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A review on particulate matter and heavy metal emissions; impacts on the environment, detection techniques and control strategies

Abstract

Population growth, Urbanization and Industrialization created many social economic environmental and health issues for Pakistan. Industries are major sources of environmental pollution specially water and air pollution due to lack of advanced technologies. This review mainly focused on the emission of heavy metals from industries, their detection methods which are available in Pakistan. Heavy metals are released into the environment through different industries and combine with other pollutants to form secondary compounds which are even more harmful to the environment. When these heavy metals combine with water and soil, they change the soil and water ecosystem functions, plant growth mechanism and disrupt the many other functions of soil. More so, groundwater contamination owing to these metals poses many serious health problems in humans and animals, and when this groundwater mixes with sea water, it threatens the health of aquatic lives and food species growing in water and bioaccumulated in the food chain of biological system. By using advanced detection, controlled and treatment technologies, ecosystem can be saved from the possible problem of heavy metal emissions and contamination.

Keywords: Heavy Metal Emission, detection techniques, Effect on ecosystem

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Introduction

Gaseous emissions from coal burning, metals processing units, smelters, petroleum products, forest fires and volcanic eruptions contain hazardous substances. These emissions contain heavy metals which not only pollute the environment, but also affect the human health, soil properties, plant life and microbial life.

Particulate matter (PM) refers to a combination of solid and liquid droplets present in air. PM can be fine or large as dust particles, smoke, soot or dirt that can be seen by naked eye. The fine particles can be seen by an electron microscope.

There are two types of particulate matter; (1) PM_{10}, these are characterized as inhalable particles having diameter in the range of 10 micrometers or less, (2) $PM_{2.5}$ are also fine inhalable particles having diameter in the range of 2.5 micrometers or less. Toxicity of fine particles is more compared to coarse particles.[1]

Potential causes of emission

Emission of PM to atmosphere results from the contribution of both natural sources and from gases by various chemical processes. In addition, major reason for their emission is human activities. Particles released directly from the sources come under the heading of primary particles, while those from gases emission come under the heading of secondary particles. Major natural and anthropogenic activities responsible for PM emissions are aerosols (marine and biogenic), off-road and on-road traffic, forest fires, burning of fossil fuels, cooking on coal or grilling on gas, smoking cigarettes, domestic, industrial, agricultural pollutants, stationary combustion processes, combustions of agricultural waste materials and construction process. Vehicular emissions are responsible for addition of PM to the atmosphere.[2] Light duty gasoline vehicles (LDGV) are also the cause of emission of PM, and it usually comprised of carbonaceous materials having minute content of water soluble ions.[3] Motor vehicles also cause PM emissions, and the major contributor to this emission results is the frictional contact among components of brake system. PM_{10} emission to the atmosphere is due to tyre wear. In the UK, the expected rubber loss from tyre wear is 53×106 kg, and it is considered to be the major contributor to non-exhaustible PM_{10}. Furthermore, road wear and road dust are also the contributor of PM emission.[4] Sea salt are sources for the emission of Na, Cl and Mg, secondary aerosols are sources for NO_3^-, SO_4^{-2} and NH^{4+} emission, and mixed fuel or industrial oil combustion are sources for SO_4^{2-}, V and Ni emission.[5] Automobile catalytic converters are reason for emission of Pd, Rh and Pt due to their use as catalysts in these devices.[6] In Hong Kong, the significant contributor to PM emission is considered to be mobile vehicle and super regional transport.[7] Ammonia (NH_3) emitted from fertilizers or livestock manure often acts as a limiting factor for the conversion of acidic components to their salts like $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3. Gaseous sulfur released from volcanic emissions or from decaying vegetation can further form secondary particles of sulfate in the atmosphere. Open sources i.e. windblown dust, road dust account for 70 % $PM_{2.5}$ emissions. While others are assumed to be due to metal processing, burning of coal for electricity generation and industrial fuel combustion is another potential cause.[8]

