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Gawronski, Stanislaw W.; Gawronska, Helena; Lomnicki, Slawo; Saebo, Arne & VANGRONSVELD, Jaco (2017) Plants in Air Phytoremediation. In: Advances in Botanical Research, 83, p. 319-346.

DOI: 10.1016/bs.abr.2016.12.008
Handle: http://hdl.handle.net/1942/25728

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Abstract

Air pollution has become a global problem and affects nearly all of us. Most of the pollution is of anthropogenic origin and therefore we are obliged to improve this situation. In solving this problem basically our only partners are plants with their enormous biologically active surface area. Plants themselves are also victims of air pollution but because they are sedentary they developed very efficient defense mechanisms, which can also be exploited in order to improve the humanosphere. For their life processes plants require intensive gas exchange, during which air contaminants are accumulated on leaf surfaces or absorbed into the tissues. Some of the pollutants are included by plants in their own metabolism while others are sequestered. In some plant species, the processes of removing pollutants from the air is conducted in a very efficient way and therefore they are used in the environmental friendly biotechnology called phytoremediation. For urban areas, outdoor phytoremediation is recommended while indoor phytoremediation can be applied in our homes and workplaces. Because in near future purifying outdoor air in order to protect human health and wellbeing does not look the most promising, an important and increasing role will be played by indoor phytoremediation.

Key words

Air pollutants, pollutants removal, air phytoremediation, indoor and outdoor phytoremediation, urban forest

1. Introduction

Impacts of air pollution on human health and wellbeing are well documented worldwide by the World Health Organization. Every year 4.3 million premature deaths occur from exposure to indoor air pollution and 3.7 million deaths are attributed to outdoor air pollution (WHO 2015), with the major health effects being respiratory and cardiovascular diseases. A striking finding of Felgin et al. (2016) showed that between 10.2 % (high income country) and 33.7% (low- and middle income countries) of stroke burden are due to exposure to air pollution. Others indicate the relationship between air pollution and neurodegenerative diseases (Calderon-Garciduenas et al. 2008). Air pollution is associated with the presence of excess amounts of chemicals and aerosols, compared to the pristine conditions, such as for example remote ocean locations. The origin of the pollutants is typically of the anthropogenic origin: particulate matter (PM), carbon monoxide (CO), nitrogen oxides (NO_X), volatile organic compounds (VOC) with most often listed in this group the polycyclic aromatic hydrocarbons (PAHs), heavy metals (HM) and sulphur dioxide (SO_2), or the result of their secondary atmospheric reactions such as PAN (peroxyacetyl nitrates) or ozone (O_3). A special group are the persistent organic pollutants (POPs) which are not released in large amounts, however, due to their environmental stability they persist in the environment for extensive periods of time. These include synthetic organic compounds, used on a large scale in human daily life such as: polychlorinated biphenyls (PCBs) that were commonly used as heat transfer liquids, polybrominated diphenyl ethers (PBDEs), used as fire retardants. The Stockholm Convention has banned the production of many of these POPs production, but nevertheless their stockpiles and abundance in already manufactured products still results in significant emissions to the environment (U.N. Stockholm Convention C.N.524.2009.TREATIES-4). Phthalates used as plasticizers in PVC plastics are not chemically bound to PVC, and are slowly released from the plastic matrix by leaching into fluids or evaporation into both indoor and outdoor air. Their high analogy to human hormones makes them suspected as endocrine disruptors. These chemicals, due to their vapour pressure and gas-solid partitioning coefficient can easily adhere to the ambient air particulate matter and undergo gas phase transport with these particulates. As a result, the main mechanism of their removal from air is particle dry deposition or alternatively, incorporation within rain droplets and precipitation (Fang and Huang 2013, Sun et al. 2014). Deposited PM particles on surfaces, such as for example plant leaves are subject to further migration with precipitation, as a substantial fraction of PM deposited on leaves is continuously washed off to the soil or on sealed urban surfaces with every rainfall (Nowak et al. 2006, Sun et al. 2014). Rain removes PM from both the air and from the surfaces of leaves contributing to air purification, however, between rainfalls plants accumulation of PM on their surface and in wax (sPM, and wPM respectively) (Popek et al. 2013) by far exceeds other dry deposition rates and ensures a much more efficient removal of pollutants from the air (McDonald et al. 2007). It is thus possible to exploit higher plants with their microbiome in an environmental friendly biotechnology for the removal of airborne pollutants associated with PM in outdoor and often also indoor locations - an example of the general process of phytoremediation.

The most important physical parameter of plants in the context of PM phytoremediation is their enormous biologically active surface area. The calculated surface area of above-ground plants' organs on earth is estimated to be at least 200 million km^2 and exceeds the earth land area of 149 million km^2 (Varma et al. 2008). Plants' leaves, needles and young twigs contribute the most to this surface area and all of them capture air pollutants. Plants leaf areas exceed by a few factors the projected by the canopies ground surface area and this characteristic is referred to as a Leaf Area Index (LAI), which depending on the group of plants equals 2-3 for grasses, 4-5 shrubs and up to 10 or more for trees. Special leaf features and structures such as leaf folding, hairs (pubescence), trichomes and wax layers have specific roles in pollutant removal and all favour the accumulation of PM.

Plants control the impact of the environment on their organs through the outermost layer of cells called the epidermis. The outer wall of this epidermis is covered with a lipid layer (wax) that forms a protective barrier for the cells from the surroundings. Plant waxes are very diverse and Barthlott et al. (1998) distinguish 23 types of waxes. Waxes are typical and at a fairly uniform structure for certain taxa, with different wax structures varying in shape, roughness, thickness of the layer and chemical composition. Trichomes, hairs, veins and rough wax are conducive for the accumulation of particulate matter on the leaf surface. During raining and snowing PM are removed from air as well as from the needles and leaves of plants which, to a large extend due to the surface electrostatic charge conducive to the accumulation. PM are localized on the surface itself, but also embedded in the wax coating leaves or needles. Deep surface penetration into the interior of the leaf tissue is very limited even for fine and ultra-fine particles, though due to their size they could only penetrate in to the plant through the stomata. The stomata, however, comprise only 0.5 to 1.5% of the leaf surface and usually are situated on the lower side of leaves.

