrene were measured in a wide range of urban microenvironments such as homes, offices, restaurants, pubs, department stores, coach and train stations, cinemas, libraries, aboratories, perfume shops, heavily trafficked roadside locations, buses, trains, and automobiles (Kim et a., 2001). For most target VOCs-including 1,3-butadiene and benzene-mean concentrations at heavily trafficked roadside locations were exceeded by those in automobiles and were comparable to those in pubs and train stations.

The results of comparison of VOCs emission of 14 gas/oil motor-driven and 3 gas-driven automobiles was proposed by Siskos et al. (2002). Method of the thermal desorption-gas chromatography with flame ionization detection made it possible to indicate that the gas-driven automobiles emit fewer VOC's.

A major contributor to indoor pollution in large cities is the outdoor environment largely via intense vehicular traffic. It was shown that in Tehran, Iran, the group of gasoline components (benzene, toluene, ethylbenzene, xylene) were principal contributors to indoor air pollution. Also, the benzene concentration was particularly high, 2-4 times greater than maximal concentrations recommended by many countries (Halek et al., 2004).

Total 48 VOCs inside the automobiles were found and analyzed with thermal desorption-GC-MS method (Zhao et al., 2005). The percentage of benzene, toluene, ethylbenzene and xylene to concentration of total VOCs was 20-30%. It was shown that concentration of the total VOCs depended on temperature and the ages of automobiles.

Fischer et al. (2000) have evaluated differences in concentrations of air pollutants outside and inside homes in streets with low and high traffic intensity in Amsterdam, the Netherlands. It was shown that total VOC were highly correlated with traffic air pollution.

Automobile Products

VOC emissions from various interior components (leather and fabric trims) of new cars was analyzed; it was shown that butylated hydroxytoluene (BHT), a common anti-oxidant, was the most common VOC. Long-chain aliphatic hydrocarbons C14-C17 were identified in most grease (lubricant) samples, and toluene and xylenes were found in adhesive samples (Chien, 2007).

BIOLOGICAL SOURCES

Building inhabitants emit metabolic products. Human exhaled breath is the source of VOCs also. The most dangerous source of indoor pollution is smoking. The source of VOCs in indoor air of biological origin include viruses, bacteria, molds, pollen, fungi, insects, bird droppings, cockroaches, flea, moth, rats and mousse, fungi, animal feces. Ornamental plants can be considered sometimes as the sources of VOSs also (Yang et al., 2009).

Smoking

It was found in the six smoking homes that environmental tobacco smoke provided a substantial contribution to concentrations of 1,3-butadiene.

Smoking homes demonstrated higher concentrations of tobacco smoke in comparison with nonsmoking homes (Kim et al., 2001).

Transient emissions of VOCs arise from smoking (Gammage and Matthews, 1988).

Burning

Volatic organic compounds can be emitted from incense burning (Lee and Wang, 2004). For example, formaldehyde and benzene concentrations from incense types commonly used in Hong Kong exceeded the standard levels.

Quantitative and qualitative estimation of VOCs that are identified before and during burning of incense showed the presence of benzaldehyde, linalool, benzyl alcohol, phenethyl alcohol., formaldehyde, and acetaldehyde in the emissions of incense both before and after burning. Incense burning produced additional compounds, such as benzene, toluene, and diethyl phthalate (Madany et al., 1995).

Human Breath

Major VOC in the breath of healthy individuals include isoprene, acetone, ethanol, and methanol. Human breath emissions of VOCs has been studied by Fenske and Paulson (1999). It was shown that humans exhale VOCs. Several studies quantified VOC emissions from human breath, with values ranging widely due to variation between and within individuals. Major VOC in the breath of healthy individuals include isoprene (12-580 ppb), acetone (1.2-1,880 ppb), ethanol (13-1,000 ppb), methanol (160-2,000 ppb). Though human breath emissions are a negligible source of VOC on regional and global scales (<4% and 0.3%, respectively), simple box model calculations indicated they may become an important (and sometimes major) indoor source of VOC under crowded conditions.

Method for sampling and analyzing VOCs in breathing air was proposed by Wang et al. (1996**)**. The results indicated that there are significant correlations between the concentration of VOCs such as benzene, toluene, and trichloroethylene in the repeated breathing air and indoor air. The correlation coefficient to benzene was 0.91, to toluene 0.98, and to trichloroethylene 0.91.

Biological and Microbial Sources

Airborne biocontaminants were measured by Black and Worthan (1999). Extractable carpet dust was collected and evaluated for biocontaminant levels before and after cleaning. Biocontaminants measured included fungi, bacteria, dust mite allergens, cat allergens, and cockroach allergens. Data indicated that carpet removed from the normal environment had no impact on the presence of airborne biocontaminants; that the carpet from the extreme environment and with visible surface mold could contribute fungi to the surrounding air, but did not contribute dust mite allergens or bacteria; that carpet cleaning efficiently removed biocontaminants from the carpet; and that the carpet cleaning processes themselves had little impact on pollutant levels in the surrounding indoor air. Data also indicated that proper control and maintenance of indoor environmental conditions and appropriate carpet maintenance can prevent significant biocontaminant growth in carpet.

Dewey et al. (1995) used gas chromatogramhy-mass spectrometry method to detect microbial VOCs formed by fungi in moldy houses. The total concentrations of 11 identified MVOC was ≤ 90 μg/m^3, mainly 1-butanol and isobutanol. A correlation between the extent of mold formation and MVOC was found for 2-hexanone, 2-heptanone, and 1-octen-3-ol.

The formation of VOCs such as propanol, acetone, 2-methyl-1-propanol, and 3-methyl-1-propanol by molds was studied by Schuchardt et al. (2001). A total MVOC emission of 2-5 μg/m^3 was assessed for strongly molded flats.

Airborn fungi and dust mite allergen were estimated in newly built Japanese dwellings in Hokkaido region. Such main organisms as *Cladosporium*, *Penicillium*, *Alternaria*, *Eurotium*, *Aspergillus* and *Rhodotorula* were detected in the dwellings. It was shown that only one fungal genus, *Rhodotorula*, had significasntly higher levels in dwellings with sich building syndrome (Takeda et al., 2009).

CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS

Most air pollutants occur in typical concentration range 1 – 1000 μg/m^3 (Organic Indoor Air Pollutants, 1999); the highest concentrations that have been detected in the USEPA BASE Study of 56 randomly selected office buildings vary from about 0.1 μg/m^3 to 450 μg/m^3 (Godish, 2001).

Typically VOCs concentrations in the buildings depend on a number of factors such as age of building, renovation, decoration, ventilation, season, location near traffic routes. All these factors will be discussed below.

A review of Brown et al. (1994) discusses concentrations of VOCs in established, new and complaint buildings. Although the mean concentrations of VOC in established buildings was generally <50 μg/m^3 (usually <5 μg/m^3), total VOC concentrations were substantially higher (e.g., 1100 μg/m^3).

Comparison of the concentrations of VOCs in indoor and outdoor air demonstrated that indoor air concentrations of many VOCs exceeds those in outdoor air (Indoor Air Quality…, 1995).

Overall median exposures to VOCs were lowest on the suburban commute, slightly higher on the New Jersey Turnpike, and highest in transit through the

Lincoln Tunnel (Lawryk et al., 1995). Median in-vehicle concentrations of benzene, ethylbenzene, m- and p-xylene, and o-xylene were 14 μg/m^3, 6.8 μg/m^3, 36 μg/m^3, and 15 μg/m^3, respectively. For a motorist who commutes 93.2 min daily (6.5% of the day), this corresponds to 12.1%, 10.8%, 14.9%, and 14.7% of the total daily exposures to these compounds. It was shown that gasoline-derived VOC concentrations in a vehicle with a carbureted engine was much higher (45.2 μg/m^3) than in the properly maintained, fuel-injected vehicle.

Phillips et al. (1997) realized a screening for up to 33 VOCs inside and outside the homes of residents in Turin, Paris, Bremen, Lisbon, Basel, and Prague occurred in 1995. Concentrations of most components were consistent with the findings of other studies, e.g., toluene, 0-250 μg/m^3 and benzene, 0-30 μg/m^3. Overall, benzene concentrations were similar inside and outside the homes, whereas toluene concentrations were higher inside vs. outside. Indoor and outdoor benzene concentrations were highest in Turin, Italy; Basel, Switzerland, had the lowest outdoor benzene concentrations overall. The prevalence of automobile use in each city might explain the differing benzene concentrations observed, irrespective of whether they were measured indoors or outdoors.

Estimation of the emissions of a total 150 VOCs from furniture coatings test chamber has shown that the concentration values varied from 4 μg/m^3 to 1288 μg/m^3 with an arithmetic mean of 173.9 μg/m^3 and a median 60.0 μg/m^3 (Salthammer, 1997). The highest chamber concentrations of individual components were found for some solvent residues such as n-butylacetate, butylglycol, 1-butanol-3-methoxy-acetate and butyldiglycolacetate. The results have shown that furniture may contribute significantly to indoor air pollution.

About 70 VOCs were analyzed in the "personal air" (personal sampler) of 13 persons living in the neighborhood of the filling stations and 6 control persons during the summer of 1996 (Heudorf et al., 1998). The mean concentrations of alkenes and cycloalkenes were below 3 μg/m^3. The mean concentrations of benzene, m/p-xylene and toluene were 4.5 μg/m^3, 6.8 μg/m^3, and 34 μg/m^3, respectively. The mean contamination of all other substances was below 3 μg/m^3, halogenated hydrocarbons were below 1 μg/m^3.

The season dependence of VOCs concentration was studied by Sakai et al. (1999). It was shown that the average VOC concentrations indoor were higher in winter than those in summer.

The concentrations of 15 VOCs including 1,3-butadiene, benzene and styrene were measured in a wide range of indoor and outdoor urban microenvironments (Kim et al., 2001). Concentrations were higher indoors, with no correlation observed between indoor and outdoor concentrations. Effect of ventilation was discussed also.

It was studied that effect of season, old and new houses, VOC concentration indoor was higher than that of the outdoor air (Yoshida et al., 2001).

The characteristics and distribution of 62 VOCs from 8 kinds of typical indoor air in South China include the total VOCs concentration of apartments, dance and sing clubs, hotels, restaurant rooms, libraries, offices, shopping malls and garages, respectively, are 0.241, 0.271, 0.471, 0.476, 0.556, 0.910, 1.177 and 2.190 μg/m^3, with the concentration. of 0.213 μg/m^3 from the top of Baiyun mountain as the background value (Wang et al., 2001).

The surveys of indoor air of private houses in Nagano Prefecture, Japan, showed that generally indoor VOC concentrations were higher than outdoor (Yamashita et al., 2001). VOC concentrations and newly built houses had higher concentrations of chemicals related so solvents and building materials.

The indoor air VOC concentration level was surveyed in the Yamaguchi Prefecture, Japan, during 1998-2000 (Sumura et al., 2002). The VOC concentration of indoor air was related to the air temperature. In winter and summer, VOC concentration showed a trend of increasing because of closed windows. The indoor VOC concentration was highest for the newly built houses, which decreased as time passed. Ventilation is the effective way of reducing indoor VOC concentration.

Seasonal cycle of VOCs in apartments was investigated by Rehwagen et al.(2003). The analysis comprised concentrations of 30 VOCs belonging to the groups of alkanes, cycloalkanes, aromatics, volatile halogenated hydrocarbons, and terpenes. It was found that the VOC load in indoor air is, on average, 10 times higher than outdoors. For the studied period there was a clear downward tendency for all VOCs in apartments in Leipzig, except for terpenes which show an upward trend in the period 1996-99. In indoor air we observe an annual cycle for the total VOC concentration as well as the sum concentrations of the above called groups. Highest concentrations occur during the winter months, approximately three times higher than the summer burden.

The spatiotemporal distribution of VOC during 1499 indoor and 222 outdoor measurements was analyzed between 1994 and 2001(Rehwagen et al., 2003).

During a monitoring campaign concentrations of VOCs were measured in indoor air of 79 dwellings where occupants had not complained about health problems or unpleasant odor (Hippelein, 2004). Parameters monitored were the individual concentration of 68 VOCs and the total concentration of all VOCs inside the room. The analytical procedure and quantification was done according to the recommendation of the ECA-IAQ Working Group which gave a definition of the total volatile organic compounds (TVOC) concentration. Using this recommendation TVOC-concentrations ranged between 33 and 1600 μg/m^3 with a median of 289 μg/m^3. However, it has been found that sampling and analyzing methods do have a considerable impact on the results, making direct comparisons of studies somewhat questionable. 47% of all samples revealed concentrations exceeding the threshold value of 300 μg/m^3 of TVOCs set by the German Federal Environmental Agency as a target for indoor air quality.

The pollution levels, characteristics, sources and related health effects of indoor VOCs after room decoration were studied (Wang et al., 2005). The TVOC concentration exceeded the national standard by 76% within one month and 0% three months later. The sources of pollution were artificial board materials used for furniture and decoration. Moreover, the complaints of the discomfort of eyes and upper respiratory tract increased as people moved in the newly decorated rooms.

The effect of inhabitants and a renovation procedure on VOCs concentration was studied by Jarnstrom (2005). The TVOC concentration reached level less than 300 $\mu g/m^3$. The results gained from a survey made among the inhabitants concluded that the symptoms had markedly decreased after the renovation.

European-style bedroom with wood flooring in newly constructed residential houses in Japan are the source of higher concentration of aldehydes, ketones, and VOCs than Japanese type room (Matsuda et al., 2005).

The effect of temperature and relative humidity on VOCs emission from the indoor building materials (furniture material, wooden floor, wall paper, paint and dye) were studied (Seo et al., 2006). It was shown that building materials emitted the highest VOCs concentration at the beginning of experiment and furniture material emitted the highest VOCs concentration. Most of the materials were affected by temperature, but paint and tile material were affected by humidity.

It was shown the correlation between temperature, relative humidity and concentration of volatile organic compounds from wooden furniture in a model room (Fechter et al., 2006). A model room was set up in a 12 m^3 test chamber, and in parallel, a scaled-down version was run in a 1 m^3 test chamber. The latter had a steady climate of 23 ^0C/50% relative humidity (RH), while the temperature and humidity conditions were varied in the 12 m^3 chamber between 18 - 28 ^0C, and 30 - 80% RH.

Onuki et al. (2006) measured the concentration of VOCs that can affect the health of young students inside a schoolroom. The measurements indicated that during the cleaning process, the concentration of diethylene glycol monomethyl ether and diethylene glycol monoethyl ether increased to more than 4000 $\mu g/m^3$, which was more than ten times the tentative goal of total VOC concentration despite air ventilation through the window during the cleaning. The indoor concentration of total VOCs decreased to 1000-2000, below 1000, 100, and 3-7 $\mu g/m^3$ at 4 h, one day, 5 days, and 73 days after the cleaning, respectively. It is recommended that ventilation be continued for several days after the cleaning to keep the VOC concentration low.