Impacts of particulate matter on the environment

Particulate matter which is considered as a heterogeneous material poses difficulties for the varieties of ecosystems and the vegetation and living species of different ecosystems. Their effects on surfaces of vegetation merely depend upon their size rather than the chemistry of particulate matter. Therefore, the loading of such components can be illustrated by their size distribution. One of the particulate matter i.e. dust affects adversely the photosynthetic activities of plants as the loading of dust results in abrasion and heating, which consequently reduces the intensity of the photon reaching leaves' surfaces and ultimately leads to reduced rate of photosynthesis. Leaf surfaces become damaged by alkaline and acidic components, while some other particulate matter becomes incorporated into plants through cuticle. Rhizosphere becomes the site for the uptake of the materials by plants, which imparts serious effects on the ecosystem. If these materials get incorporated through rhizosphere, they negatively affect the crucial nutrient cycles especially by posing devastating effects on bacteria and fungi living in the vicinity of plant roots, which take a crucial part in nitrogen cycle. Availability of various cations, including aluminum and some other alkaline cations also affects the ecosystem via the deposition of different types of particulate matter. Particulate matter affects the ecosystems in terms of climate change as the presence of various kinds of PM reduces the proportion of radiations that is required by plants which results in reduced precipitation.[9] In addition to climate change, they are also responsible for cloud condensation nuclei either directly or indirectly.[10] The effects which are produced by accumulation of pollutants of PM in one area also affect the air quality of other areas.[11] Another difficulty which is caused by fine particles is reduced visibility. Several haze episodes were visualized in china due to $PM_{2.5}$ particles, and the fog produced was found to contain much higher levels of $PM_{2.5}$.[12] Nitrogen dioxide has the ability to absorb the visible irradiations at certain concentration level which cause visibility problems. Furthermore, these problems arise due to prominent concentrations of the water vapors, carbon dioxide and ozone. NO_2 reacts with volatile organic compounds released by human activities and form photochemical smog, which not only affects the beauty of the ecosystem, but also poses problems for the living species. Nitrogen oxides are also responsible for the acidification of the water bodies. The lower pH value is harmful for the species living in water ecosystems as some organisms cannot survive under lower pH values. It further causes eutrophication which leads to excessive growth of the algae, which covers the surface of water bodies and lowers the chances of availability of oxygen to the living species, resulting in their death.[13] Plants growth also gets affected by the combination of PM with sulfur dioxide. In addition, harmful elements (fluorine or arsenic) cause damage to wild life when they fall on plants, and these plants get ingested by animals. Devastating effects in plants are produced within the leaves as they are responsible for various activities of plants due to presence of the main building blocks in them. When sulfur dioxide falls on leaves and get incorporated in to them, they convert it into less harmful form i.e. sulfate. When its concentration increases, they become unable to perform such as fast conversion of sulfur dioxide to sulfate by first converting it into sulfite leading to damaged structures, which can be seen as brown or brittle leaf surfaces. Surfaces of plants get brown patchy surfaces due to selenium. Trace elements present in air affect the process of cloud formation. Excessive presence of PM in air especially water vapors and carbon dioxide causes greenhouse effect and eventually, global warming. Warmed temperature conditions can generate floods in certain areas, while in some result in drought. It can damage the well managed ecosystems like that of northern ecosystems, where it results in the thinning of ice, which not only affect the fish, but also the humans carrying out their businesses on these permafrost.[14]

Possible emission control systems

There are many reasons for the emission of PM which poses environmental and serious health problems. Therefore, it is important to reduce the emission of PM from different sources. Dust and asphaltic air born PM emitted during synthesis of asphalt aggregate mixture can be reduced by simply following some steps. To remove the dust and other particulate matter the apparatus is attached to fiber filter dust collector. High temperature is maintained in the drum mixer, therefore asphalt mixture is added to drum in a way that it results in minimum smoke production, and the resultant dust upon aggregation of product is collected in connected fiber filter collector. Gathered dust is returned back to drum, so it gets admixed with asphalt and become coated with aggregate material.[15] Diesel engines are providing great support to human population for the transportation of goods, yet they are producing a large amount of PM which is comprised of soluble organic fraction (SOF) of hydrocarbons and carbonaceous soot. To overcome this issue, several technologies and systems are developed. One of them is the use of traps and catalysts. Mainly three kinds of traps are used, namely; wall flow filters, foam materials and fiber filters. Among them, wall flow filters have greater efficiency of approximately 90 % due to their manufacturing on the basis of shallow filtration mechanisms. In addition, catalyzed traps can be employed which are based on either shallow or deep filtration. While using them, issue arises on the contact of carbon and catalyst. This can be resolved by the use of multifunctional catalyst, liquid phase generated catalysts or oxygen spillover promoting catalysts.

Diesel oxidation catalysts were utilized for reduction of PM emission in 1996 and 1998 in the US and Europe respectively. Noble catalysts were used in them to get better results for gasoline based engines. It was a useful approach for removing hydrocarbons and CO but was not effective for the removal of soot.