Plants are higher, autotrophic organisms and for their life processes require intensive gas exchange, during which gaseous air contaminants can also be accumulated/absorbed internally. The intensity of gas exchange depends on a number of factors such as temperature, humidity, carbon dioxide concentration, light intensity, specific photosynthetic system and air pollution. During evolution, to adapt to the changing environmental conditions, plants developed different photosynthetic systems (PS) such as C_3, C_4, CAM and facultative CAM and plants with specific PS occupy different ecosystems, mainly depending on the climate. C_3 plants are dominant in the low temperate zone and cold areas, and their growth and biomass accumulation is usually lower. Such plants keep their stomata constantly open during the day to maximize CO_2 uptake (together with gaseous pollutants). C_4 plants perform the process of photosynthesis in spatially separate cells, with higher intensity of gas exchange and accumulate biomass much faster and in greater amounts. On the contrary, CAM plants conduct the process of photosynthesis in temporally separated steps. Uptake of gasses occurs during the night (open stomata) while during the day photosynthesis proceeds with the stomata closed. Such temporal separation of the CAM system steps allows plants to survive in very dry conditions. Epiphytic plants species also sometimes are exposed to dry periods and thanks to their ability to run photosynthesis via the CAM system they survive in difficult conditions, though at low efficiency of photosynthesis and growth. Interesting is the existence of facultative CAM plants that under optimal or near optimal conditions function as C_3 plants while under stress conditions they can run photosynthesis via the CAM pathway. The intensity of this process differs from typical CAM plants with closed stomata during the day to C_3 pathway (Winter & Smith 1996). Facultative CAM plant species are very interesting for air phytoremediation, as they have stomata open at night and take up CO_2 along with pollutants and during the day they carry out the other steps of photosynthesis. They can be useful for indoor phytoremediation in bedrooms; during the night CAM plants would improve the air quality absorbing CO_2 released both by these plants and humans during their sleep. This group of plants should be recommended also for cultivation in the extensive green roofs, with hot conditions during the day and the plants carrying out gas exchange at night.

The waxy surface of leaves is colonized by microorganisms, creating a phyllomicrobiome consisting on average out of $10^{6} – 10^{7}$ microorganisms cm^2 (Vorholt, 2012). De Kempeneer et al. (2004) reported that these bacteria are actively involved in the degradation of available organic pollutants such as for example toluene. This phenomenon further contributes to the air remediation by the surface of plants extending it to plant microbiome. Gaseous pollutants penetrate the leaves through stomata while surface deposited lipophilic compounds can penetrate the cuticular wax and become degraded by the endo-bacteria. It is difficult to precisely determine the role of epi- (surface) and endo-bacteria (internalized). However, washing the leaves resulting in the removal of epiphytic bacteria decreased the degradation process of organic pollutants as for example benzene confirming their substantial role in the degradation of organic air pollutants (Sriprapat & Thiravetyan 2016). The role of the plant microbiome and possibilities of its utilization have been described (Weyens et al. 2015 and in Eevers et al, 2017, this volume).

2. Aerosol air pollutants

*Particulate matter (PM)***,** nowadays the number one air pollutant in many regions of the world, is a complex mixture of chemical species within the solid or liquid particles suspended in the air defined as an aerosol. Solid aerosols can remain suspended in the air for minutes, hours to days or even months before deposition, depending mainly on size of the PM (Bidleman 1988).

Particulate matter can be directly emitted into the air and comprise primary aerosols (or can be formed in the atmosphere through particle coagulation of primary particles and incorporation of gaseous pollutants such as SO_2 and NOx forming secondary aerosols ($PM_{2.5}$, <2.5um, fine particles). Larger particles in excess of 2.5 microns in diameter are increasingly enriched with crustal elements due to the weathering process of rocks and soils (PM 2.5-10 µm, coarse particles). The smallest fraction of PM is generated almost exclusively by the anthropogenic sources and combustion, since 70% of $PM_{2.5}$ originates from combustion. A WHO report mentions that a major source of PM in urban areas of developed countries are fossil fuels and particularly internal engines combustion while it are household cooking and heating in developing countries (WHO 2015). Though the toxicity and health effects associated with the human exposure to PM are still a subject of major debate and extensive research, it is clear that different components of PM can contribute to the observed effects. These include not only native combustion borne particle components but also chemicals adsorbed on the PM when suspended in air. Recent data have shown that non-exhaust sources as such as brakes, tires and asphalt dust contribute almost equally to the total PM emitted in highly urbanized areas (Grigoratos and Martini 2015). If toxicity of non-combustion fractions of PM is equivalent to combustion fractions, the introduction of hybrid and electric cars will decrease the human risks associated with PM emissions only in part. A new discovery of Environmentally Persistent Free Radicals (EPFRs) has shed a new light on PM associated toxicity (Cormier et al. 2006, Lomnicki et al. 2008).

PM embedded in wax are more strongly associated with leaves in comparison to those located on the surface of the wax and that are more easily removed by rain or wind into the soil. In rainy regions, washing the surface of the leaves by precipitation is an efficient removal mechanism of PM associated pollutants from the air. However, PM embedded in waxes and especially lipophilic organic compounds like PAHs, PCBs, PBDEs, dioxins and the charged electrostatic PM slowly penetrate into the leaf by diffusion and only after reaching the first living epidermal cells are displaced and deposited in the cell wall or the vacuole. Raking fallen leaves and young shoots from such sites and transporting them for disposal remove PM completely from the particular sites of urban areas. The best way to dispose PM polluted litter is burning it a in strictly controlled conditions (backyard burning is absolutely not acceptable!) as, depending on amount of accumulated PM and associated pollutants they can be hazardous. The remaining ash (representing approximately 1% of the dry weight) must undoubtedly be handled as hazardous material, and disposed accordingly.

Black carbon (BC) particles comprise a significant fraction of PM originating from combustion and commonly is referred to as soot. Pure BC, commonly referred to as elemental carbon (EC), as a component of PM is not considered toxic to human health but it plays a role of a carrier or vehicle for other toxic compounds on its surface. Their adverse role is strong light absorption and heat generation and therefore directly impacting the climate change through decreasing the Earth albedo (EEA 2013). It is quite probable that BC affects plants similarly *i.e.* increase of leaves temperature and reduction of the light transmittance to the photosynthetic apparatus. According to Naidoo and Chirkoot (2004) the inhibition of photosynthesis observed in plants growing in the vicinity of coal mines partially can be explained by the negative impact of BC deposited on leaves.