Detection of halogenated hydrocarbons, esters and aldehydes in indoor air was realized by Liu et al. (2006). The average concentration of these VOCs was 33, 12 and 9 $\mu g/m^3$, respectively. It was shown that the concentrations of n-hexanal, n-octyl aldehyde, n-nonyl aldehyde, n-decyl aldehyde, Et acetate and Bu acetate had the increasing tendency with the decrease of time after decoration.

Formaldehyde is known as one of the most hazardous pollutants of the indoor air (Jacukowicz-Sobala and Kociolek-Balawejder, 2006). It is used as a preservative and disinfecting and cleaning agent in building, decorating, and insulating materials, furniture, wooden floors, carpets, and textile garments. In addition, formaldehyde in homes is released (about 10-30%) from combustion processes (tobacco smoking, fireplaces, and furnaces). Due to the widespread distribution of formaldehyde sources in houses, average levels of its concentration in indoor air are 20-60 $\mu g/m^3$ and are usually evaluated according to limits for formaldehyde concentrations.

Hida et al. (2007) reported the results of carbonyl compounds air concentration in newly built wooden houses, consisting of 20 living rooms and bedrooms of 10 houses of natural type which is furnished with natural materials, such as solid wood floors and wall panels, and 18 rooms of 9 houses of general type which is furnished with artificial materials such as bonded wood materials for floor and polyvinyl covering for walls and ceilings. The results of VOCs air concentration measurements demonstrated the following values: toluene air concentration averaged 138 $\mu g/m^3$, and the concentration of about 11% of all rooms was over the guideline value (260 $\mu g/m^3$). Toluene concentration in general type rooms was higher than in natural type rooms. Styrene air concentration. averaged 97 $\mu g/m^3$, and the concentration of about 11% of all rooms was over the guideline value (220 $\mu g/m^3$). Styrene concentration in general type rooms was higher than in natural type rooms.

RATE EMISSION OF VOCs IN INDOOR AIR

A series of source tests were conducted to determine the range of emission rates of total VOCs from portable combustion devices which are widespread in houses and restaurants in Korea (Yim et al., 2007). Range of emission rates of VOCs was from 0 to 0.119 mg/h. It is important to characterize the emission of VOCs and suggest optimum ventilation rate.

VOC measurements collected indoors and outdoors at 46 student homes in New York City and 41 student homes in Los Angeles over 2 seasons are studied by Sax et al. (2004). Significant indoor sources were observed for such compounds (mean emission rates): chloroform (0.11 mg/h), 1,4-dichlorobenzene (19 mg/h), formaldehyde (5 mg/h), acetaldehyde (2 mg/h), benzaldehyde (0.6 mg/h), and hexaldehyde (2 mg/h). Formaldehyde had substantially higher indoor emission rates in summer in New York City vs. winter (3.8 vs. 1.6 mg/h), but lower in fall vs. winter in Los Angeles (4.3 vs. 5.0 mg/h).

Procedures to estimating emission rates using transient analysis of VOC concentrations are described by Persily et al. (2003) and applied in a two-story classroom/office building. The results of the analitical yield consistent values of emission rates for building materials ranging from 0.20 to 0.40 mg/m^2h when normalized by floor area. Occupancy-related emissions were more difficult to estimate and covered a wider range from roughly 0.1 to 1.5 mg/m^{2}h.

Concentrations of 54 VOCs and ventilation rates were measured in 4 new manufactured houses over 2-9.5 months following installation and in 7 new site-built houses 1-2 months after completion (Hodgson et al., 2000). Generally, the ratios of emission rates at low and high ventilation rates decreased with decreasing compounds volatility. Changes in VOC emission rates in manufactured houses 2-9.5 months after installation varied by compounds; only some of them showed a consistent decrease in emission rate over this period.

Zhu et al.(1999) developed a method for estimating VOC emission rates from hydrocarbon solvent-based indoor materials has been developed. The estimation is based on the assumption that the emission rate of individual VOCs is proportional to its molar fraction in the evaporative mixture at the time, its saturated pure vapor pressure and total remaining VOCs in the material. The estimated total VOC emission rates were in good agreement with the experimental results.

Guoa et al. (1999) proposed two computational methods to estimate the emission rate of volatile organic compounds from solvent-based indoor coating materials based on knowledge of product formulation. The first method was based on mass transfer models with two key parameters, total vapor pressure and average molecular weight for total VOC (TVOC); the second method was based on a simple, first-order decay model with parameters estimated from the properties of the source and the environment. All model parameters are readily obtained.

An examination of VOC emission rates from new carpet was provided by Hawkins et al. (1992).

EFFECT OF EXTERNAL FACTORS ON VOCs EMISSION IN INDOOR AIR

The concentration of volatile and semivolatile organic compounds depends in a complex manner on the interaction of sources of VOCs and internal conditions: structural situation inside the house, room climate, ventilation regime, air velocity, temperature, relative humidity, and the season (Volland et al., 2005).

The effect of ventilation rate on the ratios of emission rates of VOCs α-pinene, formaldehyde, hexanal, and acetic acid in new manufactured and site-built unoccupied houses have shown that the ratios of emission rates at low and high ventilation rates decreased with decreasing compounds volatility (Hodgson et al., 2000). In poorly ventilated buildings, indoor concentration of VOCs was higher than outdoor concentration (Kim et al., 2001).

The effect of air velocity, temperature, and humidity of air on long-term VOC emissions from building products was studied by Wolkoff (1998). Ten different climate conditions were tested: four different air velocities from 1 cm/s to

9 cm/s, three different temperatures (23, 35, and 60 ^{0}C), two different levels of relative humidity (0% and 50% RH), and pure nitrogen instead of clean air supply. Primary source emissions were not affected by the air velocity after a few days to any great extent. Both the temperature and relative humidity affected the emission rates, but depended strongly on the type of building product and type of VOC.

It was shown by Volland et al. (2005) that the concentration of volatile and semivolatile organic compounds (VOC and SVOC) in indoor air is the result of a complex interaction of sources and the specific situations within a contaminated building – structural situations, room climate, ventilation habits and the season. Indoor air is a dynamic system; the parameters, which determine the concentration in indoor air are the source strength and the emission characteristics of the source. The source strength is a function of the diffusion potential and the vapor pressure of the pollutant/emitter and therefore a function of temperature and relative humidity. Besides this, the varying air exchange rates and ventilation habits influences the concentration of organic pollutants in indoor air.

Otson et al. (1998) studied the relationship between air exchange rate and indoor VOC levels. It is often assumed that the air quality is better in "leaky" than in airtight buildings. To test this anecdotal hypothesis, data from two Canadian surveys were examined. Indoor measurements of 28 VOCs were made by a passive sampling method during the 24- to 48-h study periods in both studies, and air exchange rates were detected by the perfluorocarbon tracer approach. The air exchange rates ranged between about 0.1 to 2.5 air changes per h in 54 test homes in the Greater Toronto Area (GTA). Other information on building age and construction, renovation activities, and occupant activities that potentially influenced indoor VOC concentrations in the homes was collected by means of a questionnaire. It was established that the relationship between the air exchange and indoor VOC concentrations is tenuous.

Interaction of VOCs with indoor materials was estimated by Meininghaus et al. (1999) who used a small-scale screening method. The investigators have used experimental set-up where indoor materials were placed as a membrane separating two air compartments. Both compartments, consisting of field and laboratory emission cells, were constantly flushed with air; one air stream contained a mixture of 20 VOC, and concentrations in both compartments were measured after 1 h. It was shown that ten materials usually covering extensive surfaces indoors were consecutively exposed to the vapor mixture at concentrations typically found in indoor environments. Under the experimental conditions, five of these materials exhibited a permeability high enough that VOC could be detected on the other side. VOC mass transport into and through indoor materials was confirmed by this experiment; the set-up allows quick screening of indoor materials with respect to their sorption capacity and permeability.

Different coated wood based products and furniture have been investigated by Jann and Wilke (1999) on the emission behavior of VOCs by means of different emission test chambers combined with an appropriate sampling and analyzing procedure. The effect of external parameters such as temperature, relative humidity, air exchange rate, loading rate, air velocity and clean air supply on the emission behavior of the materials and thus on the materials aging has been established.

The effect of environmental conditions on biocontaminants were studied by Black and Worthan (1999). Two environmental regimes were used normal conditions (70-75^{0}F and 40-60% relative humidity) and extreme conditions with elevated temperature and high humidity (80-90^{0}F, 85-95% relative humidity). Biocontaminants measured in carpets included fungi, bacteria, dust mite allergens, cat allergens, and cockroach allergens. Data indicated that carpet removed from the normal environment had no impact on the presence of airborne biocontaminants; that the carpet from the extreme environment and with visible surface mold could contribute fungi to the surrounding air, but did not contribute dust mite allergens or bacteria; that carpet cleaning efficiently removed biocontaminants from the carpet; and that the carpet cleaning processes themselves had little impact on pollutant levels in the surrounding indoor air. Data also indicated that proper control and maintenance of indoor environmental conditions and appropriate carpet maintenance can prevent significant biocontaminant growth in carpet.

An investigation of the emissions of VOCs from a floor adhesive and an acrylic latex caulk in an environmental test chamber where temperature, humidity, and air flow were controlled has shown the desirability of high air exchange rates during the application of caulks, adhesives, and other similar materials indoors. Increased ventilation causes rapid volatilization of organics and high emission rates, but the high air flow promotes reduced indoor concentrations of organics by dilution and increased air exchange (Tichenor and Mason, 1986).

Highly volatile organic compounds and HCHO were found as pollutants in indoor air of primary schools as well as in the schoolchildren's homes (preferentially children's rooms and bedrooms). Results showed that the HCHO concentration of the outdoor air was generally less than that of the indoor. In newer school buildings, contamination levels markedly exceeded the guide values of 0.1 ppm for class-rooms and for residential accommodation recommended by the Federal Health Office of Germany. Among the school rooms, the highest concentrations were registered in teachers' and secretaries' rooms, whereas the various gymnasiums had a low level contamination. Classrooms in the clean-air areas (mainly new school buildings) displayed higher contaminations of halogenated compounds than the classrooms in the older school buildings. It was shown that the children's rooms in single- and 2-family homes mostly displayed higher concentrations of hydrocarbons than children's rooms in multistory blocks of flats (Prucha et al., 1989).

The results of a field study of soil-gas transport of VOCs into a building at a site contaminated with gasoline were reported by Fischer et al. (1996). The authors have explained the appearance of a sharp gradient in soil-gas VOC concentrations between 0.1 and 0.7 m by a partial physical barrier to vertical transport in combination with microbial degradation. A careful attention to the identification and separation of physical and biotic effects must be paid.

The effects of dampness in newly built dwellings in Japan were studied in a series of works (Saijo et al., 2004, 2009; Takeda et al., 2009).

FATE AND TRANSPORT OF VOLATILE ORGANIC COMPOUNDS IN IDOOR AIR

The main problem phytoremediation of indoor air is minimization of VOCs emission through application of various ornamental plants. The principal stages of VOCs fate and transport include primary emission, sorption, sink-source behavior and secondary emissions of VOCs.

Sorption includes the action of either absorption or adsorption. Adsorption occurs when a VOC is trapped on solid with a large surface area, forming a molecular or atomic film. There are two types of adsorption (Oyama, 2000): the first (physical adsorption) means holding pollutant molecules in place in the pores by relatively weak physical attraction forces of a dipole or van der Waals nature; the second (chemical adsorption) is related to participation of chemical bonding forces.

Absorption is the incorporation of a substance in one state into another of a different state (e.g., liquids being absorbed by a solid or gases being absorbed by a liquid).

Sorption of VOCs

A review of Smith and Bristow (1994) offers an information about specifications, test methods, low emitting materials, and infinite sinks for textile products to determine the type and severity of problems and to find alternatives to improve indoor air quality. The following topics are discussed as primary emissions of VOCs, sink-source behavior and secondary emissions, biological factors, testing and modeling; human exposure assessed.

Building materials were found to be able strongly affect indoor air quality (Lee et al., 2005). It is necessary to mention especially porous building materials which are not only sources of indoor air pollutants such as VOCs but they are also strong sinks of these pollutants. The knowledge of VOC transfer mechanisms in these materials is an important step for controlling the indoor VOC concentration levels, and for determining the optimum ventilation requirements for acceptable indoor air quality. The authors investigated primary and secondary VOC source and sink behavior of porous building materials and proposed a new analytical model based on the fundamental theories of mass transfer mechanisms in porous materials. The proposed model was assessed with experimental data, namely emission tests of carpets and sorption tests of wood chipboard. The model presented in this paper can predict both primary and secondary VOC source (emission) or sink (sorption) behavior of porous building materials. Since the model considers diffusion and adsorption/desorption within the material, and convection over the material surface, the simulation using the model can readily provide the effects of material properties and airflow properties on the primary and/or the secondary behavior, hence, it can provide a better understanding on the mechanisms and to keep the indoor VOC concentration within a desirable level.

Such a natural product as biodiesel, a methanol trans-esterified product of rape seed oil, was proposed by Bay et al. (2006) to use as a high-boiling solvent well-suited for VOCs absorption. The main task of this investigation was to determine the type of biodiesel (winter biodiesel with volatile additives and summer biodiesel without volatile additives), molar mass and dilution activity coefficients using gas chromatography (GC) and headspace GC methods.

The activity coefficients of VOCs in different absorption media were determined by Weisweiler and Winterbauer (1995). It was shown that the molecular structure of a washing liquid is responsible for its absorption behavior.

The comparison of experimental investigation of fate and transport of nicotine emitted from either cigarette combustion or evaporation of liquid nicotine with several models based on possible nicotine interactions with the chamber was performed by Van Loy et al. (1996). Nicotine decay processes considered were first-order, irreversible deposition; second-order chemical decay; reversible linear sorption on chamber surfaces; reversible non-linear sorption with a surface catalyzed reaction; and fully irreversible sorption with limited surface sites. None of the tested models was fully consistent with experimental data. Clearly, nicotine interactions with indoor surfaces are very complex; available models are not adequate to properly describe physical and chemical processes which can occur.

Dynamic behavior in indoor air of semivolatile VOCs such as nicotine and phenanthrene with carpet and wallboard was studied by Van Loy et al. (2001). The sorption capacity of stainless steel was of similar magnitude for nicotine and phenanthrene. Sorption of nicotine on carpet and wallboard was much stronger, with equilibrium partitioning values 2-3 orders of magnitude higher. The sorption capacities of phenanthrene on carpet and wallboard were smaller, approximately 10-20% of the stainless steel values. Kinetic sorption parameters were determined by fitting a mass-balance model to the experimental results.

A review of Otson and Fellin (1992) is dedicated to principal problems of indoor air pollution by VOCs, particularly covering sources and emissions, including tobacco smoke, other combustion sources, building materials and furnishings, consumer products, and outdoor sources; source-occurrence relationship, including environmental tobacco smoke, HCHO, other building materials, furnishings, and human activities, and outdoor air. This review reflects also the fate of VOCs, including dilution and dispersion, sorption and deposition, transformations, and mathematical models.

As was shown by Hers et al. (2001), there is a soil vapor migration of VOCs into buildings that provokes potential inhalation exposure and risk to human health. The authors admit that soil vapor intrusion into buildings is complex, highly dependent on site-specific conditions, and may vary over time, complicating the interpretation of indoor air measurements. The problem how studies that use indoor air testing to assess subsurface risks could be improved is discussed.