The Peugeot-Citroen Société' Automobiles system utilizes SiC wall flow monolith for its improved physical characteristics and better filtration performance. It further utilizes active regenerative strategy, pre oxidizer and Ce fuel additives. This system has apparently no disadvantages except of its high cost, and currently being used in approximately 1000000 cars with lower proportion of PM release.

Continuously regenerating-trap (CRT) system was developed by Johnson Matthey. CRT system comprised on a trap (wall flow trap) with an upstream flow referred to as preoxidiser. The preoxidiser reduces at least 3% of $NO_{(x)}$ and converts approximately 90% of hydrocarbons to carbon monoxide. It works at a lower temperature, oxidizes hydrocarbons and CO and brings about the conversion of NO to NO_2, and further carries out burning the and conversion of PM into carbon dioxide and NO. Its limitation is its sensitivity to high sulphur content.

Toyota Motors system controls the emission of PM and NO by using active oxygen with Pt hosted by metal oxides, which are put on filtration device. The oxygen is generated by the conversion of NO to nitrate compound. The surface nitrates produced brings about the conversion of HC and CO to carbon dioxide. Nitrates convert themselves to nitrogen and NO. This system provides the efficient suppression of CO, PM, HC and NO.[16] The reduction of emission of PM from coal combustion sources is mandatory. To achieve this, several technologies have been developed.

Hybrid ESP/BAG technology is well known to reduce the PM emission from coal combustion and was developed in 1990. For this purpose, a pulse get filter bag is attached with ESP as the use of ESE also minimizes the releasing content of PM, and when filter bags are attached to them additionally, the emission can further be reduced by 4

to 8 times, minimizing the space among bags. This technology is cost-effective and also reduces spaces required for construction purpose.

Novel Tsinghua hybrid ESP/BAG particulate collection technology (THEBPC) is a more advanced approach. To enhance the effects of ESP, bags louver type collecting tubes were utilized for the collection of electrostatic charges. During processing, the PM containing gas is passed first through ESP and collector plate, which removes approximately 90% of PM, and the dust is collected in bags. The re-entrained particulate enters into the ESP zone via opening present at collection plate for secondary electrostatic capturing.

Bipolar electrostatic agglomeration comes under novel electrostatic agglomeration techniques. In this, agglomeration of particles is brought about by first charging half of the particles positive and remaining one as negative. After charging them, they are passed from mixing chamber where they get agglomerated. This approach is found to reduce the emission of PM_{10} up to 45 %.

Magnetic filtration is used for gathering fine ferro or paramagnetic particles. In this, particles are collected on a filter which is comprised of ferromagnetic wires and is fixed in a strong magnetic field. A highly non uniform field is produced when applied magnetic field magnetizes the attached wires, which results in the attraction of fine particles to wire. For PM, the collecting efficiencies were higher for higher mass concentration and increased aggregation time.[17]

Metal dissolution by acid rain

The term acid rain or acid deposition can be elaborated as the transmission of strong acids and acid yielding substituents from the atmosphere to the earth surface. Acid rain comprised of gases, ions and particles incorporated into the atmosphere through the emissions of $SO_{(x)}$, $NO_{(x)}$, ammonia and particulate matter. Acid rain drains off metals and also contributes in alteration of elements interaction i.e. calcium, magnesium, sulfur, nitrogen and hydrogen. By doing so, it affects a number of ecosystems. It has effects on the ecosystem via hydraulic cycle.[18] For understanding the dynamic of acid rain, its real time measurements are performed and dry deposition contribution is considered in two ways. That is, acidic particles with greater solubility are responsible for enhanced acidity, while buffered particles are responsible for reduced acidity.[19] Among various metals, aluminum is considered as the most abundant due to its presence in earth crust in combined form either in form of bauxite or other minerals. Acid rain acts as key and dissolves the aluminum as Al^{3+} ions and certain other metals like lead and mercury and carries them to water resources. Though acid rain leads to acidity of water which is damaging to fish, yet the Al^{3+} ions carried to water in form of acid rain affects more badly the water ecosystem. If Al^{3+} contaminated water is used by humans, its accumulation in the body can cause Alzheimer, neurological and bone disorders.[20] Lead usually exists in soil matrix in bonded form and due to its large release from industrial processes, and its adverse effects upon ecosystems and humans. Trials are in progress to reduce its release. Therefore, the soils are now stabilized by cement, but when acid rain falls on cement stabilized soil, it causes the leaching or dissolution of lead.[21]