Environmentally Persistent Free Radicals (EPFRs) are a recently discovered class of combustion related pollutants. They are inherently associated with the PM, as they are formed at the gas-solid interphase and lead to the surface bound species. EPFRs are conjugated species between an organic fraction and metal centers embedded in the PM. The association between the metal and organic adsorbent (in general small aromatic compounds) results in an electron transfer from the organic molecules to the metal center forming organic radical species, though bound to the surface. The organic forms of the EPFRs are generally of phenoxyl or semiquinone type structures, with the unpaired electron localized around oxygen, and stabilized by resonance. A unique characteristic of such species is their lifetime – while usually organic radicals have a lifetime of microseconds to milliseconds (and seconds in extreme cases) EPFRs are relatively stable with lifetime of hours, days or even months in ambient air (thus 'environmentally persistent') (Vejerano et al. 2012, Gehling and Dellinger 2013). Recent studies implicate EPFRs to be responsible for observed health effects of PM in humans (Kelley et al. 2013, Saravia et al. 2013, Reed et al. 2015). In fact, it was suggested that based on the concentrations of EPFRs it is possible to compare the exposure of PM to the amount of smoked cigarettes (Gehling and Dellinger 2013). The mechanism of their toxicity results from redox reactions with a net output of hydroxyl radicals which are extremely potent oxidizers and toxic to living organisms, and resulting in oxidative stress (Khachatryan et al. 2011). So far the effects of the presence of EPFRs on either plants or their associated microbiome upon deposition of PM has not been investigated. However, based on the known chemistry and behavior of EPFRs it is plausible that generation of hydroxyl radicals within thin water films on the surface of the leaves may result in the degradation of the protective wax layer and also be toxic to the microbiome. More studies are required in this field. It is also quite possible that through evolutionary processes some bacteria developed resistance to EPFRs or even can destroy them thus having a symbiotic protective function for their host plants. This will also contribute to the overall phytoremediation activity, as the PM collected by plants are neutralized in respect of the presence of EPFRs.

Semivolatile organic pollutants (SVOCs) are a large group of known toxicants formed during incomplete combustion of coal, oil and any other organic matter. Lower combustion temperatures and substoichiometric concentrations of oxygen increase formation of these products including PAH, biphenyls, phenolics, dioxins and many others. Compounds with low vapour pressure are partitioning to the surface of combustion formed particles such as carbon black or refractory oxide nanoparticles, forming soot and fly ashes. Individual PAHs are different in environmental behaviour depending on the number of aromatic rings in the structure as well as their relative arrangement. Five and 6 rings are solid and very persistent in the environment and subject to environmental- and bioaccumulation. Noteworthy are the two most carcinogenic 5 ring PAHs i.e. benzo (*a*) pyrene and the more carcinogenic but fortunately present in lower quantities dibenzo (*a*, *h*) anthracene. Due to their stability, the fate of such PAHs is usually dependent on organisms capable to decompose them enzymatically such as by wood-rotting fungi; however, this is a very slow process. In Europe, Poland is one of the most polluted countries with benzo (*a*) pyrene (WHO 2015) resulting from the dominant role of coal-based energy and the large number of old cars. However, similar situations are found in many places around the world.

Along with the progress in science the list of organic pollutants is increasing constantly, converting once praised new chemicals into banned and dangerous substances. A good example are the polychlorinated biphenyls (PCBs) originally introduced by Monsanto or polybrominated diphenyl ethers (PBDEs) and recently diethyl phthalates. Though, in developed countries, the production of PBDEs in was abandoned in the 1970-ies they are still released into the environment from old electronics, printed circuit boards, old furniture upholstery, construction and lighting equipment.

Besides SVOCs removal by PM deposition on the surface of leaves, many plants are capable to metabolize them making them perfect air remediation tools. PCBs from the air enter plants through the cuticle. Part of them remain trapped within the cuticle (Moeckel et al. 2008) and the remaining part penetrates into the cells and is metabolized possibly by cytochrome P-450 as shown for cells of pine needle and eucalyptus leaves by Chen et al. (2014). Winter melon (*Benincasa hispida*) is taking up di (2-ethykhexyl) phthalate (DEHP) very efficiently from the air through its leaves, shoots and even flowers, what makes this species much more effective than commonly recognized phytoremediation species like *Brassica chinensis* and *B. campestris*. These results indicate that *B. hispida* is a good candidate for phytoremediation of phthalates (Wu et al. 2013). However, although it is a valuable vegetable in the warmer regions of the world it cannot be used for consumption when cultivated as phytoremediation species.

Heavy metals (HM) present in air PM mainly originate from combustion of fossil fuel. Heavy metals are sometimes associated with larger, coarse particles in areas of active mining and where mine tailings are present. The list of HM is quite long, but lead (Pb), zinc (Zn), cadmium (Cd), arsenic (As), mercury (Hg), chromium (Cr) VI and copper (Cu0) are very often dominating. Their presence in plant tissues should be interpreted with some caution since even metals that are very toxic and unnecessary to plants such as Cd and metalloids like As are very easily taken up from the soil and translocated to the above ground parts of plants. Also other elements like zinc (Zn) and slightly less copper (Cu) and manganese (Mn) are subject to similar translocation mechanisms and all of them can get toxic for plants at high levels. Other elements such as Pb, Ni, Cr, V and generally also Fe are poorly taken up from soils and generally do not translocate to the aerial plant parts, and their presence in leaves and twigs indicates absorption from air (Ny and Lee 2011, Sæbo et al. 2015).

Increased concentrations of Pb and Cr in leaves confirm that they penetrate into these tissues via the epidermis as their uptake from the soil is minimal (Megremi 2010). In cells, toxic forms of metal(loid)s like As V and Cr VI are reduced to less toxic forms *i.e.* As III and Cr III. Plants have an even more effective defence mechanisms *i.e.* methylation of As, Cr and Se and release of methylated forms to the air. With high levels of As in the soil, some plant species release significant amounts of As into the air, However, recent studies suggest that As methylation occurs already in the soil by rhizo-bacteria and that plants absorb methylated As (Lomax et al. 2011).