The exposure of various materials (carpet, gypsum board, upholstery, vinyl and wood flooring, acoustic tiles, and fruit) to eight gaseous VOCs such as isopropanol, MTBE, cyclohexane, toluene, ethylbenzene, tetrachloroethene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene offered an information concerning the interactions between VOCs and indoor surface materials (Won et al., 2001). Dynamic responses in VOC concentrations were used to determine linear adsorption and desorption rate coefficients and equilibrium partition coefficients. Carpet was identified as the most significant sorptive sink for non-polar VOCs, while virgin gypsum board was observed to be a significant sink for highly polar VOCs. The effects of relative humidity on sorptive interactions between non-polar VOCs and indoor materials were studied.

The main objective of experiments that were conducted by Schlitt and Knoppel (1997) was to assess that fraction of VOCs released during the use of household products which is not vented but sorbed to indoor surface materials. Test chamber was used in which a liquid detergent for floors and tiles was applied and the compounds emitted and their concentrations determined. The impact of adsorption on the removal of VOCs from indoor air was established.

The measurements of adsorption on and desorption from wool carpet, nylon carpet, polyvinyl chloride (PVC) floor coverings, cotton curtain material and the empty chamber were conducted by Jorgensen et al.(1999); experiments were performed with α-pinene and toluene in concentrations of 160-300 $\mu g/m^3$. The ranking of the materials, with respect to their sorption capacity, was established: the adsorption of α-pinene was higher than the adsorption of toluene for all the materials. The experiments were carried out during both the adsorption and the desorption phase. Based on the results obtained, it can be recommended that sorption experiments should be performed as desorption phase experiments.

A VOCs sorption model with an arbitrary inlet concentration. is proposed by Deng et al. (2007). This model is based on the diffusion within the material and the mass transfer through the air boundary layer and uses Laplace transform and convolution theorem. Experimental results on VOCs sorption in an environmental chamber are in good agreement with the proposed model. The influences of model parameters such as the diffusion and the partition coefficients, and the rate of the adsorption have been investigated.

Three semi-empirical sorption models were compared with the experimental data that were obtained with 20 VOCs in a 50-m^3 room furnished with painted wallboard, carpet and cushion, draperies and furnishings by Singer et al. (2004). Results indicated that sorption usually didn’t greatly affect indoor concentrations of methyl-tert-Bu ether, 2-butanone, isoprene and benzene. In contrast, sorption appears to be a relevant indoor process for many of the VOCs studied, including C8-C10 aromatic hydrocarbons, terpenes, and pyridine. These compounds sorbed at rates close to typical residential air change rates and exhibited substantial sorptive partitioning at equillibrium. Polycyclic aromatic hydrocarbons, aromatic alcohols, ethenylpyridine and nicotine initially adsorbed to surfaces at rates of 1.5-6 h^{-1} and partitioned 95-99% in the sorbed phase at equillibrium.

A thermogravimetric analyzer was applied to measure three VOCs, toluene, 1,2-dichlorobenzene, and 1,1,1-trichloroethane, on polyacrylonitrile carpet fibers by Elkilani et al. (2003). Linear isotherms were observed in all cases with Henry coefficients values of 0.063-0.941 mm. Results of additional experiments conducted in a simple test chamber containing a single VOC source showed the carpet fibers acted as a significant sink causing a prolonged elevation of VOC concentrations in the air within the chamber. An unsteady-state model was proposed, which adequately described these adsorption and desorption phenomena occurring in the test chamber and yielded realistic values of adsorption and desorption rate constants.

A comparative analysis of existing sorption models is realized in review of Zhang et al. (2002). Existing sorption data can make it possible to understand better the phenomenon of VOC sorption on building materials better and to direct future research. There are two approaches in developing sorption models – the first one proposes first order adsorption/desorption rate models which are simple and easy to use, but it is necessary to obtain the model parameters from experimental data by curve fitting. The second approach is based on equilibrium interface models, which can be obtained through independent measurements, but lacking material property data and demands high computing costs. Experimental estimation of the sorption of VOCs on building materials is usually realized by the widely used small-scale chamber test method. It is necessary to take into account chemical properties of VOCs, physical properties of materials, and environmental conditions, such as temperature, humidity, and air velocity.

Two types of scale-up experiments were conducted to validate the surface sink model that was developed, based on small-scale chamber experiments (Won et al., 2001). It was demonstrated that adsorption and desorption by indoor surface materials can have significant impacts on the level of VOCs indoors. Authors indicated the conflicting results that were obtained from a large-scale laboratory experiment and a field test: the level of sorption in the field test was observed to be at least 9 times greater than was predicted by the surface sink model.

It was found that indoor materials can act as VOC buffers, reducing peak concentrations but prolonging the presence of compounds in air (Meininghaus et al., 2000). The impact of such processes as diffusion and sorption on indoor air quality is discussed. For some materials, effective diffusion coefficients were only 1 order of magnitude below that found in air. Two types of concrete showed a very high sorption capacity for Et acetate. Regarding gypsum board walls, it was concluded that diffusion through the material can contribute to reducing the room air concentration, especially at low ventilation rates. Results can be go into account during consideration of ventilation requirements in such rooms.

The paper of Schlitt and Knoppel (1997) is dedicated to the emission of VOCs mixture that is released during the use of household products; it is not vented but sorbed to indoor surface materials. The impact of adsorption on the removal of VOCs from indoor air has also been studied either in the chamber or in a real living environment (a small apartment (58 m^2) where the same VOC mixture was allowed to vaporize as in the chamber study. The adsorbed amount depended on the polarity and volatility of the individual compounds.

VOCs content and temporal kinetic of VOCs emission in 20 Kuwaiti houses was studied by Bouhamra and Elkilani (1999). 17 predominant compounds (benzene, toluene, xylene, styrene, trimethylbenzene, butylbenzene, propylbenzene, dichloroethylene, trichloroethane, dichloropropane, dibromomethane, chloroform, tetrachloroethane, tetrachloroethylene, chlorotoluene, dichlorobenzene, fluorobenzene) were identified. Related factors such as outdoor concentrations, surface area of walls and furnishings, and air exchange rates were incorporated in a transient mass balance model which also considered the phenomenon surface sorption and source emission. Surface sorption rate constants for each VOC under study were evaluated; they were 0.2-0.96 m/h depending on the VOC chemical nature. The experimental data correlated with developed model satisfactorily if the surface area for sorption was estimated not only on the surfaces of walls, ceiling and floor, but also those of all components of interior, such as those of furniture.

Three alternative, diffusion-limited mathematical models to account for the interaction of VOCs with indoor sinks was proposed by Dunn and Chen (1993). In such a way, diffusion mechanisms may play an important role in this interaction.

The paper of Meininghaus and Uhde (2002) performed experiments that underlined the important role of diffusion within materials during process of VOC adsorption by indoor materials that reduce peak concentrations; subsequent desorption will prolong the presence of a compound indoors.

Mixture of VOCS

The problem of sorption effects that were produced by combinations of indoor materials and VOCs have been investigated by Van Der Wal et al.(1998). It was shown that such parameters as the adsorption time, the desorption time, the concentration of the pollutants and the temperature had influence on the sorption.

Close agreement of experimental data that were obtained by placing samples of vinyl flooring inside a small stainless steel chamber and exposing them to absorption/desorption cycles of n-dodecane and phenol, and a developed model that predicts mass transfer between a flat slab of material and the well-mixed air within a chamber or room was found (Kumar and Little, 2003). A strategy to characterize the rate of absorption and desorption of VOCs by diffusion-controlled building materials was validated.

The sorption of single VOCs was compared to the sorption of the combination of the VOCs and the sorption of single material surfaces was compared to the sorption of the combination of material surfaces (Jorgensen and Bjorseth, 1999). The sorption compounds were α-pinene and toluene, and the material surfaces were wool carpet and nylon carpet. It was established that the presence of two chemical compounds at the same time gave correspondingly higher sorption compared to experiments with one compound at a time. The results indicated that the desorbed masses of individual compounds and the effect of combination of two materials were additive.

The process of VOCs sorption in residential rooms with furnishings and material surfaces just as in furnished chamber designed to simulate a residential room was studied by Singer et al. (2007). A mixture of VOCs was rapidly volatilized within each room. The 3-parameter sink-diffusion model provided acceptable fits for most compounds and the 4-parameter 2-sink model provided acceptable fits for the others. The purpose of the study was to develop and validate a microbalance set-up aimed at investigating VOC adsorption by indoor materials under controlled relative humidity at ambient pressure.

HEALTH EFFECTS AND TOXICITY OF VOLATILE ORGANIC COMPOUNDS

It was reported that industrial exposure to VOCs are generally ten to hundred times that of non-industrial home and office environment; home and office environments are typically two to one hundred times higher than that found outside. The most consistent effects of VOCs exposure in indoor air include irritation of the eyes, nose, and throat, headache, lightheadedness, nausea (Hess-Kosa, 2002).

In spite of relatively low concentration emission of VOCs can provoke sick building syndrome through the irritation of sensory systems, neurotoxic effects, skin irritation, nonspecific hypersensitivity reactions, odor and taste sensations (Godish, 2001).

Some of VOCs such as benzehe, styrene, tetrachloroethylene, 1,1,1,-trichloroethane, trichloroethylene, dichlorobenzene, methylene chloride, and chloroform can induce mutagenic or carcinogenic effects (Godish, 2001).

The most detailed list of possible health effects that are produced by VOCs is presented in the book “Indoor Air Quality. A comprehensive reference book” (1995) M. Maroni, B. Seifert, T. Lindall eds., Elsevier Science. The most potential effects of VOCs are irritation of eyes and respiratory tract, narcotic action and depression of the central nervous system. Many of VOCs are known as human or animal carcinogens. The other health effects are related with the affect of heart, kidney and liver.

The booklet "Indoor Air Package" that is intended for the health professionals (http://www.epa.gov/iaq/pubs/hpquide.html) confirms that VOCs emission in indoor air is responsible for rhinitis, epistaxis (associated especially with formaldehyde), pharyngitis, cough, wheezing, worsening, asthma, conjunctival irritation, headache or dizziness, lethargy, fatigue, malaise, nausea, voming, anorexia, cognitive impairment, personality change, rashes, myalgia (hypersensitivity pneumonitis, humidifier fever), hearing loss, allergic skin reaction.

Many volatile organic compounds are readily absorbed into our bodies, the effects of which have not been elucidated. It is known that inadequate indoor air quality can result in "multiple chemical sensitivity", "new house syndrome", and "sick building syndrome" (Ando, 2002; Shinohara et al., 2004) and a cross-section of physical symptoms for those exposed (e.g., allergies, frequent fatigue, asthma, headache, a feeling of uneasiness) that negatively affect their "quality of life" (Hayashi et al., 2004; Ingrosso, 2002; Kostiainen, 1995). For example, 2-ethyl-1-hexanol in the 2-32 $\mu g \cdot m^{-3}$ concentration range is associated with "sick building syndrome" which can cause asthma in humans (Norbäck et al., 2000).

Allergy. From: allergy.immunodefence.com

Asthma. From: walgreens.com

Let's discuss the results of scientific investigations of health effects of VOCs in indoor air.

The concentration of total volatile organic compounds (TVOCs) determine the human response: concentration of TVOCs < 0.20 mg/m^3 is found to be comfortable; the range 0.20-3.00 mg/m^3 means the irritation; the range 3.00-25.00 mg/m^3 is acutely uncomfortable; concentrations > 25.00 mg/m^3 correspond to toxic action on human organism (Hunter and Oyama, 2000).

It was investigated that the indoor environment, particularly at home, has been recognized as a major source of exposure to allergens and toxic chemical. Some evidence of a link between the indoor environment and asthma was found by Richardson et al. (2005), who discusses reasonable evidence for one causative factor for asthma in the indoor environment - house dust mite allergen. Asthma results usually when VOCs cause hyperactivity of the airways with narrowing of the air passages; the person feels a tightening sensation of the chest and breathing difficulties associated with coughing and wheezing (Hess-Kosa, 2002).

The respiratory effects of VOCs were studied by Pappas et al. (2000). The main authors' conclusion is that VOCs have been implicated as causative agents in asthma and building-related illness. VOC exposures caused dose-related increases in lower respiratory, upper respiratory, and non-respiratory symptoms, with no significant change in lung function.

Since 1993, the New York State Department of Health, funded by the Agency for Toxic Substances and Disease Registry, has collected data about the effects non-petroleum hazardous substances **(**Welles et al., 2004). The chemical categories most frequently associated with events, and with events with adverse health effects were VOCs. The most frequently reported adverse health effects were respiratory irritation, headache, and nausea or vomiting.

The nature of the VOCs that are ubiquitous in indoor environment and the evidence for adverse health effects associated with exposure to some of these compounds are discussed in the review of Rumchev et al. (2007). The main conclusion is that the indoor environment can be of crucial importance because modem society spends most of their time indoors, and exposure to VOCs may result in a spectrum of illnesses ranging from mild, such as irritation, to very severe effects, including cancer.

The combined toxicity of gaseous mixture of dominant VOCs (formaldehyde, benzene, methylbenzene, dimethylbenzene, ethylbenzene) and ammonia in indoor air of newly decorated rooms was investigated by Ou et al. (2004). The Kunming mice were used as test-objects. It was shown that the gaseous mixture prepared in this study showed adverse effects on blood, liver, heart and lung of mice, especially sensitive for female mice. Reticulocute count could be used as a sensitive index reflecting the damage induced by the toxicity of air mixture.

A review of Beall and Ulsamer (1981) is dedicated to the problem of health hazard of indoor air pollution by toxic volatile organic compounds, solvents, polymer compound, pesticides, aldehydes.

The empirical equations were elaborated to relate the toxicity of various types of VOCs (hydrocarbons, esters, ketones, alcohols, and several others) were proposed by Lyublina and Rabotnikova (1971).

It is shown in review of Zhu et al. (2007) that many kinds of VOCs exist in the indoor air and the chemical reaction occurs among the pollutants when O_3 and NO_2 exist simultaneously. This reaction can severely impact the indoor air quality and produce some adverse effects on human health.

Effects of combustion products, passive smoking, VOC, formaldehyde, indoor microbes on the people's health were analyzed (Qian and Dai, 2006). Causes of leukemia and "sick building syndrome" were discussed. It was indicated that owing to the decoration material industrial sector not well managed as well as related laws and regulations not complete in China, the quality of construction materials is generally inferior to consist with the rapid economic development. In addition, regional protectionism and slack enforcement of laws have resulted in the indoor air pollution as a critical problem to seriously harm the human health.

Sick building syndrome is discussed with laws and regulations, pollutant chemical concentrations, immunological studies, and case studies (Takigawa, 2006).

VOCs were sampled in buildings where people with non-specific building-related symptoms perceive health problems and in buildings where they do not (Sunesson et al., 2006). The obtained VOC data was evaluated using multivariate methods, to investigate possible systematic differences in air quality of “problem” and “non-problem” buildings. It was shown that that air samples of the two groups of building were chemically different.