Acidic emissions

When meteorological analysis was performed for all weather kinds, acidic emissions were found to be the cause of acidity. $NO_{(x)}$ and $SO_{(x)}$ are considered to be responsible for acidic emissions. Anthropogenic sources of nitrogen oxides emissions are high temperature combustion phenomena, especially from power plants and automobile industry. Moreover, house gas heater and stoves are responsible for its release. Short time exposure to nitrogen oxide leads to problems in lung function, while its longer exposure may cause alterations in lungs. It is also involved in the formation of ozone which is associated with health implications. Nitrogen oxides have impacts on vegetation from fertilization to nutrient imbalance, forest carbon storage, acidification of soil and water which consequently reduces the productivity of plants and contracted biodiversity.[22]

Major source towards the emission of sulfur oxides is electric utilities especially those from coal combustion and smelting of metals. Coal containing higher content of sulfur is responsible for $SO_{(x)}$ emission in the atmosphere about 69 % in the United States. $NO_{(x)}$ emission results from transportation means.[23] $NO_{(x)}$ and $SO_{(x)}$ additions to the atmosphere are due to industrial, residential and combustion processes. More so, industrial manufacturing processes are also responsible for acidic emissions.[24] Exposure to higher concentrations of sulfur oxides generates breathing problems for asthmatic patients, while its less exposure can as well cause whizzing, shortness of breath and chest tightness. SO_2 is responsible for bronchitis, lung cancer and emphysema in humans.[25] Sulfur oxide toxicity can lead to severe illness, disability and eventually death.[26] Together with $NO_{(x)}$, it results in acid deposition which in turn is responsible for acidification of soil and water bodies, weathering of stones, sculptures and monuments.[27] $SO_{(x)}$ contributes to $PM_{2.5}$ and poses visibility problems.

Heavy metal detection techniques

Qualitative and quantitative techniques are used for the detection of heavy metals just like other pollutants. In recent years, many investigations have been focused on developing new methods. Electrochemical techniques in many ways play an important role. Microwave calcination is for metals. Similarly, ion chromatographic and voltametric analysis were also reported in literature.[28] Many active instrumental analytical techniques are also being used to measure the concentration of heavy metals in different environmental media. The most common techniques are atomic absorption spectrometry, inductively coupled plasma mass spectrometry, atomic emission/ fluorescence spectrometry inductively coupled plasma optical emission spectrometry, X-ray fluorescence, neutron activation analysis and anodic striping voltammetry (AVS).[29]

Atomic spectroscopy

Atomic spectroscopy comprises of atomic absorption, atomic emission, and fluorescence. Each nucleus atom is surrounded by boarder electrons. It is based on the principle that each element has specific number of electrons. And an atom possesses most stable configuration in ground state. When energy is supplied to an atom, it gets absorbed with a known amount of energy and in the process, electron is promoted to the least stable excited state. As it is in an unstable state, atom spontaneously releases the absorbed energy and comes back to its ground state. The process of excitation and de-excitation of atom involves three fields of atomic spectroscopy.[30]

Atomic Absorption Spectrometry (AAS)

It is a quantitative analytical technique, generally known for the determination of almost more than 70 trace elements. This technique works on passing the light of specific wavelength by radiation source of an element. Hollow cathode lamp is the main part of this technique. The reduction in the amount of light intensity reaching the detector is seen as a measure of the concentration of element in the original sample. Atomic absorption spectrometer comprises of a light source, an atomizer for sample placement, monochromator, detector and a plotting of collected data (Figure 1).[31]

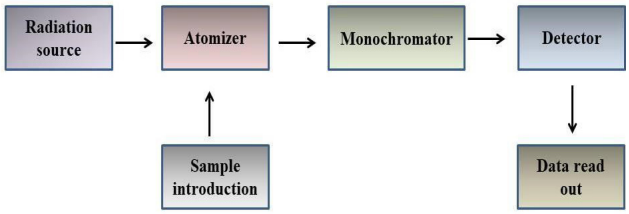

Figure 1 Working of atomic absorption spectroscopy.