Both, organic compounds of high molecular weight (Wild et al. 2006) and HM (authors own data) slowly, through physical diffusion, penetrate through the wax into the living cells of the epidermis where they are sequestered in the vacuole or cell wall.

Aerosols moving near the ground encounter plants as ‘obstacles’, equipped with folded leaves, often covered with trichomes or hairs and possessing an electro-magnetic charge, what together effectively increases the accumulation of PM on their surface (Pough et al. 2012, Popek et al. 2013, Gawronska & Bakera 2015).

All plants accumulate PM on their surface meaning, all are involved in air phytoremediation and act as biofilters (Bakker et al., 1999, Barack, 2002, Farmer 2002). However, research performed on a large number of trees and shrubs revealed that they can differ by more than 10-fold in their PM accumulation ability (Sæbo et al. 2012, Popek et al. 2013).

The following tree species are known as potentially good phytoremediation species: *Pinus sylvestris*, *Betula pendula, Fraxinus pensylvanicus, F. excelsior, Pyrus caleriana, Sorbus intermedia, Populus sp., Alnus spaethi, Robinia pseudoaccacia, Sophora japonica Elaeagnus angustifolia, Ligustrum lucidum, Quercus ilex, Tilia europea* ‘Pallida’. Equally excellent functions for phytoremediation perform shrubs that are growing closer to the ground like: *Pinus mugo; Syringa meyeri; Spireae sp., Stephanandra incisa, Taxus media, T. baccata, Hydrangea arborescens; Acer campestre, Physocarpus opulifolius; Sorbaria sorbifolia; Forsythia x intermedia* (Dzierzanowski et al. 2011, Saebo et al. 2012, Popek et al. 2013, Wang et al. 2013, 2015, Sgringa et al. 2015). In the densely built-up city centres where the surface for growing plants is limited following climbers can fulfil a role in phytoremediation: *Hedera helix; Parthenocissus tricuspidata, P. quinquefolia, Vitis riparia* and *Polygonum aubertii* (Borowski et al. 2009, Ottele et al. 2010 and own not yet published data). Also herbaceous plants deserve attention as phytoremediation plants: *Achillea millefolium, Berteroa incana, Polygonum aviculare, Brickellia veronicifolia, Flaveri trinervia* and *Aster gymnocephalus* (Weber et al. 2014).

Conifers plants are excellent for air phytoremediation due to the abundant wax layer on the needles and, as evergreens, they are active in pollutant accumulation during the whole year. These species keep needles for more than one year and being so efficient in retention of pollutants, they eventually can die because of too ” heavy loads” of pollutants. The only genera very tolerant and well surviving contamination with PM in this group is the yew (*Taxus sp*.) with a very efficient self-cleaning mechanism.

For their effective remedial properties, conifers should be more frequently recommended for planting however at an adequate distance from the emission source and at moderate pollution intensities. When creating “green filters”, significant declines in PM were reported already at 100 meter distance from the edge of a highway (Fuller et al. 2009).

3. Gaseous air pollutants

The main gaseous air pollutants are CO, NO_x, SO_2, O_3 and some organic compounds. One of the main greenhouse gases causing human concern is CO_2, which for the plant is the essential molecule in the process of photosynthesis and in an elevated concentrations, to certain extent, promotes the synthesis of plant biomass. Gaseous air pollutants enter into the plants mainly through the stomata and through wax and cutin, though at a marginal level.

Carbon monoxide (CO) in the environment raises larger concerns for humans for whom it is acutely toxic already at 750 ppm. Plants, however, tolerate CO to a relatively high concentration. CO originates from the combustion of organic materials in conditions with limited oxygen.

Toxicity of CO in humans results from binding with the active site of hemoglobin, obstructing oxygen transport. CO is metabolized by plants either by further oxidation to CO_2 or is reduced and incorporated to amino acids. There exist large differences between species in the ability of uptake of this gas by plants (Bidwell and Bebee 1974). From a list of 35 investigated woody plant species 17 were characterized by high ability to fix CO. Among trees these are: *Acer saccharum, A. saccharinum, Gleditsia triacanthus, Pinus resinosa, P. nigra*, *Fraxinus pennsylvanica*. and two shrubs species *Syringa vulgaris* and *Hydrangea sp.* Two popular ornamental indoor plant species in moderate climate (and gardened in subtropical and tropical zones) *Ficus variegata* and *Phenix roebelenii*, also metabolize CO efficiently (Bidwell and Bebee 1974).

Nitrogen (N), an important building block of proteins, is after carbon the second most important element for plants. In nature it occurs in several different forms, however plants can only absorb fixed nitrogen (*i.e.* other than in the molecular form N_2). The atmosphere is often contaminated with nitrogen containing gasses such as NO_x and NH_3. In urban areas nitrogen oxides (primarily NO_2) are the dominant N-containing pollutants due to vehicular emissions. The negative environmental impacts of NOx are associated with: (i) active participation in the

UV radiation assisted ozone formation cycle (however the net increase of ozone requires also co-presence of volatile organics), (ii) acid rain formation and (iii) recently discovered post-translational modification of allergenic proteins as a result of their nitration (Reinmuth-Sezlet et al. 2014). Significant intensification of such processes is observed in polluted air (Zhao et al. 2016, Lu et al. 2014, Bryce et al. 2010). However, plants are capable to utilize nitrogen in the form of NO_2. Some years ago Morikawa et al. (1998) investigated the ability of 217 herbaceous and woody species to take up NO_2 and discovered up to 600-fold differences in NO_2 uptake and assimilation between them. They reported the following woody species to be the most efficient: *Magnolia cobus*, *Eucalyptus viminalis*, *E. grandis*, *E. globulus*, *Populus nigra*, *Populus sp*., *Robinia pseudoacacia*, *Sophora japonica*, *Prunus cerasoides* and as herbaceous species: *Nicotiana tabacum* and *Erechtites hieracifolia* calling them NO_2-filice (Morikawa et al.1998). Further investigations of 70 species of woody plants recommended for the cultivation in the vicinity of heavy traffic roads revealed greater differences in the response to NO_2. Among the tested species *Robinia pseudoacacia*, *Sophora japonica*, *Populus nigra* and *Prunus lannesiana* proved to be the most interesting species tolerant to high levels of NO_2 and efficiently assimilating this form of nitrogen. Therefore, they are the recommended for air phytoremediation (Takahashi et al. 2005).