The influence of a typical indoor contaminant burden on the development of allergies and upper respiratory tract infections in children with an allergy-risk was studied by Rolle-Kampczyk et al. (2005). During this investigation typical tobacco smoke related indoor VOCs as well as excretion of certain VOC metabolites in urine were measured. It was established that residences with a high burden of passive smoking showed higher benzene concentrations than nonsmoking ones. That’s why significant differences between the excretion of VOC metabolites could be found between passive smoking and unburdened children. Exposure to increased concentration of toluene provoked atopic symptoms like eczema which was found to be associated with the excretion of the VOC metabolite of toluene S-benzyl-mercapturic acid.

A total 350 adults from 224 flats with decorated indoor have undergone health examination (Liu et al., 2005). It was shown that 107 members of 350 (30.57%) have demonstrated vary symptoms, which largely with nervous system symptom. These symptoms as well concentration of formaldehyde and VOCs decreased with the time passed after decoration of the flats. Authors proposed to use opening the windows and ventilation as means of decreasing the effect of VOCs on human health.

O total 200 newly decorated apartments were investigated from the point of view the effect of inhalated VOCs and housing decoration. Indoor concentrations of formaldehyde, BTEX-compounds and TVOC were measured in typical apartments, offices, houses where decoration and painting occurred (Gao et al., 2006). Results showed that the percentages of people who had different discomfortable symptoms in the workers in the painting workshop were higher than that in common people. More of the people living in the houses newly decorated for two years felt the unpleasant smell compared with the people whose houses had been decorated for more than two years. The main conclusion is that it is necessary to pay more attention to the pollution of VOCs in newly decorated houses.

It was concluded that blood levels of VOCs may be more indicative of personal exposures than are air concentrations; no studies have addressed their relationship with respiratory outcomes (Elliott et al., 2006). The problem was studied whether concentrations of 11 VOCs that were commonly identified in blood from a sample of the U.S. population (953 adult participants 20-59 years of age) were associated with pulmonary function. After adjustment for smoking, only 1,4-dichlorobenzene (1,4-DCB) was associated with reduced pulmonary function; exposure to this VOC related to the use of air fresheners, toilet bowl deodorants, and mothballs, at levels found in the U.S. general population, may result in reduced pulmonary function.

Analysis of VOCs and semi-VOCs emitted from varnishes based on acrylic and alkyd resin has shown that they showed a very pronounced decay behavior which was not complete after 28 days, but releases were no longer measurable after 90 days; none of tested varnishes released persistently toxic substances (Wensing et al., 2006).

The effect of various VOCs such as benzene, toluene, ethylbenzene, xylenes, and styrene (BTEX) on indoor air quality of typical photocopy centers in Taiwan was studied by Lee et al. (2006). All photocopy centers in this study had a lifetime cancer risk which was related to the high level of benzene.

The group of investigators (Fiedler et al., 2005) tested the health effects among women of controlled exposures to VOCs, with and without O_3, and psychological stress. Health effects measured before, during, and after each 140-min exposure. Mixing VOCs with O_3 was shown to produce irritating compounds including aldehydes, hydrogen peroxide, organic acids, secondary organic aerosols, and ultrafine particles. Exposure to VOCs with and without O_3 did not result in significant subjective or objective health effects. Stress appeared to be a more significant factor than chemical exposures.

The relationship between an unusual combination of indoor air contaminants in a school and adverse health outcomes such as respiratory irritation, asthmatic symptoms, eye and general symptoms, and increased occurrence of common viral respiratory infections among the attending children was established by Putus et al. (2004). A leaking roof and damp floors, together with gaseous leaks from the sewage system, led to a combined exposure of hydrocarbons, 2-ethylhexanol from plastic floor coverings, and moisture-associated microbes. Chemical contaminants from the sewer system and damp construction materials were identified as the source of the problem. Authors concluded that remediation of the school building improved the indoor air quality and the health status of the children.

The effect of indoor pollutants on the health condition of old people, between the ages of 60 and 95 years, living close to Paris in a social collective habitat was investigated (Coelho et al., 2005). Among the main ways that old people are exposed to pollutants are difficulty in maintaining the residence, preference for staying in the kitchens, substantial use of cleaning chemicals. But the principal risk for health status of old people is provoked by poor ventilation.

The Committee for Health Evaluation of Building Products has developed test criteria and an evaluation scheme for VOC emissions from building products suitable for indoor usage (Daeumling et al., 2005). The evaluation scheme sets quality standards relevant to health for future production of building products for use indoors and fosters the development of particularly low-emission products.

Humans may be long-term exposed to complex VOC mixtures via indoor air. The review of Hepfner et al. (2005) reflects the problem of toxicity, especially with the genotoxicity of C4-9-aldehydes, particularly hexanal and nonanal, butanal, pentanal, heptanal and octanal that have been found in indoor air. Sources of C4-9-aldehydes are burning processes, environmental tobacco smoke, surface coatings, floor coverings, laying materials, wood and wood-based materials, various consumer products etc. It was shown that data on the toxicity, genotoxicity and carcinogenicity of C4-9-aldehydes are either scarce or unavailable. The present state of knowledge demands further biological studies.

A review of Zhao and Jin (2004) considers the source, variety, and adverse impact to people's health of VOCs.

The discussion includes countermeasures against sick school, e.g. hypersensitivity caused by VOC (Uchiyama, 2004).

Data collected from 170 homes within the Avon Longitudinal Study of Parents and Children determined which household products were associated with highest TVOC concentrations (Farrow et al., 2003). These data were collected over a period approximating 6 months of pregnancy and the first 6 months of infant life. Higher TVOC concentrations were associated with air freshener and aerosol use. Infant diarrhea and earache were statistically significantly associated with air freshener use; diarrhea and vomiting - with aerosol use. Headache experienced by mothers 8 months after birth was significantly associated with air freshener and aerosol use; maternal depression - with air freshener use. Results suggested a link between using products which increase indoor TVOC concentrations and an increased risk of certain symptoms among infants and mothers.

Total VOCs and formaldehyde are among typical indoor pollutants that was found in schools; these compounds are responsible for commonly reported building-related health symptoms (Daisey et al., 2003).

Indoor air quality in a Canadian elementary school is discussed by Probert et al. (2000). It is proposed that health and education officials must work together to address environmental health concerns in schools demonstrating leadership and commitment to improve children's education, health, and well being.

A study of total MVOC emission for strongly molded flats shown that no health risk due to MVOC was found (Schuchardt et al., 2001). The health risk caused by other mold products like spores and toxins is discussed.

It was determined 21 VOCs in the environmental tobacco smoke (ETS), that is suspected to be a major source of exposure to many of the compounds identified as toxic air contaminants (Daisey et al., 1998). The variabilities in the ETS emission factors among six brands of cigarettes were relatively small. The concentrations of most of the VOCs did not change over the 4-hours periods of the experiments, while concentrations of 3-ethenylpyridine, phenol, o-cresol, and m,p-cresol showed consistent decreases over time, indicating removal by means other than the very low air infiltration rate, e.g., deposition onto the chamber surfaces.

The review of Daisey et al. (2003) is dedicated to a number of indoor air quality problems in schools; the causal relationships between pollutant exposures and health symptoms were studied. Low HCHO concentrations possibly increased risks for allergen sensitivities, chronic irritation, and cancer. Authors have suggested that health symptoms in schools were related to exposures to VOCs, molds and microbial VOCs, and allergens.

The search of Cooper et al. (1995) showed that many of the VOCs possess toxic properties when studied at acute, relatively high-level exposures. Toxic effects were reported also for a few of the chemicals, such as benzaldehyde, α-terpineol, benzyl acetate, and ethanol, at relatively low dose levels of 9-14 mg/kg. In order to understand the effect of chronic, low-level exposures, validated analytical methods for the quantitative characterization of polar organic compounds at low concentrations will be required to make such work possible. The main conclusions are the following: better criteria are needed to study emission of substances into the indoor environment, adequacy of ventilation, additive or synergistic effects of mixtures of chemicals and toxicity of microorganism decomposition products; objective clinical tests to assess the effects of indoor pollutants on health and indices for Indoor Environmental Quality in assessing buildings need to be improved.

Some important problems connected with methods of analysis of VOCs from building materials, determination of their emission rates, especially under high-temperature exposure from computer and inside car compartments are discussed in a review of Isagawa et al. (2004)

Up to 60 million people working indoors are suffered with eye, nose and throat irritation, headache and fatigue (Anderson et al., 2007). The principal cause of these symptoms are VOC emitted from building materials, cleaning formulations, or other consumer products. In addition, new compounds (glyoxal, methylglyoxal, glycolaldehyde, diacetyl) appeared as the result of VOCs reactions with OH^- or NO_3^- radicals or O_3 in indoor environments. Experimental and computed identification of these compounds as sensitizers may help explain some health effects associated with indoor air complaints.

A review of Rumchev et al. (2007) confirmed the thesis that modern society spends most of their time indoors, and exposure to VOCs may result in a spectrum of illnesses ranging from mild, such as irritation, to very severe effects, including cancer.

Qualitative and quantitative evaluation of VOCs emission from wood and wood-based materials that commonly used in furniture, interior furnishings, and building products in Denmark, just as irritative and toxicological effects of VOCs is described by Jensen et al. (2001).

A review of Leslie (2000) concerning health risks from indoor air pollutants is related to public alarm and toxicological reality. Authors discuss biological pollutants such as bacteria, non-biological pollutants like VOCs, O_3 and combustion products, and the means of health risks amelioration.

It is known that indoor air pollution plays an important part in developing sensitization to and triggering of respiratory disease symptoms. The studies of Stewart et al.(2000) examined the effect of exposure of children from ages 4 to 15 years to a number of indoor chemical pollutants such as respirable suspended particulate [$PM_{2.5}$], environmental tobacco smoke, VOCs and formaldehyde, NO_x, house dust mite allergen, presence of visible or measurable moisture, and mold and fungal allergens. In addition, temperature and humidity were monitored to assess their role in the expression of asthma in young children.

VOCs play a significant role as causative agents in asthma and building-related illness (Pappas et al., 2000). To determine whether a mixture of VOCs could impair lung function or cause airway inflammation among subjects without bronchial hyper-responsiveness, the authors conducted a series of experiments with controlled VOCs exposures to filtered air. It was concluded that reducing VOC concentrations to substantially <25 mg/m^3 is required if a non-irritating work environment is desired.

Analysis of chlorinated hydrocarbons and volatile aromatic hydrocarbons in indoor air showed that most citizens were likely to have exposure, at nearly the same levels of official regulations, with these hazardous substances as carcinogens, not outside but inside living places (Tamakawa et al., 1997). Possible sources including so-called fun-heater (petroleum stove), dry-cleaned clothes, moss repellent cakes, manicure materials, and bleaching agents were discussed.

Formaldehyde is known to be one of hazardous pollutant (Jacukowicz-Sobala and Kociolek-Balawejder, 2006). It causes, even at low exposure levels, burning sensations in the eyes, nose, and throat, and contributes to sick house syndrome. Long-term exposure induces sensitization to formaldehyde, which may develop into an allergic reaction. According to the toxicity and exposure levels of formaldehyde, it is necessary to take measures to reduce formaldehyde concentrations in indoor air. There are some simple ways of limiting its emission, i.e., buying wood products, furniture, and decorating materials with low formaldehyde content, ensuring adequate ventilation, temperature moderation, and reduction of humidity levels. Some general methods of air purification are proposed such as adsorption of formaldehyde on activated carbon or other adsorbents with functional groups reactive to formaldehyde (usually primary and secondary amine groups), and an alternative technique, oxidation, including heterogeneous catalytic oxidation with air, photocatalytic degradation, and oxidation of formaldehyde using potassium permanganate filters.

It is necessary to mention a very interesting approach to estimate the relationship between indoor environmental factors in newly built dwellings and sick building syndrome (SBS) which was proposed by Japanese scientists (Takeda et al., 2009; Saijo et al., 2004, 2009). The symptoms of SBS were surveyed by standardized questionnaires which were distributed among the occupants of the dwellings. The following typical characteristics of the residents were controlled: age, gender, smoking status, history of allergy disease, pets at home, time spent in the dwellings and size of the household (Saijo et asl., 2004); occupation (full-time or part-time, retired or unemployed) (Saijo et al., 2009). The principal characteristics of the dwelling included: structure of dwelling (wooden, reinforced concrete, steel-reinforced concrete), age of dwelling, renovation of dwelling over the past two years, wooden flooring, wall materials, dampness, pet in dwelling, presence of smokers, use of room fragrance and insect repellents (Takeda et al., 2009). The questionnaire contained the questions about the medical history of the occupants (asthma or allergies), general symptoms (fatigue, feeling heavy-headed, headache, nausea/dizziness); eye symptoms (itching, burning or irritation of the eye); nasal symptoms (irritated, stuffy or runny nose); throat and respiratory symptoms (hoarse, dry throat, cough), skin symptoms (Takeda et al., 2009).

METHODS OF SAMPLING AND ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

All the methods of VOCs analysis consist of such principal stages:
1) sampling (sample trapping from the air and collection); 2) sample preconcentration and enriching; 3) removal of VOCs from air sample to the analytical device; 4) detection and identification of VOCs.

Sampling and Preconcentration

There are two methods of sampling – active sampling that is based on application of actively drawing air through a sorbent device, and passive sampling that realized the process of diffusion of the sample due to concentration gradient (Organic Indoor Air Pollutants, 1999).

A sorbent is a material used to adsorb VOCs. Preliminary sample enriching permits to achieve the required sensitivity and selectivity of the analytical device. The most preferable method for enriching VOCs is application of *solid sorbents*. There are three main types of solid sorbents such as *inorganic sorbents*, *porous* *materials* based on carbon, and *organic polymers*. Comparative analysis of solid sorbents is proposed by Uhde (1999) (In: Organic Indoor Air Pollutants, 1999). VOCs can be tested by carbon based sorbents (activated charcoal, carbon molecular sieves, graphitized carbon black) and porous polymers (styrene polymers and phenyl-phenylene oxide polymers).

Removal of VOCs sample from the sorbent

The principal ways to remove the sample from the sorbent are thermal desorption and solvent extraction. *Thermal desorption* means utilization of heat to increase the volatility of compound that is analyzed and to transfer it from the sorbent to analytical device. *Solvent extraction* is a methods that makes it possible to separate compounds on the basis of their different solubilities in water and organic solvent.

Two carbon based solid sorbents such as carbon molecular sieve and coconut shell activated carbon were studied at 38 private houses (Tsuji et al., 2005) in Kanagawa prefecture, Japan. A conventional GC/MS system and an active air sampling system with a suction pump (100 mL/min), as the standard analytical procedure was used.

The dual-column configuration that consisted diffusive (passive) samplers was proposed (Begerow et al., 1996). The VOCs were adsorbed onto charcoal during a four-week sampling period and subsequently desorbed with carbon disulfide. After injection, using a cold split-splitless injector, the mobile phase was split via a Y-connector and led onto two capillary columns of different polarity switched in parallel. Such a system provided additional information about the VOC components that can be obtained for verification purposes. Detection was in both cases performed by connecting each column with tandem non-destructive electron-capture detector (ECD) and flame ionization detector (FID) switched in series. By this procedure sensitivity is increased because no effluent splitting was required.

A simple sampling method and a highly sensitive analytical method which are based on application of a passive sampling-thermal desorption-GC/MS system was used by Kobayashi et al. (2003), for the detection of VOCs in indoor air. Diffusive uptake rates of such compounds as carbon tetrachloride, trichloroethylene, toluene, tetrachloroethylene, ethylbenzene, m,p-xylene, o-xylene, styrene and p-dichlorobenzene, were calculated from the results of simultaneous measurement by passive and active sampler indoors and outdoors. It was shown that the concentrations of toluene, ethylbenzene, o-xylene and m, p-xylene were significantly higher in newly built house and renovated house.

Aromatic hydrocarbons emitted from various building materials, such as medium-density fiberboard, particleboard (PB) and wood-based flooring (laminate flooring and engineered flooring) were studied with portable gas-chromatograph which is designed to measure certain aromatic compounds in indoor air. Compounds separated through the column were detected by a semiconductor gas sensor and the concentration of the target compounds automatically calculated and shown (Kim et al., 2006).

The small chamber method was used to study the emission of VOCs in different indoor environments (Wolkoff, 1990). It was found that VOC emissions detected by small chamber method were strongly depended upon the wood species and the type of product; the concentration of VOC depended upon other factors such as time of the day, age of the building, activities and(or) number of persons, position of measurement, and the temperature.

The application of small chamber method to the analysis of VOCs emitted from the grain surface of 36 leathers made it possible to establish types, concentration and attenuation of the emission rate of VOCs (Kita, 2005).

Sorbent tubes for sampling of gases and vapors including types of adsorbents, the adsorption process (humidity effects and multicomponent systems), and the desorption process (thermal desorption and solvent desorption) are described in review of Quintana et al. (1992).

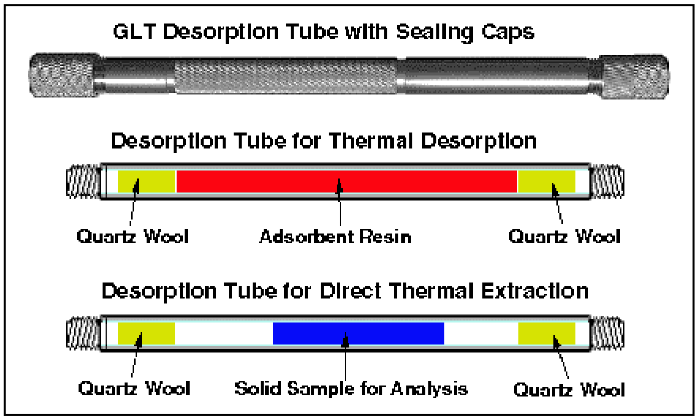
A review of Uhde (1999) is dedicated to solid sorbents as a convenient mean to enrich the contents of VOCs from indoor air. Properties of some solid sorbents, comparison of active vs passive sampling for collecting of air samples, thermal desorption vs solvent extraction for removing the sample from the sorbent, breakthrough volatiles, water affinity in GC/MS chromatograms, as well as degradation products and sorbent background are discussed.

The use of sorbents has been proposed to remove VOC present in ambient air at concentrations in the parts-per-billion (ppb) range performance of sorbent materials, is described (Scahill et al., 2004). High efficiency of this method is achieved by increasing the challenge gas flow rate: sorbent bed mass ratio and decreasing both the in-bed sorbent mass and sorbent particle size. The method can be used to screen sorbent materials VOC removal from indoor air applications.

Study of sorptive properties of trap systems for selective enrichment of VOCs from tobacco smoke samples was performed by Buszewski et al. (2008). The procedure of sampling and sample preparation for analysis of highly volatile compounds (VOC) and their derivatives such as ethylene, propylene, acetaldehyde and acetone is the most difficult stage of VOCs detection. For this purpose single- and multibed sorbent tubes were prepared, filled with the following materials: Tenax TA, Carbotrap, Carbopack C, Carbosieve SIII, Carboxen 569. Sorbent traps were also used to detect selected VOC (acetone, acetaldehyde, 2-butanone, benzene, toluene, m,p-xylene) in gas phase of tobacco smoke from single cigarette.

Sampling and analysis of the chamber air was done by Tenax/Thermal desorption followed by analysis with GC/MS (Jann et al., 1999). Different coated wood based products and furniture have been investigated on their emission behavior of VOCs by means of different emission test chambers combined with an appropriate sampling and analyzing procedure. It was possible to detect the concentration lapse for a large spectrum of compounds over a wide range of volatility down to concentrations. of 1 µg/m^3.

The emission behavior of VOC of different hardcopy devices in combination with suitable air sampling and analytical procedures was investigated in different emission test chambers (2 different 1-m^3-chambers and one 20-m^3-chamber). Air sampling and analysis for VOC were done by Tenax TA and subsequent thermal desorption (TDS) in connection with GC/MS (Jann et al., 2003).



Tenax TA. From: http://www.sisweb.com/art/sptd/tube5.gif

It was shown that the reproducibility of the analytical method based on the activated C capture sampling-GC-MS analysis of the VOC in 1-100 µg/m^3 concentration range is good (Yoshida, 2002).

Determination of VOCs samples in indoor air of new houses by thermal desorption-GC/MS system after collections by both air toxics tube-pump method and Carbopack B tube-diffusion method is described by Mori et al. (1997).

The application of the technique of preconcentrator-GC-MS provided rapid measurement method for the detection of hazard VOCs from indoors air (Wang et al., 2001).

A thermal desorption/GC-MS method using Tenax and Carbotrap multisorbent cartridges for the detection of 28 target VOCs is described by Heavner et al. (1992). Techniques used for method validation include detection of limit of detection, limit of quantitation, repeatability, room temperature storage stability, breakthrough volume, and sampler collection efficiency.

Different methods of detecting VOCs and SVOCs in indoor air including preconcentration by solvent desorption and thermodesorption are presented by Hansen (1997).

Twenty-eight VOCs were either adsorbed passively or actively, desorbed with CO_2 or with the newly developed thermal desorption method (Hallama et al., 1997). The main conclusion of the authors is that thermal desorption was more convenient and yielded better results in many cases, especially in combination with passive sampling of volatile solvents.

A method of thermal desorption-gas chromatography for detection of VOCs such as halogenated hydrocarbons, esters and aldehydes in indoor air was applied by Liu et al. (2006). The average concentrations and temporal behavior of VOCs was studied.

Thirty compounds (mainly benzene, toluene, and xylenes) were identified by the combination of gas chromatography and electron impact mass spectroscopy for monitoring and analysis of indoor air (Bo and Chen, 2005).

The method, that canister sampling followed by condensation by liquid nitrogen and GC-MS analysis was used as a standard method for hazardous air pollutants, is suitable for indoor air investigation (Zheng et al., 2002).

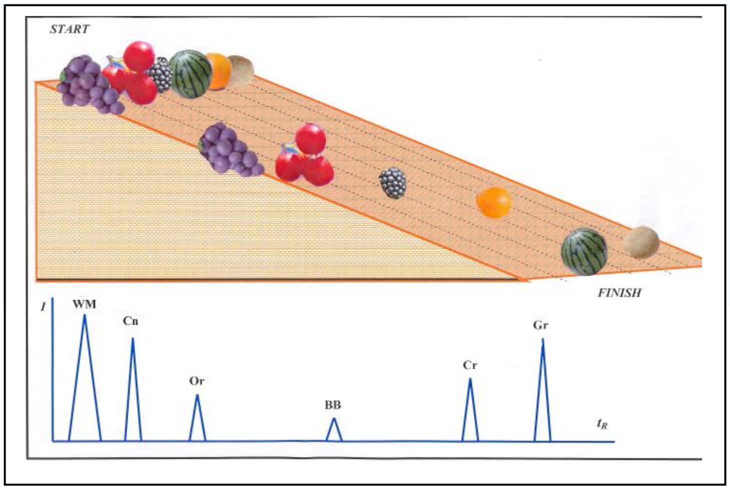
Solid-phase microextraction (SPME), as a simple and solvent-free new method, that is applied to the analysis of VOCs in indoor environments which can affect the health and well-being of inhabitants (Yuan et al., 2001). A SPME fiber coated with an extracting phase, liquid or solid, was used. This method is fast and simple, it can be used without solvents and is charactarised with high sensitivity. The analysis was carried out using gas chromatograph equipped with mass spectrometer detector.

VOC emission of several selected liquid-based consumer products have been studied in static chambers (Zhu and Cao, 2000). These measurements were based on the hypothesis that the concentration of VOC in the static chamber increases linearly over time when the concentration in the chamber air is significantly lower than the surface concentration of the emission source. VOCs in the chamber were collected using passive samplers and detected by solvent extraction and GC-MS analysis.

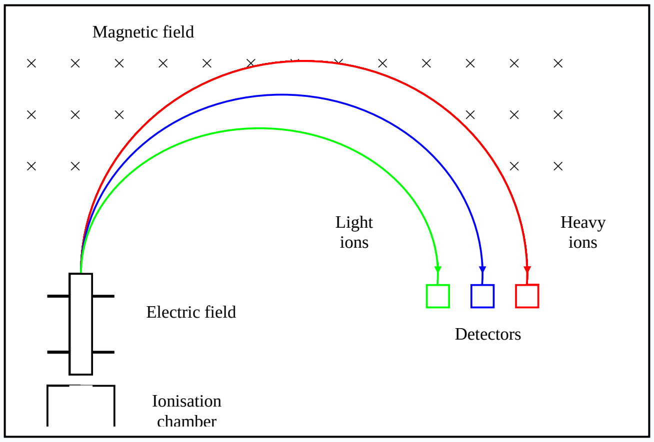
Emissions in grease-laden cooking operations exhaust was studied by Welch and Norbeck (1998). Sampling and analytical techniques were integrated with standard test methods specifying appliance operation, cooking procedures, and ventilation parameters.

Gas Chromatography and Mass Spectrometry

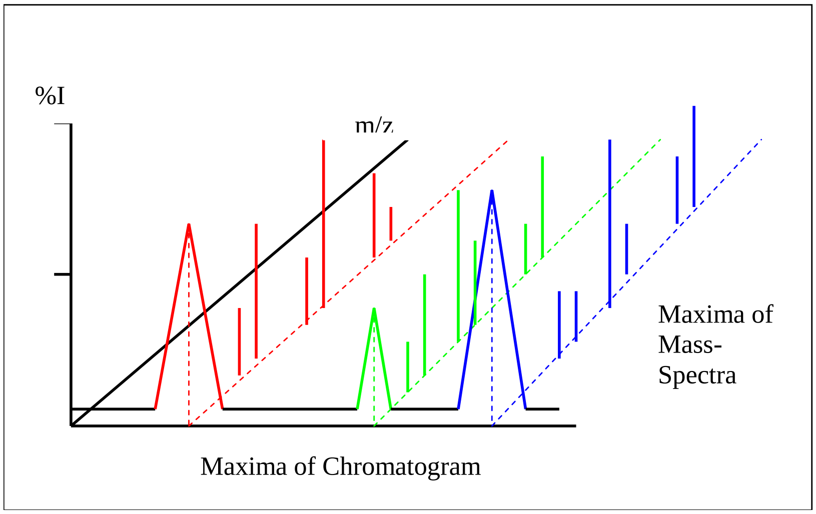
Gas Chromatography (GC) is analytical techniques that is based on vaporization of the sample and separation of mixtures due to passing a mixture dissolved in a mobile phase through a stationary phase. Each component of the mixture can be presented as spectral peak in the chromatogram spectrum.



Mass spectrometry is an analytical technique that measures the mass-to-charge ratio of charged particles that are accelerated by the electric field and are separated according to their masses and charges in a magnetic field.



Gas chromatography-mass spectrometry (GC/MS) is a combination of gas chromatography and mass spectrometry methods which is used to identify different substances within a test sample. This method is effective in separation of compounds into various components and identification of specific substances.



GC-MS method was used for simultaneous detection of semi-volatile organic compounds (SVOC) in indoor air (Yoshida et al., 2004). The selected 73 SVOC were collected using combined adsorbents (quartz fiber filter disk and Empore disk). Forty compounds (19 plasticizers and flame retardants, 19 insecticides, 1 synergist, 1 fungicide) were detected accurately and precisely.

GC-MS System. From: http://www.gmu.edu/departments/SRIF/tutorial/gcd/gc-ms2.htm

Single ion mass chromatography is based on the application of a small mass window for detection of a very specific mass while other masses are ignored. A method of identification and quantification at a level of 0.3 μg/m^3 using systematic single-ion chromatograms (SICs) was developed by Tsuchiya et al. (1996). Air samples were taken in 3-layered sorbent tubes (glass beads, Tenax TA, Ambersorb XE-340) and trapped compounds were thermally desorbed into the helium stream of a gas chromatograph/mass spectrometer (GC/MS) analytical system. Total quantities of VOCs were measured using a flame ionization detector (FID). Individual compounds were analyzed by a GC/MS. For the identification of compounds in the main stream GC effluent, both the specific GC retention and mass spectra were used.

Analysis of the VOCs and HCHO concentrations in indoor air and personal exposure level that was carried out with GC-MS/SIM and HLPC is described by Dai et al. (2005). It was shown that the pollution level of VOCs in indoor air with newly-fitment and newly-built was the highest, later rapidly drop down to indoor air quantity standard value after 3 months.

Electron Impact is one of the ionization method in mass spectrometry. An air sample is introduced into the electron ionization source where the collision of the sample molecules with high energy (about 70 eV) electrons takes place. Accelerated sample ions are focused to the mass analyzer. Combination of electron ionization and mass spectrometry provides useful information about the structure elucidation of small organic molecules. The combination of electron impact mass spectroscop**y** and gas chromatography was used for monitoring and analysis of indoor air during painting for arenes and VOCs (Bo and Chen, 2005). An air sample was taken for the detection of arenes (mainly benzene, toluene, and xylenes), and the volatile gaseous mixture above the paint-diluent was taken for the analysis of VOCs. The detection limits of arenes in air samples were in the range of 0.1 to 0.2 ng.

The comparative analysis of the application of three methods of VOCs analysis such as a flame-ionization-detector (FID) method, a gas chromatography/mass spectrometry (GC/MS) method, and a method employing a photoacoustic infrared (IR) gas monitor in laboratory and field conditions is proposed in the review of Hodgson (1995).

GC-MS method was applied for investigation on the emission levels of VOCs from surfaces of furniture elements, both in the course of finishing processes and during ordinary utilization of finished products (Stachowiak-Wencek and Pradzynski, 2005).