NH_3 (ammonia) is also considered to be one of the primary N-containing air pollutants The major sources of atmospheric NH_3 are agricultural activities, animal feedlot operations, and domestic waste water effluents. All plants are able to take up ammonium directly from the air to a certain extent. Adverse effects on vegetation occur when the rate of foliar uptake of NH_3 is greater than their level of tolerance (Rogers & Aneja 1980, Krupa 2003, Ghaly & Ramikrishnan. 2015).

Ecosystem pollution with nitrogen gasses cannot be viewed from the amounts of NO_2 or NH_3 but must be seen in the context of total deposited N. Data suggest that a critical load of 5-10 kg ha^{-1} $year^{-1}$ of total N can be deposited on more sensitive terrestrial ecosystems (heaths, bogs, cryptogams) and 10-20 kg ha^{-1} $year^{-1}$ would be tolerated by forests. Crop plants could tolerate higher than the earlier listed values of nitrogen from air, but it is highly dependent on soil conditions (Krupa 2003).

Biogenic volatile organic compounds (BVOC) are natural organic compounds should also be taken into account as substances polluting the air as they are released to the environment in considerable quantities. Plants as sessile organisms use such compounds in order to defend themselves against pathogens, herbivores and other stress factors. Typically, these are compounds of low molecular weight, including isoprenes, monoterpenes, sesquiterpenes and other C10-C15 chemical structures (Curtis et al. 2014). BVOCs are easily released to the atmosphere in gaseous form, and in the presence of NOx and light, they contribute to photochemical reactions involved in the formation of secondary pollutants. Introduction of biogenic and anthropogenic VOC shifts the equilibrium of the atmospheric processes in which NO and NO_2 are involved towards higher ozone contents (Calfapietra et al 2013). Production of BVOC by the plants is still intensively investigated, also because of the possibility of EPFR formation when adsorbed on PM. The phenomenon of O_3 and EPFR creation should be taken into account in the current recommendations to increase greenery in urban areas. Studies allowed distinguishing between two groups: low BOVC and high BOVC emitting plants. The low BVOC emitting group of plants includes genera such as *Malus, Camphora, Citrus, Pyrus* and species as *Ginko biloba* and *Juglans nigra*. To high-emitting BVOC plants belong the following genera: *Salix, Quercus, Populus, Pinus* and *Liqidamber* (Benjamin and Winner 1998, Karl et al. 2009, Calfapietra et al. 2013, Curtis et al 2014).

Ozone contained in the troposphere is among the main threats to plants. Although all plants are susceptible to ozone, inter- and intra-species differences in ozone tolerance were found, and depend on the existence of a genetically determined efficient antioxidant system. In recent years, studies have been undertaken on the active protection against the ozone damage in plants by the application of synthetic antioxidants *i.e.* ethylene urea (EDU). European ash (*Fraxinus excelsior*), previously damaged by ozone during subsequent years was successfully protected against ozone injury after application of EDU (Paoletti et al. 2011).

To summarize, during evolution, plants colonized different environments by developing abilities to cope with all kind of stresses including air pollution. Plants with their large, conducive to pollutants accumulation surface, are the most efficient and natural tool in the hands of a man for decreasing air pollution and with our knowledge will be effectively and widely used for this purpose.

4. Plants as a barrier for air pollutants

The primary processes of plants are based on gas exchange to obtain CO_2. However, during this process, they inevitably also absorb contaminants present in the air. Consequently, they play a role as biological air filtering systems. The scale of this positive role of plants can vary, from large areas of forest, which can protect a city or even regions, to small scale, with only a few indoor plants in apartments or offices. It does not matter what is the scale, the intended use of plants in this context, is to reduce air pollution and to protect human health and well-being as well as improving the environment for other organisms, improve climate and even enhance the monetary value of properties. The positive functions of trees and forests were object of many studies and a very good example is one conducted by D. Nowak et al. (2014). They estimated that trees and forests in 2010 removed 17.4 million tons of air pollutants throughout the United States, with human health effects valued at 6.8 billion US dollars, including avoidance of more than 850 human deaths. The positive role of forests on climate and the environment, both globally and regionally is clearly large. As air pollution became one of the major threats in many parts of the world, forests may play a very positive role, which is a good argument to invest in afforestation policies. On smaller scales, parks and plant barriers can play a similar role in order to improve environmental goods and services. A fully overgrown stand was shown to stop most of the pollution within a distance of the first 20 meters, with as dominant species *Tilia platyphyllos* (Popek et al. 2015) and *Quercus ilex* (Sgrigna et al. 2016). In case of pollutants emitted by vehicles, the concentration can be lower close to the road, because pollutants are blown further on where the particles are partially stopped, leading to increased pollutant concentrations (Popek et al. 2015; Sgrigna et al. 2016). To obtain a good protective role of parks in the cities, the belts probably need to be at least 20 meters wide, with a canopy consisting of trees and shrubs. The mixture of species, age and the proper space for the air to move into the filter, is beneficial for a good effect. In a belt of 50 meters in width, a decrease in PM with more than 50% was observed (Popek et al 2015). Especially fine and coarse PM decreased, with a much lower decline of the ultrafine fraction. The results presented indicate that forests and parks are sanctuaries with much cleaner air than there where people spend most of their time. Especially the places where people live, play and work, should have the best conditions. Particularly people with cardiovascular and respiratory problems are very sensitive to PM, and for young children, it is crucial for the development of their health. City planners should include such aspects when planning parks, in which the outside belt of trees should possess a high capacity for air pollutant biofiltration.