The problem of sampling workplace atmospheres for VOCs is discussed by Hey (2007). When resources are available, VOC analysis may be performed at the site using sophisticated field analytical equipment, but this equipment is costly and difficult to maintain in defensible analytical calibration. Alternatively, the atmosphere may simply be sampled and the samples sent to the laboratory for analysis. Such field sampling is typical and may occur in one of two modes: the capture of whole-air samples using evacuated canisters, or the capture of the VOC contaminants only using sorbent tubes. Both methods of atmosphere sampling are used frequently. There are, however, significant common factors between these two analytical systems, namely: the use of a gas chromatograph, the use of a mass selective detector, the need for internal and calibration standards, and a quality assurance protocol procedure. It seems that a single procedure and analytical system that can accommodate both sample modes would be useful.

The application of static chamber is based on the assumption that the concentration in the static chamber increases linearly over time when the concentration in the chamber air is significantly lower than the surface concentration of the emission source. Thus, VOCs emission factors can be detected by their concentrations in static chambers (Zhu and Cao, 2000). In this method, VOCs in the chamber air were collected using passive samplers and detected by solvent extraction and GC-MS method. Emission factors of seven selected liquid-based consumer products have been detected.

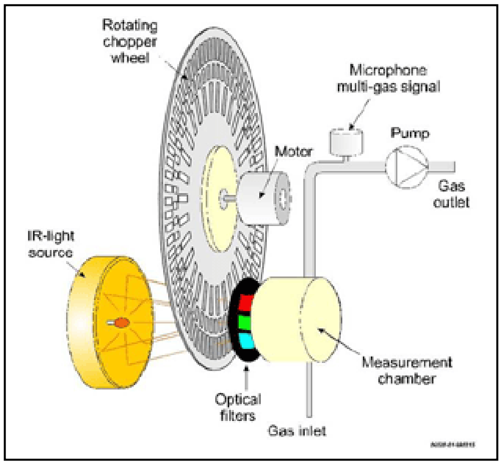
Flame Ionization Detector (FID) is a techniques that is applied for analysis materials coming off gas chromatography column. The source of ionization is hydrogen-air flame that burns such a temperature that is enough to pyrolyze organic compounds and produce charged ions. These ions are attracted to the collector and induce electric current which corresponds to the proportion of reduced carbon atoms in the flame. Usually this method is provides the analysis of hydrocarbons.

Photoionization Detector (PID)

PID is a gas detector that uses the source of ultraviolet radiation to break molecules to positively charged ions that can be counted by detector. The sensitivity of such a detector is 1-10,000 ppm.

Photoacoustic Spectroscopy

This method is based on the irradiation of the sample with light (laser) beam of light which induces local heating and thus a pressure wave from the sample. By measuring dependence of pressure of the sample on the wavelength a photoacoustic spectrum of a sample can be recorded that can be used to identify the absorbing components of the sample.



Principles of photoacoustic spectroscopy. From: lumasenseinc.com

Sensitive and selective detection of certain VOCs in a patient's breath could enable the diagnosis of diseases that are very difficult to diagnose with contemporary techniques. For instance, an appropriate VOC biomarker for early-stage bronchial carcinoma (lung cancer) is n-butane (C_4H_{10}). A new optical detection method of VOCs detection was proposed by (Wolff et al., 2005). This method that is based on photoacoustic spectroscopy (PAS). The authors performed very sensitive and selective measurements on butane. A detection limit for butane in air in the ppb range was achieved.

Comparison of solvent desorption-gas chromatography-mass spectrometry (SDGCMS) method, thermal desorption-gas chromatography-mass spectrometry (TDGCMS) method and photoacoustic radiometry for monitoring chlorinated hydrocarbons was performed by Solid et al. (1996).

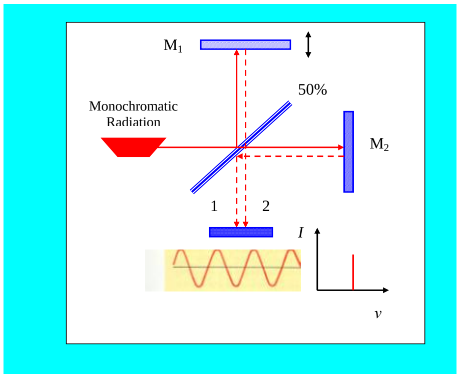
Photoacoustic radiometry (PAR) is optimal methgod from the point of view precision and costs of the measurements. PAR cannot replace GCMS, since knowledge of the plume analyte constellation is required to initialize the PAR. However, PAR is excellent for observing changes.

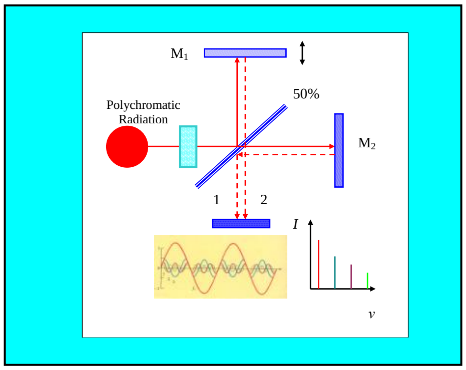
Fourier Transform Spectroscopy

This analytical technique is based on the measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation.

One of the main devices for measuring the temporal coherence of the light is the Michelson or Fourier transform spectrometer which consists of the source of light, beam splitter, movable and fixed mirrors, and detector.

If the source is monochromatic and the movable mirror is moved at a constant rate, the detector signal oscillates with a single frequency. The radiant power can be recorded as a function of time as the cosine oscillation (time domain) or as a function of frequency as spectral line (frequency domain). A plot of the output power from detector versus the mirror displacement is called *interferogram*. If the source is polychromatic, each input frequency can be considered to produce a separate cosine oscillation; the resulting interferogram is a summation of all cosine oscillations caused by all frequencies in the source.





The recorded signal is mathematically manipulated using a Fourier transform technique to produce a spectrum that can be used to identify specific contaminants and their concentrations.

The application of Fourier transform IR and dispersive IR spectrometry to the continuous monitoring of VOCs in indoor air and on the effects of daily human activities on VOC levels in indoor air were studied by Lee et al. (1993).

The FTIR-based photoacoustic spectroscopy (PAS) made it possible to quantify low concentrations of VOCs in air (Baldwin et al., 1992). It was established that band intensities were proportional to VOCs concentrations and sensitivity was a few ppm.

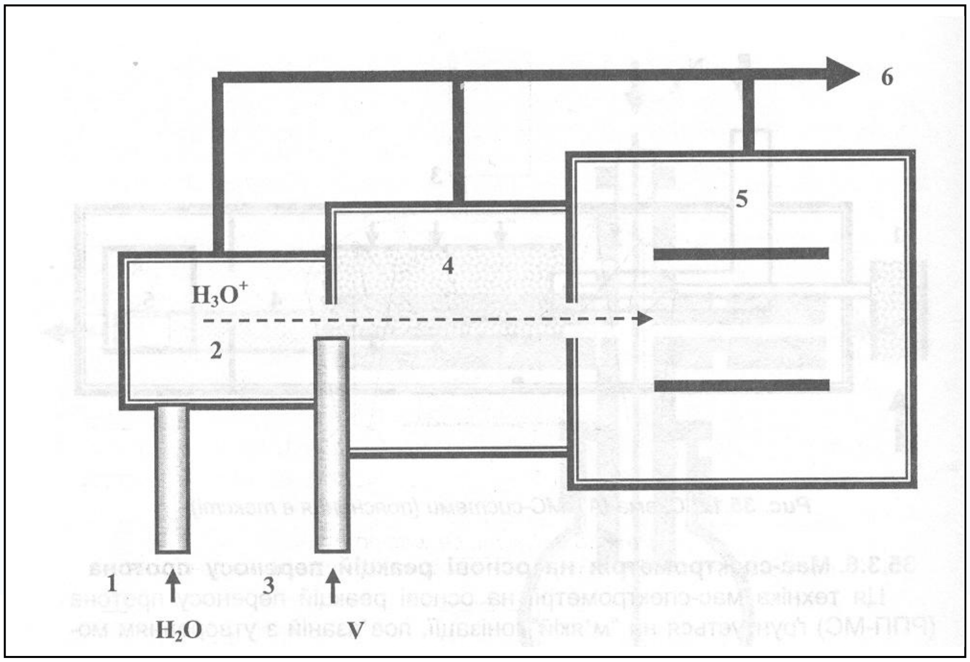
It is known that the zeolite 13X has good surface properties to adsorb several types of VOCs. Gas phase Fourier Transform-Infrared Spectrometer (FT-IR), which responds more quickly to instantaneous changes in the gas concentrations was used to estimate adsorption of several types of VOCs by zeolite (Wu et al., 2007).

A simultaneous quantitative measuring method of indoor air multi-component VOCs based on FTIR combined with chemometrics was proposed (Xu Li-eng et al., 2006).

Plants have a large capacity to transfer water from soil to the atmosphere. Soluble pollutants may be carried with that water. Method of Fourier Transform IR spectrometry was used for estimating the transfer rate of solvents that vary in volatility and solubility: trichloroethylene, trichloroethane, chloroform, dichloromethane, di-Et ether, and methyl-t-Bu ether (Davis et al., 1998). An extractive FTIR spectrometer measured gas phase concentrations above plants which had their root system immersed in water containing the pollutants.

Proton Transfer Reaction Mass Spectrometry

This method realizes the chemical ionization which is based on proton-transfer reactions; H_3O^+ is used as the reagent ion. The air sample is continuously drawn into a reaction chamber of PTR-MS where it encounters the reagent ion. Volatile organic compounds containing a polar functional group or unsaturated bonds have proton affinities larger than of H_2O and therefore will react with H_3O^+ in a proton transfer reaction which is accompanied with proton transfer between H_3O^+ and VOCs. The amount of analyte (R) in the sample air is determined by a simple formula relating the H_3O^+ count rate, the RH^+ count rate, the rate constant for the ion-molecule reaction, and a fixed reaction time.



Proton Transfer Reaction Mass Spectrometer: 1 – inlet of H_2O vapor; 2 – reaction chamber; 3 – inlet of air with VOCs; 4 – drift chamber; 5 – entrance of mass-spectrometer; 6 - pump

Proton Transfer Reaction Mass Spectrometer (PTR-MS) provides real-time, online quantification of VOCs in indoor air. The instrument is characterized with fast response time of about one second. A series of reviews are dedicated to the theory, principles of operation, instrumentation, detection limit, and practical application of PTR-MS for analysis of VOCs (Tani, 2003; Kato et al., 2004).

A proton transfer reaction mass spectrometer (PTR-MS) system has been developed which allows for online measurements of trace components with concentrations as low as a few pptv (parts per trillion by volume). Studies of VOC emissions from decaying biomatter and online monitoring of the diurnal variations of VOCs in ambient air are typical examples of environmental applications of proton-transfer-reaction mass spectrometry (Lindinger and Jordan, 1998)

The development of PTR-MS as a tool for the analysis of VOCs is described by Lindinger et al. (2001). This method allows detection of some VOCs in the parts per trillion by volume range and can be applied for studying many aspects of VOC analysis in environmental applications (Hansel, 2004).

Combining VOC separation by gas chromatography (GC) with simultaneous, parallel detection of GC effluent by PTR-MS and electron impact MS, an unambiguous interpretation of complex PTR-MS spectra is feasible. This novel development is discussed based on characteristic performance parameters, e.g., resolution, linear range, and detection limit (Lindinger et al., 2005).

Hansel et al. (1998) has reported that the sensitivity of a PTR-MS system was improved by nearly 2 orders of magnitude, so that now online monitoring of VOCs at a few pptv concentration is possible. This was demonstrated using calibration data down to 20 pptv and data on the diurnal variation of C9-alkylbenzene and its 13C-isotope in ambient air obtained at the western outskirts of Innsbruck, Austria.

An experimental system consisting of a PTR-MS, CO_2 analyzer, diffusion devise and leaf enclosure was used to measure the uptake of VOCs by *Golden Pothos* (*Epipremnum aureum*) (Tani et al., 2007). The results of the investigation were compared with a measurement system based on gas chromatography analysis and it was shown that the use of a PTR-MS based system can significantly increase the certainties in detecting the rate of VOC uptake by plants.

Proton transfer reaction-time of flight mass spectrometer (PTR-TOFMS) has been developed for real time measurement of atmospheric VOCs by a linear combination of H_3O^+ ion source, drift tube in which VOC is ionized, ion transport duct and TOFMS (Tanimoto et al., 2006). This system may be applied to the measurement of areal distribution of VOCs in urban air and VOC sources etc.

A PTR-MS system was used to monitor selected hydrocarbon emissions from in-use vehicles (Rogers et al., 2006). Selected hydrocarbons including methanol, acetaldehyde, acetone, Me tert-Bu ether (MTBE), benzene, and toluene were among the vehicle exhaust emission components monitored. This method is characterized with fast response and sensitivity and provides a valuable tool to study the impact of driving behavior on the exhaust gas emissions.

Similar application of PTR-MS for measuring VOCs concentrations online in diesel engine exhaust as a function of engine load was realized by Jobson et al. (2005).

New Generation of Instruments

Different analytical methods and instrumentation for the detection and analysis of VOCs in the different air environments are described by Siskos et al. (1997). The main category of methods concerns automated gas chromatographs (GC) equipped either with flame ionization detector (FID) or photoionization detector (PID). For outdoor measurements spectrometric methods can often be used such as Differential Optical Absorption Spectrometry (DOAS) and Fourier Transform IR (FT-IR). Recent advances have made available methods such as

Direct MS analysis (D-MS) and Membrane Introduction MS analysis (MI-MS) for the direct detection of VOCs. Recently, biosensors are used for the *in situ* detection of VOCs.

Analysis and VOCs detection from latex paints was described by Lorenz et al. (2005). The comparison of a PVC adhesive was detected by infrared (IR) spectroscopy, pyrolysis GC, and FID. A test chamber was used to detect exhalations from a floor covering, where volatiles were captured in an adsorber tube and then detected by thermodesorption and GC. VOCs in latex paints were detected by IR spectroscopy and pyrolysis GC.

The review of Parmar and Rao (2006) focuses on recent developments of the analysis of VOCs in ambient air. The new generation instruments are automated gas-chromatographs, fast gas chromatographs, multi-dimensional gas chromatographs, differential optical absorption spectroscope, Fourier transform IR spectroscopy, and time-of-flight mass spectrometer. This instrumentation facilitated real-time monitoring of VOCs also.

SICK BUILDING SYNDROME PREVENTION AND CONTROL

Indoor air quality improvement and prevention of hazardous effects of VOCs can be resolved through the thorough control of indoor air quality, application of systems of ventilation of indoor air and its cleaning (Dyer et al., 1996; Leovic et al., 1999; Inoue, 1999; Torii, 2000; Ro, 2002; Kadosaki, 2003; Gao et al., 2006; Liu et al., 2003, 2005; Cooper, 2007).

The prevention and amelioration of indoor environmental pollution begin with the control of the sources. Environmentally friendly building materials must be developed and used to construct "healthy buildings," basically preventing indoor environmental contamination and creating a healthy and comfortable living environment. It is necessary to mention the application of multilayer flooring material for reducing sick house syndrome (Hong et al.,2006); utilization the eco-material without harmful gases and reducing or removing them through the additional treatment to the building materials (Lee et al., 2005); development of new types of fiber panels and coatings as potential low-emitting alternative materials (Leovic et al., 1999) and water-based products that can be introduced to the wood coating industry to replace the high VOCs and high hazardous air pollutant materials (Huang et al., 1996); application of porous carbon material in environmental protection (Rong et al., 1999); limitation of recycling paper for printers and copiers (Jann et a., 2003; Gehr et al., 2004). The application of little out-gassing architectural materials and technology that is based on raising the room temperature is perspective from the point of view of removal the generated contaminant in the room (Ro, 2002).

Techniques for removal of trace VOCs from air that utilizes preferential ionization and electric migration of ions was proposed by Ito et al. (2002); the technology of VOCs removal from indoor air by negative air ions is described by Wu et al. (2004).

A ventilation of office environment with fresh air and removal of printers and photocopiers from office personnel working places are effective also (Dyer et al., 1996; Morrison et al., 1998).

Use of water-based aerosols and UV light is perspective for preventing sick building syndrome and VOCs removing (Niikura et al., 2006).

Development of an effective UV-irradiated titania-photocatalytic reactor was effective to improve removal efficiency of indoor volatile organic contaminants (Namiki et al., 1998).

Photocatalytic oxidation (PCO) of VOCs is a highly attractive alternative technology to purify and deodorize indoor air (Chapuis et al., 2002). This study demonstrated that a common fluorescent visible light lamp can effectively remove, via PCO, low concentrations of VOCs from slightly polluted air.

One of the promising technologies for the purification of indoor air that has emerged over the last decade is termed phytoremediation.

PHYTOREMEDIATION

Definition

The term *phytoremediation* comes from the Greek *phyto* (plant) and Latin *remedium* (restoring balance, or remediating); it means a complex of processes that provides the use of plants to remove, transfer, neutralize, or destroy contaminants from surrounding mediums that contain them (Yang et al., 2007).

This term has appeared in a 1991 funded proposal by U.S. Environmental Protection Agency Superfund Program (Raskin et al., 1994) although the technology of application of plants in land farming is known for at least 300 years (Phytoremediation. Transformation and Control…,2003).

Historically phytoremediation technology was realized at first to extract contaminants from soil and water (Phytoremediation of soil and water contaminants,…, 1997; Phytoremediation of contaminated soil and water,… 2000; Pivetz, 2001).

Plants both absorb and release volatile organic compounds and the use of plants for improving indoor air quality is increasingly being tested (Shemel, 1980; Wolverton, 1986; Darrall, 1989; Lohr and Pearson-Mims, 1996; Darlington et al., 2001; Wood et al., 2002*a,b*; Yoo et al., 2006). Plants are known to absorb air pollutants *via* their stomata during normal gas exchange. Several pollutants have been shown to be sequestered or degraded *in situ* or after transfer to other locations in the plant (Schmitz et al., 2000; Shemel, 1980; Son et al., 2000). Likewise, some air pollutants are removed by absorption or adsorption to the plant surface, microorganisms or soil particles (Jen et al., 1995; Orwell et al., 2004; Son et al., 2000; Wolverton, 1986; Wolverton and Wolverton, 1993; Wood et al., 2002*a,b*).

Several studies are dedicated to the application of plants to clean indoor air from volatile organic compounds (Ugrekhelidze et al., 1997; Wood et al., 2002*a,b*, 2006; Orwell et al., 2004) and formaldehyde (Kim et al., 2010).

Critical analysis of phytoremediation technologies is given by Trapp and Karlson (2001). Phytoremediation methods have advantages – they are cheap, are accepted by the public and, compared to physical or chemical approaches, are ecologically advantageous. However, there are characterized with certain limitations − the processes involved are complex, and a full clean up may require many years. It is necessary to account the effect of plants on the water balance of a site, redox potential and pH, and microbial activity of the soil. These indirect influences may accelerate degradation in the root zone or reduce leaching of compounds to groundwater. Compounds taken up into plants may be metabolized, accumulated, or volatilized into air. Authors underline that the lack of experience about possibilities and limitations seems to be a hindrance for a broader use of phytoremediation technologies.

Plants as objects of phytoremediation have certain advantages such as fast growth rate, high biomass, hardiness, tolerance to pollutants (Cherian and Oliveira, 2005).

Phytoremediation is realized through various mechanisms such as (Kvesitadze et al., 2006):

phytotransformation (*phytodegradation*) – the uptake, accumulation, and transformation of the organic toxic contaminants from soil, air and water by plants; all these processes lead to chemical modification of the contaminants through plant metabolism and enhancement of their toxic activity;

phytoextraction – absorption of contaminants by root system and translocation of them into plant biomass;

rhizosphere degradation – the process by which contaminants are destroyed by soil microorganisms at the zone that surrounds the root system of the plant;

phytostabilization – production of chemical substances that are able to immobilize contaminants in the surroundings by sorption, precipitation, and complexation;

phytovolatilization – ability of plants to remove contaminants from soil or water and release them into the atmosphere as a result of phytotransformation to more volatile or less polluting substances.

Uptake, Fate and Transport of VOCs in Phytoremediation Systems

A series of studies are dedicated to the application of phytoremediation technology to removal VOCs from indoor air.

Several indoor plant species have been shown to remove gaseous benzene and toluene, two important indoor volatile pollutants (Ugrekhelidze et al., 1997;

Wolverton et al., 1989; Wood et al., 2002*a,b*). For example, *Spathiphyllum willisii* Schott., *Dracaena deremensis* Engl. and *Kalanchoe blossfeldiana* Poelln. effectively removed benzene while *Chrysalidocarpus lutescens* H. Wendl. and *Phoenix roebelenii* O'Brien readily removed toluene and xylene (Cornejo et al., 1999; Wolverton et al., 1989). *Howea forsteriana* (C. Moore & F. Muell.) Becc. was better than *S. wallisii* and *D. deremensis* in the removal of *n*-hexane but not benzene (Wood et al., 2002*a,b*); and the efficacy of *D. deremensis* differed from that of *H. forsteriana* indicating individual species display different responses depending on the gas present.

Group of investigators (Cornejo et al., 1999) proposed to use plants for the decontamination of air. They have used several species of plants to determine their ability to remove VOCs such as benzene, trichloroethylene (TCE) and toluene from air. Plants were exposed to the pollutants singly or in mixtures in an airtight chamber, where concentrations of the pollutants, temperature and CO_2 level were monitored. The main objective of this investigation was to evaluate the idea that phytoremediation techniques might be used to lower the concentrations of indoor air pollutants, such as volatile or semi-volatile organic compounds. It was shown that pollutant removal efficiency varied in response to plant species and the pollutant; such species as *Pelargonium domesticum, Ficus elastica* and *Chlorophytum comosum* removed efficiently benzene from air. *Kalanchoe blossfeldiana* appeared to take up benzene selectively over toluene, and TCE was removed efficiently from the air by *C. comosum*.

The capacities of plants for removal of VOCs from indoor air were studied by Wood et al. (2002*a,b*). Three plant species, *Howea forsteriana* Becc. (Kentia palm), *Spathiphyllum wallisi* Schott. "Petite" (Peace Lily), and *Dracaena deremensis* Engl. "Janet Craig" were used in these experiments. The results demonstrated the capacity of an indoor potted-plant systems to remove VOCs such as benzene and n-hexane and the ability of these systems to act as an integrated biofilter in removing VOCs.

Purification capability of potted plants, such as rubber plant, Boston fern, golden pothos and snake plant for removing atmospheric formaldehyde was investigated by Oyabu et al. (2003).

The paper of Wood et al. (2006) reports the results of a field-study on the effects of potted-plant presence on total VOC levels, measured in 60 offices (12 per treatment) with two “international indoor-plant” species. Fourteen VOCs were identified in the office air. The results indicate that airborne TVOC levels above a threshold of about 100 ppb stimulate the graded induction of an efficient metabolic VOC-removal mechanism in the microcosm. These results and the investigations of Orwell et al. (2006) demonstrate that potted-plants can provide an efficient, self-regulating, low-cost, sustainable, bioremediation system for indoor air pollution, which can effectively complement engineering measures to reduce indoor air pollution, and hence improve human wellbeing and productivity.

The effects of plants, such as *Sansevieria trifasciata* and *Clivia miniata* on the clean-up of indoor air ad absorption of VOCs were studied by Guo et al. (2006). It was shown that in the certain range of pollutant concentrations, *Sansevieria trifasciata* could absorb 64.4% of the total content of formaldehyde, 61.4% of di-Me benzene and 64.8% of TVOC while *Clivia miniata* could absorb 70.1% of formaldehyde, 33.6% of di-Me benzene and 56.5% of TVOC within a week.

The study of Liu et al. (2007) was dedicated to the ability of ornamental plants to remove VOCs from air by fumigating 73 plant species with 150 ppb benzene, an important indoor air pollutant that poses a risk to human health. The following plant species were found the most effective at removing benzene from air: *Crassula portulacea, Hydrangea macrophylla, Cymbidium* Golden Elf., *Ficus microcarpa* var. *fuyuensis, Dendranthema morifolium, Citrus medica* var. *sarcodactylis, Dieffenbachia amoena* cv. *Tropic Snow; Spathiphyllum Supreme; Nephrolepis exaltata* cv. *Bostoniensis; Dracaena deremensis* cv.

The fate of organic compounds into leaves of various plants was studied by Ugrekhelidze et al. (1997). It was shown that [1-614C]benzene and [1-14C]toluene vapors penetrate into hypostomatous leaves of *Acer campestre*, *Malus domestica*, and *Vitis vinifera* from both sides, whereas hydrocarbons are more intensively absorbed by the stomatiferous side and more actively taken up by young leaves. Benzene and toluene conversion in leaves occurs with the aromatic ring cleavage and their carbon atoms are mainly incorporated into nonvolatile organic acids, while their incorporation into amino acids is less intensive. Intact spinach chloroplasts oxidize benzene, and this process is strongly stimulated in light.

A Dissertation of X. Ma (University of Missouri, 2004) is dedicated to the investigation of fate and transport of VOCs in phytoremediation systems**.**

A new methodological approach which is based on the application of a dual-vacuum, continuous high-flow chamber system for accurately determining the fate of VOCs in plants is proposed (Orchard et al., 2000).

The experimental system provides a natural plant environment, complete root/shoot separation, the ability to quantify phytovolatilization and mineralization in both root and shoot compartments, continuous root-zone aeration, and high mass recovery. The plant in such a system must be sealed in a chamber that allows rapid exchange of air to remove the water vapor lost in transpiration, to resupply the CO_2 consumed in photosynthesis, and to resupply the O_2 consumed in root-zone respiration. Such a system makes it possible to avoid contradictory observations regarding the uptake and translocation of VOCs by plants which are explained by inadequate airflow through the foliar region that results in high humidity, which dramatically reduces transpiration and may reduce contaminant flux; root stress that is induced by oxygen depletion in static root zones and increase root membrane permeability; the absence of separation of the root zone from the shoots.

The immediate application of spider plant (*Chlorophytum elatum* var. *vittatum*) as air-purification system in energy-efficient homes that have a high risk of HCHO contamination of the indoor air due to outgassing of urea-formaldehyde foam insulation, particleboard, fabrics, and other synthetic materials was proposed (Wolverton et al., 1984). The spider plant was more efficient in comparison with the either golden pothos (*Scindapsus aureus*) or nephthytis (*Syngonium podophyllum*).

Phenanthrene is a polycyclic aromatic hydrocarbon that consists of three fused benzene rings. This compound is found in pure form in cigarette smoke and is known as irritant and photosensibilizator of human skin. The transportation and transformation of ^{14}C-phenanthrene in a closed ‘plant-lava-nutrient solution-air' chamber system was studied by using radioactivity technology (Jiang et al., 2001). At the end of 64-days experiment the distribution sequence of ^{14}C activity in the components of closed chamber system was the following: root (38.55%) > VOCs (17.68 %) > lava (14.35%) > CO_2 (11.42%) > stem (2%).

The ability of foliage plants of *Hedera helix* L. (english ivy), *Spathiphyllum wallisi* Regal (peace lily), *Syngonium podophyllum* Schott. (nephthytis), and *Cissus rhombifolia* Vahl. (grape ivy) to remove two indoor VOCs, benzene and toluene. was evaluated by Yoo et al. (2006).The results indicated an interaction between gases in uptake by the plant, the presence of different avenues for uptake, and the response of a single gas was not necessarily indicative of the response when other gases are present. Changes in the rates of photosynthesis, stomatal conductance, and transpiration before and after exposure indicated that the volatiles adversely affected the plants and the effects were not consistent across species and gases.

Removal of tobacco smoke from indoor air under light and dark conditions as affected by foliage plants is described by Yoon et al. (2009).

Prof. Stanley Kays and his horticultural team of the University of Georgia, USA, explained that they have identified five "super ornamentals" of 28 indoor plants tested that had the highest rates of contaminant removal during phytoremediation (Fosgate, 2010). These are the red ivy (*Hemigraphis alternata*), English ivy (*Hedera helix*), variegated wax plant (*Hoya cornosa*), asparagus fern (*Asparagus densiflorus*), and the purple heart (*Tradescantia pallida*), the study says.

Phytotransformation

There are two approaches concerning the realization of phytotransformation technology. The first one is the involvement of plant enzymes that can transform toxic compounds and detoxify them. The second is related to creation of transgenic plants that can transform contaminants.

A review of Bock et al. (2002) covers such important topics concerning the phytoremediation technologies with particular emphasis on phytotransformation, i.e., the enzymic conversion of organic compounds within plant tissues following plant uptake. The principal topics are related to organic compounds uptake and transformation (uptake and translocation, enzymic phyto-transformation);

rhizosphere biodegradation; modeling plant-contaminant interactions; cell suspension cultures to understand polychlorinated biphenyl, polycyclic aromatic hydrocarbon, and nonylphenol metabolism by plants (uptake and extraction from plants); and plant peroxidase enzymes and polychlorinated biphenyl metabolism (materials and methods, results and discussion).

Enzymes and Genes involved in the Phytoremediation of VOCs

Over 100 metabolic enzymes from plants that are identified can be used in phytoremediation (Phytoremediation. Transformation and Control of Contaminants, 2003). These enzymes are able to detoxify various organic pollutants. For example, the cytochrome P-450 that is found in most plants and mammals, participates in oxygenation reactions for many natural and xenobiotic compounds. The most common reaction catalyzed by cytochrome P450 is a monooxygenase reaction, e.g. insertion of one atom of oxygen into an organic substrate while the other oxygen atom is reduced to water. The name *cytochrome P450* is related to the by absorbance of light at wavelengths near 450 nm.

Genetic engineering techniques provides the creation and application of transgenic plants that can possess a gene or genes that can be transferred from a different species; the DNA molecules from different sources that belong to other species or even different kingdoms can be combined *in vitro* into one molecule and create a new gene. The genetic engineering of plants can achieve sustainable *in situ* recycling for antropogenic chemicals and produce hybrid or *de novo* enzymes to transform and mineralize xenobiotic contaminants (McCutcheon and Schnoor, 2003).

Plant P 450 monooxygenases represent the largest family of plant proteins that can be used in phytoremediative applications. Review of Rupasinghe and Schuler (2006) discuss the methodology that helps to understand the interactions of P 450 monooxygenases with substrates.