Streets and roads with intensive traffic are sources of linear pollution that are difficult to control. Vegetation can be useful to reduce the pollutants emitted by transport vehicles at such places. The vegetation in the vicinity of transport routes can fulfill a useful role in all its growth forms, as trees (Tong et. al. 2016, Popek et al. 2013, Sæbo el. al. 2015), shrubs (Popek el. al. 2013, Sæbo el. al. 2015) and herbaceous plants (Weber at al. 2014). One of the most air-polluting environments are highways, which also produce noise pollution. To combat the latter negative impact on the environment usually noise screens are used. Screens protect better against noise pollution than plants, but pollutants are dispersed. They are transported with the air streams, some passing over the screens, and they may be deposited on the screens or on the road, being easily re-suspended by the next vehicles that are passing. Tong et al. (2016), evaluated the protective role of noise screens as a solid barrier only (i), solid barrier covered with vegetation as green wall (ii), vegetation barrier (iii) and the combination solid-vegetation barrier (iv) as to compared to free space in the vicinity of the road. Solid barriers (i) increased PM concentrations along the roadside though part of the PM was dispersed above the barrier. Solid barriers with vegetation cover (ii) slightly reduced the PM concentration but the best result was obtained with a combination of a vegetation barrier (iii) and a solid barrier with vegetation (iv) since both significantly reduce PM concentration. The authors used evergreen conifer plant species with low BVOC emission and high LAI, in order to obtain a biofiltering function the whole year around. The results of this experiment indicated an additional positive effect for drivers. Long trips on motorways surrounded by solid noise screens become tedious, which increases the chance for accidents. Trees behind the screens both change the landscape and create a surface for the deposition of air pollutants. When buildings are constructed close to the road they form canyons. In such canyons, trees may reduce the concentrations of NO_2 and PM by 40% and 60% respectively (Puogh et. al. 2012), although there exist also papers reporting the opposite (Jin et al. 2014). The latter might be due the fact that trees lower wind speed in and ventilation of the streets. In this respect, two factors are important: (i) the density of the “phytobarrier” and the location of the vegetation. The most frequently used method of measurement for density of the barrier is Leaf Area Density (LAD) (Petroff et al. 2009, Puogh et. al. 2012). A comprehensive overview of urban vegetation and air particle dispersion and deposition was made by Janhall (2015), highlighting several significant relationships. Phytobarriers need to be permeable enough to let air to penetrate through it but solid enough to keep moving air close to the surface of the vegetation. In developing the optimal solution for the best pollutant deposition in street canyons the model of plant distribution developed by Gromke et al. (2016) can be helpful. An optimal situation can be achieved by using the appropriate species and pruning the barriers to the best height and porosity. Retention is higher in case the plants are equipped with trichomes, rough wax and an abundant microbiome (fungal mycelium) (Sanchez-Lopez et al. 2015). PM deposition in street canyons can be increased, without the problems outlined above, if climbing vegetation is used to form green walls in the cityscape (Ottele et al. 2010).

With wide streets, limited dispersion is not a problem. Usually, there is also more space for plants, so that deposition areas can be established for the pollution in order to improve air quality. Other groups of plants should also be used, such as shrubs and herbaceous plants. These plants grow lower than trees, and can be located closer to the edge of the road without disturbing neither the driver's view for traffic and road signs, nor air movements. Pollutants deposited on herbaceous plants are removed by mowing and removing the grass during the season. Herbaceous plants possess more shallow roots and also take up some pollutants (mainly heavy metals) from the top layer of the soil, thus the harvested biomass of these plants also removes some pollutants from the soil. Removal of air pollutants should take place on all possible levels both regional and local as well as inside our own homes and offices (see below).

5. Indoor phytoremediation: main pollutants and recommended plants

In many parts of the world air pollution still continues and will remain a problem threatening the health of people and the environment for a long period of time. The purpose of this subsection is to illustrate the problem and to present measures that can be taken to protect people from negative effects in houses, apartments and workplaces. Indoor air pollution has been recognized as a public hazard globally. In developed countries polluted air occurs from polluted outdoor air and products and materials with which are used in apartments and offices. In contrast, in underdeveloped countries it comes mainly from household cooking and heating and in some places partially also from transportation. Nowadays, many people spend most of their time indoors where the air is often more polluted than outside because there are additional sources of pollutants. The scale of the problem is indicated by the recognition by the WHO as a ”sick building syndrome” (SBS) disease. Particular attention should be paid to this problem in newly constructed buildings because in these VOC emissions are the highest and only decrease over time. Usually, the emission of formaldehyde represents a significant risk factor for the SBS symptoms. At this point, it is important to monitor the indoor pollution and to increase awareness of residents (Takigawa et al. 2010). Heating systems and air conditioning equipment that are functioning in buildings and apartments need to be very well maintained because their use sometimes leads to increased ionization and ozone in the air (Britigen et al. 2006). Plants biofiltrating indoor air, which in recent years was referred to as indoor phytoremediation, is of high interest because of (i) the low cost, (ii) the ease of implementation and maintenance of this environmental friendly technology, and (iii) the fact that some species possess a surprisingly high efficiency of uptake of pollutants. The use of potted plants to remove VOCs from indoor air and a list of assessed species have been reviewed by Cruz et al. (2014a).

The list of indoor air pollutants is very long, starting from chemical impurities coming from outdoor sources: vehicle exhaust, plumbing vents and building exhaust, radon and combustion byproducts as well as from indoor sources: volatile organic compounds (VOC) from adhesives, upholster, carpeting, copy machines, cleaning agents, tobacco smoke, combustion byproducts from stove and fireplace, biological contaminants: pollen, bacteria, viruses, fungus, molds etc. Gaseous pollutants are the most difficult to remove from the air, which also not often achieved by air-conditioners. Therefore, here the valuable ability of plants comes to the fore, since during gas exchange they simultaneously absorb and inactivate pollutants.