The induction of individual components of the plant microsomal monooxygenase system have been studied by Khatisashvili et al. (1997). The induction of individual components of the plant microsomal monooxygenase system and xenobiotic oxidation specificity in NADPH and NADH synergism with NADPH have been studied. The possibility of cytochrome P 450 switching over from biosynthetic into detoxication pathway and transformation of monooxygenase mechanism of oxidation into peroxidase according to plant age have been demonstrated.

It is known that cytochrome P 450 2E1 (CYP2E1) is a key enzyme in the mammalian metabolism of several low molecular weight VOCs, such as trichloroethylene (TCE), vinyl chloride (VC), carbon tetrachloride (CT), benzene, chloroform, and bromodichloromethane (BDCM), which are all common environmental pollutants that pose risks to human health. A transgenic tobacco (*Nicotiana tabacum* cv. Xanthii) that expresses CYP2E1 with increased activity toward TCE and ethylene dibromide was developed (James et al., 2008). In experiments with tobacco plant cuttings exposed to VOCs in small hydroponic vessels, the transgenic tobacco had greatly increased rates of removal of TCE, VC, CT, benzene, toluene, chloroform, and BDCM, compared to wild-type or vector control tobacco, but not of perchloroethylene or 1,1,1-trichloroethane.

In addition, detoxification of xenobiotic compounds can be realized through the conjugation to small natural molecules such as glutathione, sugar, and malonate. Among enzymes that can catalyse such reactions are glutathione-*S*-transferase (GSTs) and glycosyl-transferases they are found in all organs of plants. Properties and functions of these enzymes are described by Schwitzguebel and Vanek (2006).

The problem of detoxification of formaldehyde by the spider plant (*Chlorophytum comosum* L., tobacco plants *Nicotiana tabacum* L. and by soybean (*Glycine max* L.) cell-suspension cultures was studied by Giese et al. (1994). The results supported the idea of indoor air decontamination with common room plants such as the spider plant – the shoots of this plant are able to take up and extensively metabolize gaseous formaldehyde.

One of the detoxification enzyme, glutathione S-transferase (GST), that can reduce the toxicity of organic chemicals, was purified from broccoli (*Brassica oleracea* var. italica) by Lopez et al. (1994).

Glutathione-dependent flormldehyde dehydrogenases were isolated by Giese et al. (1994) from shoots and leaves of *Equisetum telmatea* and from cell-suspension cultures of wheat *Triticum aestivum* L. and maize *Zea mays* L. This glutathione-dependent formaldehyde dehydrogenase is identified as a progenitor of the plant alcohol dehydrogenase superfamily. Common indoor plants were active in the phytoremediation of formaldehyde in the air. A role of gene duplication and mutation, as well as genetic rearrangements is generally well established for the evolution of isoenzyme families (Sandermann, 1999).

The article of Martinez et al. (1996) is dedicated to a detoxification enzyme such as glutathione-dependent formaldehyde dehydrogenase (class III alcohol dehydrogenase) derived from *Arabidopsis thaliana*.

The following table generalizes the principal plants that have been used for phytoremediation technology, and air pollutants.

Plants	**Pollutant**	**References**
Spathiphyllum willisii Schott.	benzene	Cornejo et al., 1999; Wolverton et al., 1989
Dracaena deremensis Engl	benzene	–
Kalanchoe blossfeldiana Poelln.	benzene	–

Chrysalidocarpus lutescens H. Wendl	toluene, xylene	–
Phoenix roebelenii O'Brien	toluene, xylene	–
Howea forsteriana (C. Moore & F. Muell.) Becc.	*n*-hexane	Wood et al., 2002
Pelargonium domesticum	benzene	Cornejo et al., 1999
Ficus elastica	benzene	–
Chlorophytum comosum	benzene, trichloroethylene	–
Howea forsteriana Becc. (Kentia palm)	benzene, *n*-hexane	Wood et al., 2002
Spathiphyllum wallisi Schott. "Petite" (Peace Lily)	benzene, *n*-hexane	–
Dracaena deremensis Engl. "Janet Craig"	benzene, *n*-hexane	–
Sansevieria trifasciata	formaldehyde, benzene, VOCs	Guo et al., 2006
Clivia miniata	formaldehyde, benzene, VOCs	–
Crassula portulacea, *Hydrangea macrophylla,* *Cymbidium* Golden Elf., *Ficus microcarpa* var. *fuyuensis,* *Dendranthema morifolium,* *Citrus medica* var. *sarcodactylis,* *Dieffenbachia amoena* cv. *Tropic Snow;* *Spathiphyllum Supreme;* *Nephrolepis exaltata* cv. *Bostoniensis;* *Dracaena deremensis* cv.	benzene	Liu et al., 2007
Chlorophytum elatum var. *vittatum*	formaldehyde	Wolverton et al., 1984
Hedera helix L., *Spathiphyllum wallisi*	benzene, toluene	Yoo et al., 2006

Regal, *Syngonium podophyllum* Schott. (nephthytis), *Cissus rhombifolia* Vahl.		
Chlorophytum comosum L., *Nicotiana tabacum* L. *Glycine max* L.	formaldehyde	Giese et al.,1994
Hemigraphis alternata, English ivy (*Hedera helix*), variegated wax plant (*Hoya carnosa*), asparagus fern (*Asparagus densiflorus*), and the purple heart (*Tradescantia pallida*)	VOCs	Kays et al. (cit. by Fosgate, 2010)

Crassula portulacea . From: succulent.chat.ru

Hedera helix L. From: www.tom-garten.de/

Spathiphyllum wallisii. From: http://www.houseofplants.co.uk/Spathiphyllum_wallisii_FL.htm

Dracaena deremensis. From: http://en.wikipedia.org/wiki/Dracaena_deremensis

Kalanchoe blossfeldiana. From: http://en.wikipedia.org/wiki/Kalanchoe_blossfeldiana

Chrysalidocarpus Lutescens. From: http://www.alibaba.com/product-gs/51031628/Chrysalidocarpus_Lutescens/showimage.html

Ficus_benjamina. From: http://en.wikipedia.org/wiki/Ficus_benjamina

Howea forsteriana. From: staff.mcs.uts.edu.au

The studies of Orwell et al.(2004) was the first attempt to show that microorganisms of the potting mix rhizosphere were the main agents of removal of benzene, as model VOC, by seven potted-plant species/varieties. The results demonstrated of soil microbial VOC degradation from the gaseous phase. These investigations lead to developments in microbially-based biofilter reactors for cleaning VOC-contaminated air on the basis of plant/soil-microorganism interactions.

Burken et al. (2005) developed unique sampling techniques that made it possible to study the fate of VOCs in phytoremediation systems. Tissue sampling and diffusion traps were used to determine how VOCs are transported in and diffuse from vegetation, particularly woody species, how plants can interact with different contaminated media, showing transport of contaminants occurs from the vadose zone (vapor phase) as well as the saturated zone (aquatic phase). The results have shown that diffusion from the xylem tissues to the atmosphere is a major fate for VOCs in phytoremediation applications. These techniques were also utilized to observe the impact of engineered plant/microbe systems, which utilize recombinant, root-colonizing organisms to selectively degrade compounds and subsequently alter the fate of VOCs.

Volatilization

It was shown that trichloroethylene and 1,1,2,2 -tetrachloroethane were taken up by hybrid poplar trees and released to the atmosphere though the process of volatilization that took place directly from the transpiration pathway and occurs through diffusion from the conductive xylem tissues (Burken and Ma, 2002). It was shown during laboratory investigations that the flux of the VOCs depended on vertical distance up the stem, evapotranspiration rates, and the concentration of VOCs in the feed solution. This research provides the first definitive measurements of diffusion directly from the xylem tissues in live plants and of VOCs released to the atmosphere in a field-scale phytoremediation application.

Experimental techniques was used to study the pathways for phytoremediation of VOCs, particularly methyl-tertiary-butyl-ether (MTBE), distinguishing between uptake of the (MTBE) along with water transpired by living plants and the passive, physical process of volatilization (Ramaswami and Rubin, 2001). Estimation of MTBE transpiration stream concentration factor root concentration factor, just as mass balance studies confirmed the hypothesis that phytovolatilization may be the primary pathway for MTBE phytoremediation.

It was studied during recent investigations concerning the fate of chlorinated solvents in phytoremediation, particularly, such processes as plant uptake, metabolism, rhizosphere degradation, accumulation, and volatilization of organic contaminants, including chlorinated solvents. The agreement of experimental data with theoretical models confirmed that VOCs volatilize from stems and that the resulting diffusive flux to the atmosphere is related to exposure concentration and to height up the stem; xylem transport, including advection, dispersion, and diffusion through cell walls with subsequent volatilization to the atmoshere, is a major fate for VOCs in phytoremediation (Ma and Burken, 2004).

Uptake and Absorption of VOCs by Leaves

This process means a diffusion of a VOC into a liquid to form a solution. Absorption concerning the remediation plants includes the penetration of VOCs from ambient air through stomata into leaves where they adsorbed on the lipophilic surface of leaf wax. The wax is an active sorbent of the lipophilic toxic compounds and doesn't permit them to penetrate further into leaves. Air contaminants can penetrate into a leaf through stomata or epidermis. The opening and closure of stomata are controlled by the potassium ions which regulate the movement of the guard cell of the stomata. The thickness of wax cuticle that covers epidermis depends on the plant species and the age of the leaf. Contaminants are accumulated on the lipophilic surface of leaf and penetrate into the leaf structure (Kvesitadze et al., 2006).

Although VOCs emission from plants is well known, nevertheless, it is not clear whether or not plants can act as sinks for VOCs (Miebach, 2003). Sunflower (*Helianthus annuus* L.) was used as test plant to examine effect of exposure to different VOCs in laboratory conditions under well controlled external parameters. Method GC-MS was used for concentration estimation of individual VOCs. A possible uptake by the plants was detected from the concentration differences between chamber inlet and outlet. If a significant uptake by the plants was observed, the flux densities were detected using the leaf area as a normalization factor. By variations of light intensity stomatal aperture was changed allowing to determine the passway of the individual VOC into the plant. For the compounds such as acetaldehyde, acetone, EtOH, isoprene, limonene, and MeOH no uptake by sunflower was observed; these substances were only emitted even if the plants were exposed to VOC concentrations more than 50 ppb. For (E)-3-hexenol, hexanal, octanal, and nopinone significant concentration differences between chamber inlet and outlet were found. These losses could not be explained by reactions in the gas phase or interferences at the walls of the analytic equipment. The data showed no significant deposition onto the plant's cuticula but good relations between stomatal aperture and loss of the VOC. These relations showed a limitation of the uptake by diffusion through the stomata for (E)-3-hexenol, hexanal, and octanal. For nopinone an internal resistance for the uptake was found. Furthermore, calculations showed that a solution of the compounds in the apoplasic water could not explain the uptake rates implying a metabolization of (E)-3-hexenol, hexanal, and octanal. Author considers that dry deposition of VOCs on plant surfaces cannot be neglected as a sink.

Biotransformation of [1-6-14C]benzene and [1-14C]toluene in English ryegrass (*Lolium perenne* L.) seedlings was investigated (Chrikishvili et al., 2006). Vapors of these compounds. were absorbed by the leaves of this plant. Benzene and toluene were oxidized, forming phenol and benzoic acid, respectively; a portion of them was bound by low-molelular-weight peptides forming conjugates. After removing plants from the atmosphere with [1-6-14C]benzene and [1-14C]toluene, the radioactivity of the conjugates gradually decreased. The process of biotransformation was accompanied by the evolution of $^{14}CO_2$, indicating the breakdown of these conjugates, by oxidative transformations of portion of phenol and benzoic acid along with peptide conjugation, and disruption of the aromatic ring. By this pathway, nonvolatile carboxylic acids, such as muconic, fumaric, succinic, malic, malonic, glycolic, and glyoxylic, were formed. Using electron microscopy, a damaging effect of benzene on the cell ultrastructure of English ryegrass leaves was shown, and this toxic effect depended on the benzene concentration.

Participation of the cuticle but not the stomata of the leaves in the foliar uptake processes for VOCs is reported by Beattie and Seibel (2007). The authors studied the uptake kinetics for gaseous phenol and p-cresol into the leaves of maize seedlings in a closed system over periods up to 23 hours. When leaves were exposed to mixtures of phenol and p-cresol, the air concentrations of the compounds rapidly decreased, showing residence times of 4-6 hours. The stomata of the leaves were mostly or completely closed, suggesting that uptake was primarily through the cuticle. The involvement of a cuticular uptake pathway was confirmed based on increased uptake into two cuticular mutants of maize. In addition, the authors studied the location of ^{14}C in leaves exposed to ^{14}C-phenol. Those fact that significantly more ^{14}C accumulated in the terminal parts of the leaves than in the central and basal regions has demonstrated that a gaseous VOC, or its breakdown products, accumulates in a spatially non-uniform manner in leaves following foliar uptake. These findings support a role for plants as natural, or deliberate, attenuators of airborne pollutants, and suggest potential availability of these compounds to the leaf surface microflora.

An experimental method to measure foliar uptake and translocation of VOCs in plants is proposed by Jen et al. (1995).The soybean foliage that was chosen as a sample in this experiment was located in a flow-through exposure chamber to determine phytotoxicity of VOCs; an air-tight chamber was used for exposure of whole plants to radiolabeled test compound (^{14}C-toluene). It was shown that deposition velocities were greatest in the light phases than during the dark phases of exposure, suggesting that stomatal uptake as well as surface deposition contributed to toluene uptake. ^{14}C was translocated from foliage to the roots. These data indicate that deposition of VOCs to vegetation may constitute an important mechanism leading to herbivore exposure to volatile hazardous organics at waste sites.

CONCLUSIONS

The problem of search, identification and analysis of volatile organic compounds (VOCs) in indoor air is rather actual because of hazardous effects of these compounds on the health and well-being of building occupants. The further progress is based on thorough control of indoor air quality, application of environmentally friendly building materials and creation of a healthy and comfortable living environment, development new analytical methods for screening VOCs and technique for removing the most hazardous VOCs from indoor air.

Indoor air quality has progressively deteriorated, compromising the health of individuals exposed. Indoor plants absorb volatile organic pollutants and therefore could be used for phytoremediation of air quality.

Phytoremediation technologies have certain advantages – they are low-cost and ecologically clean; the ornamental plants provide efficient and self-regulating bioremediation system for indoor air pollution.

Nevertheless, these technologies demand to solve a lot of problems ncerning the searching the most effective phytoremediation systems on the basis of understanding the principal passways of the individual VOCs into the plant and mechanisms of removal VOCs from indoor environment.

Successful screening and practical application of suitable plants with high phytoremediation potential can be used for improvement of human wellbeing.

"Why some plants are very effective at remediation—while others show little promise—is a mystery. That's one of the things we want to learn," explained Professor Stanley Kays in his interview to UGA News Service (February 11, 2010). "We also want to determine the species and number of plants needed in a house or office to neutralize the problem contaminants. Further research could help scientists refine the concept".

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