The following VOCs are most commonly found in homes and offices: formaldehyde, benzene, toluene, xylene, carbon monoxide, naphthalene, nitrogen dioxide, ammonium, polycyclic aromatic hydrocarbons including benzo [*a*] pyrene, trichloroethylene, cigarette smoke and others. Sometimes the list contains even several hundreds of compounds. In the presently constructed buildings, formaldehyde is most often listed on the first place of pollutants and a great number of investigations among indoor phytoremediation are devoted to this compound. Despite the fact that it is already over 20 years old, the work of Giese et al. (1994) dedicated to the detoxification of formaldehyde is still very interesting. One of the investigated species was the spider plant (*Chlorophytum comosum*), which is a very common ornamental plant in apartments and offices. Plant were exposed to ^{14}C-formaldehyde for 24 hours and analyzed. Results showed that about 88% of the radioactivity was recovered in the plant, and was incorporated into organic acids, amino acids, free sugars, and lipids as well as cell-wall components. The authors identified also two dehydrogenases (including one glutathione dependent) involved in oxidative detoxification of formaldehyde (Giese et al. 1994). The role of the enzyme formaldehyde dehydrogenase in the degradation of formaldehyde was also endorsed by others (Xu et al. 2011). The activity of formaldehyde dehydrogenase in three plant species: *Chlorophytum comosum, Aloe vera* and *Epipermum aureum* (7.8, 2.8 and 4.4 nmol min^{-1} mg^{-1} protein respectively), confirms the role of *Chlorophytum* as a good air phytoremediator plant. Kim et al. (2010) evaluated capacity of 86 species of plants for removing formaldehyde from indoor air. The most efficient species are: *Osmunda japonica, Selaginella tamariscina, Davallia mariesii, Polypodium formosanum,* *Psidium guajava, Lavandula* spp., *Pteris dispar, Pteris multifida,* and *Pelargonium* spp., that are removing more than 1.87 µg $m^{-3.}$ cm^{-2} of leaf area over 5 h. Based on efficacy of formaldehyde removal authors divided tested species into three groups: excellent, intermediate and poor removal. Species classified as excellent (removing more than 1.2 ug $m^{-3.}$ cm-^{2} of leaf area over 5 h) are taken into account as the best candidates for phytoremediation in places where formaldehyde may appear as a health threatening gas. The results of this valuable work contribute to the development of indoor phytoremediation. Indoor plants are cultivated in a prepared growing medium or in soil. Both substrates are rich in microorganisms which also participate in the degradation of VOC, using them as a source of carbon and energy. Gas exchange with soil is facilitated by watering plants which ‘pushes’ air out of the soil followed by a period of drying which allows ‘new’ batch air (with contaminants) to penetrate into the soil pores. The participation of both, the aerial parts of plants and the root zone in the formaldehyde removal during the day and night was assessed using two species, *Fatsia japonica* and *Ficus benjamina*. During the day both species were equally well removing formaldehyde by both the aerial parts and the root zone. However, during the night the above ground parts of the plants removed less than one tenth of what was achieved in the soil where in the process of removing of formaldehyde is performed by soil and rhizobacteria microorganisms (Kim et al. 2008). Xu et al. (2011) demonstrated that cultivation of plants like *Chlorophytum comosum, Aloe vera* and *Epipermum aureum* resulted in almost equal proportions of 50% formaldehyde removal by both microorganism and plants. Aromatic hydrocarbons like benzene and its derivatives toluene, xylene ethylbenzene (known as BTEX) are common air pollutants in apartments and offices. They enter to indoor from the outside air but are also emitted by internal sources in the room. Applied ^{14}C-benzene is taken up by plants and in a first step hydroxylated to phenol or pyrocatechol. A further step is cleavage to muconic acid and in a next step fumaric acid. These metabolites were confirmed by the high radioactivity of these products. The research was conducted with three woody plant species: *Acer campestre, Malus domestica* and *Vitis vinifera* (Ugrekhelidze et al. 1997). One of the first publications describing the removal of benzene from indoor air presented data for seven taxa: *Dracaena* 'Janet Criag', *Dracaena marginata, Epipermnum aureum, Schefflera* 'Amate', *Spathiphyllum* 'Petite', *Spathiphyllum* 'Sensation', *Howea forsteriana*. Tested dracaenas are from different species and differ in their efficiency of benzene removal. Differences between cultivars of *Spathiphyllum* show potential of improving efficiency during breeding processes (Orwell et al. 2004). During their search for plant species removing benzene from indoor air Liu et al. (2007) evaluated 73 species exposing them during two hours to fumigation with this gas. Results showed high differences between tested plant species in their ability of benzene removal. Out of the 73 species 23 did not change the benzene level in the air, 13 species removed between 0.1and 9.99%, 17 species removed between 10-20% and another 17 species removed 20-49% of benzene; three species even showed able to remove 60-80% of the gas. Out of the 73 species 10 were selected for the second experiment, in which plants were exposed to fumigation for two days: *Crassula portulacea, Hydrangea macrophylla, Cymbidium* ' Golden Elf ', *Ficus microcarpa* var. *fuyuensis, Dendranthema morifolium, Citrus medica* var. *sarcodactylis, Dieffenbachia amoena* 'Tropic Snow', *Spathiphyllum* 'Supreme', *Nephrolepis exaltata* 'Bostoniensis' and *Dracena deremensis* 'Variegata'. After standardization of the results to plant leaf area and extrapolation to room size, the authors concluded that for indoor phytoremediation of benzene the best were *Crassula portulacea*, *Hydrangea macrophylla*, and *Cymbidium* ‘Golden Elf ‘ while *Dracena deremensis* 'Variegata' was the least effective (Liu et al. 2007). Sriprapat and Thiravetyan (2016) investigated the ability of eight plant species for removing benzene from the air: *Syngonium podophyllum, Sansevieria trifasciata, Euphorbia milii, Chlorophytum comosum, Epipermnum aureum, Dracena sanderiana, Hedera helix* and *Clitoria ternatea*. All species efficiently removed benzene, but the best was *Chlorophytum comosum*. These authors also underlined the importance of the plant microbiome, especially both the endo- and phyllobacteria, in this process.

Another common air polluting VOC is toluene, which is removed by several plant species commonly grown in homes and offices: *Schefflera elegantisima, Philodendron* spp. 'Sunlight' and *Hedera helix* (Kim et al. 2011) and *Hedera helix* ‘Gitte’ that was investigated in the work by Cruz et al. (2014b). In order to evaluate the removal of the aromatic hydrocarbon xylene from the air, Sriprapat et al. (2013) tested 15 species. The best species in this study was the recently very popular in public places, very resistant to drought and low light intensity *Zamioculcas zamiifolia* (Sriprapat et al. 2013). Toabata et al. (2016) demonstrated that this species can also successfully remove another VOC, ethylbenzene, from the air.

Yang et al. (2009) assessed 28 ornamental plant species for their ability to remove five volatile indoor pollutants: benzene, toluene, octane, trichloroethylene (TCE) and α-pinene. Huge differences in the efficiency of removal of these compounds were found between the different plant species. Out of the 28 species only *Hemigraphis alternata, Hedera helix, Hoya carnosa* and *Asparagus densiflorus* were efficiently removing all five pollutants. Others as

Tradescantia pallida displayed high removal efficiencies for four of the five VOCs. *Fittonia argyroneura* very effectively removed benzene, toluene and TCE, *Ficus benjamina* effectively removed octane and α-pinene while *Polyscias fruticosa* remove only octane.

In most laboratory tests plant species are assessed in relation to one chemical compound while in real life conditions plants usually have to cope with cocktails of several pollutants. Therefore, experiments using cocktails of pollutants are crucial. Plants exposed to a mixture of pollutants are removing them with varying efficiencies depending on plant species and type(s) of pollutant(s). Removal efficiency of a mixture of benzene, trichlorethylene (TCE) and toluene from polluted air was evaluated using following species of ornamental plants: *Pelargonium domesticum*, *Ficus elastica*, *Chlorophytum comosum* and *Kalanchoe blossfeldiana*. All species were good in removing benzene and toluene. TCE was preferably taken up by *C. comosum* but the removal of benzene and toluene was decreasing (Cornejo et al. 1999). Orwell et al. (2006) reported an effect of synergy was. When *Dracaena* 'Janet Criag' was exposed to a mixture of toluene and xylene in ranges between 1 and 10 ppm, these gases were more efficiently removed in comparison to when is was exposed to each of them individually.

6. Future research needs

Because people in their homes and offices try to maintain optimal climatic conditions for life and since in our everyday life, we use fragrances and many other substances of plant origin (Rehind 2014) there is chance that plants can improve human wellbeing. In many areas of the world the same ornamental plant species are grown. This has the advantage that the results of the investigations on the main pollutants removal can be applied at many places.

In case of indoor phytoremdiation, the world can almost be considered as one global village. Despite the fact that over 20 years passed since the first book of the "father" on indoor phytoremediation Dr. Wolverton (1996) was published and the knowledge already is quite extensive, still much is left as open questions and to be done. Indoor phytoremediation arouses growing interest of society, which often asks what species are recommended to maintain air in homes and offices safe and how many plants should be cultivated. Regarding plant species we already have at our disposal a significant amount of information, but knowledge on how many plants and what should be the leaf surface are needed for an adequate pollutants removal is still limited. One of the first real scale trials to reduce indoor air pollution was carried out with the very good indoor phytoremediation species *Dracaena* *deremensis* 'Janet Craig'. Three and 6 plants of this variety were placed in office rooms and it turned out that just 3 plants reduced pollution level by 75% below the threshold level of 100 ppb. These potted plants were equally effective in both air-conditioned and non air - conditioned rooms (Wood et al. 2006).

In an attempt to solve the lack of adequate practical experience, Thomas et al. (2015) developed a mathematical model that takes into account the amounts of plant material, building air volume, VOC concentrations and air exchange. After a positive validation this model can become a very valuable tool in the implementation of the technology of indoor air phytoremediation.

Another area in which indoor phytoremediation can be a valuable ally to limit is to combat the negative effects of smoking tobacco. The reason for undertaking this study was the finding that nicotine is present in many foods of plants origin. The first clue was that the very common ornamental plant *Epipremnum aureum* takes up and transports nicotine to its above ground organs. This species does not metabolize the nicotine and in higher concentrations it is even toxic for the plants resulting in an acceleration of the aging process (Weidner et al. 2005). Innovative are the results of a study with peppermint (*Mentha x piperita*) as a model plant. The results demonstrated that peppermint takes up nicotine from a soil with plant debris and also absorbs it from air contaminated with tobacco smoke (Selmar et al. 2015). The presence of nicotine in many plant foods allows to suppose that many plant species possess the ability to take up this pollutant from the environment. This opens up new possibilities for indoor air phytoremediation research in order to find the most effective ornamental plants to protect nonsmoking family members from indirect smoking effects.

There is still a strong need to apply indoor phytoremediation for the immediate protection of human health. Already in 1996, Wolverton and Wolverton conducted a pioneering experiment of placing in the same house in the living room plants and treating the adjacent bedroom as controls without plant. The experiment was carried out for 3 months and was repeated at another season of the same year. In the room with plants humidity was higher than in the plant-free bedroom. Concurrently, microbial levels were more than 50% higher in a room without plants despite lower humidity. These results indicate that the plants generate a more friendly environment *i.e.* with lower numbers of microbes and a higher air humidity. With the today's possibilities of molecular analyses, we should more concentrate on the role of the microbiomes associated with plants. In the above case, the plants' microbiomes might act as counterparts against pathogens within microbial ecosystems. In future, strategies can probably be developed of management of the environment in homes, apartments and offices that would be beneficial to human (Berg et. al. 2014).

Phytoremediation of indoor air also opens up new possibilities for human wellbeing. A good example is provided by Boraphech et al. (2016) who used the popular plant *Sansevieria* spp. for removal of trimethylamine (TMO) (responsible for so called fishy odor) from air. Both living plants and non-living plant material removed the smell. Massive secretion of TMO by the human body is called as fish odor syndrome, a rare metabolic disorder causing weak (or none) oxidation of trimethylamine to trimethylamine oxide. When the oxidizing enzyme is in disorder, TMO is accumulated in excess and released from the body through sweat and urine but also in the breath, causing a strong odor resembling the smell of rotting fish. Especially difficult experience with this disease is during childhood when peers do not accept such a person claiming that she/he does not care about hygiene. Currently, some drugs are available that reduce the disease state and also proper diet may be helpful, but it was demonstrated that help also might came from indoor phytoremediation, thus it can be said that phytoremediation marched with help into medicine (Boraphech et al. 2016).

Summarizing it can be concluded that with help of the properly chosen plant species there is a chance to create a sanctuary for a more safe and pleasant life.

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