Heavy metals are detected and collected by placing a sample in an atomizer. The light coming from the radiation source passes through the sample, and the light from the standard solution passed through the sample as well and reached to the monochromator, where incoming light is scattered by a number of lenses and mirrors to focus the radiation. The detector is typically a photomultiplier tube that converts the light signal to an electrical signal, proportional to the light intensity. The standard solutions for all the heavy metals are prepared in three to five different concentrations to obtain a calibration curve by diluting stock standard solution of concentration, 1000 ppm. These standard solutions of heavy metals are placed in hollow cathode lamp to determine the desire heavy metal.[32]

Flame Atomic Absorption Spectrometer (FAAS)

Flame atomic absorption spectrometer is a precise technique used to determine the traces of heavy metals in parts per million. It usually contains nitrous oxide in its atomizer. Nebulizer is used to introduce the sample in the atomizer. It is a fast analytical method for samples and can be carried between 10 to 15 seconds. Some metals like zirconium, arsenic cannot be detected by FAAS due to the insufficient temperature range for their detection, while traces of lead, Cadmium, nickel, chromium, manganese, Zinc, Cooper and iron can easily be detected under this technique.[33]

Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

Graphite furnace atomic absorption spectrometer is also an atomization technique utilised in determining the precise concentration of metals in parts per billion levels. In this technique, samples are mixed with modifiers prior to their introduction into an atomizer, having graphite tube to dispense the sample. Sample is passed through a series of steps like heating, drying, ashing in order to remove excess of solvent. Thereafter, the remaining atomized sample is retained within the tube and the light path for a prolonged period of time, which leads to an improvement in sensitivity. It has excellent detection limits for majority of heavy elements, as a small sample size of 20 µl is required for analysis. However, limited working range, slow analysis, and high cost are the limitations of this technique.[30]

Hydride Generation Atomic Absorption Spectroscopy (HGAAS)

HGAAS also plays an important role in detecting the heavy metals like arsenic, selenium ad tellurium etc. through atomization technique. In this technique, volatile hydride is produced by sodium borohydride reaction in a continuous glide system, and then transported to the heated quartz cell which acts as atomizer along the optical axis of conventional AAS by using argon gas. In the atomizer, hydride is converted into gaseous metalloid analyte atoms in the path light source, and the produced signals are measured by the quantity of light absorbed. This technique is restricted to positive elements. The quality of the results depends on different parameters, such as the valency of an analyte, gas pressures, concentration of acid and the cell temperature. Thus obtaining a quality data in this technique requires a great operator competence.[34]

Atomic Emission and Fluorescence Spectroscopy (AES and AFS)

Metals like (Ca), potassium (K), magnesium (Mg) and sodium (Na) can be detected by AES, while heavy metals such as arsenic and mercury can be detected by AFS technique. In the AES technique, atoms move to higher electronic states by absorbing light, and when they return to the ground electronic state, they subsequently release the absorbed light. Each element emits light at a characteristic wavelength, which is isolated by a grating and detected via a spectrometer. The wavelength of the atomic spectral line provides the identity of the element, while the intensity of the emitted light is proportional to the number of atoms of the element, while in AFS, both absorption and emission phenomena are observed. The atoms in a ground state are generated in a Flame and are excited by focusing a beam of light into the atomic vapor. Subsequent emission from the decay of the atoms excited by the source light is measured.[35,36]

X-ray Fluorescence (XRF)

It is a physical phenomenon which works on the principle of interaction of X-ray light with the matter. It is a fluorescence technique for the elemental analysis of potassium (K), calcium (Ca), silicon (Si), sodium (Na), magnesium (Mg), iron (Fe), phosphorous (P), sulphur (S), aluminium (Al), manganese (Mn), copper (Cu), and zinc (Zn). X-ray spectrometer comprises of an X-ray source, sample chamber, detector, and a computer for data plotting.

Future suggestion

Efforts are being made for the treatment of waste water and soil contamination far away from the source of emission. There should be a proper system of checking the water quality before discharge into the environment and water bodies. Air should be monitored before emission into the environment, because once it got released, it is highly impossible to remove from the atmosphere. Old installed pollutant removal technologies must be replaced by advanced high-performance technologies, Environmentalist and expert human resource personnel should be hired for proper monitoring and mitigation of the pollutant emissions. A lot of space for research is available in the area of inventing new advanced technologies for in situ pollutant capturing and treatment at lower cost. This should be a focus point of new researchers, investigators and inventors in the field of science and technology.

Conclusion

Industrial revolution is good for the mankind, but their negative impacts on the environment should properly be addressed. Particulate matter and heavy metal emissions are the cause of many health problems and harmful for the environment, especially for water and air. Majority of the areas in Pakistan have heavy metal contamination in ground water, which are causing many diseases when the polluted water is consumed, specifically for new-born babies. Heavy metals also paly their catalytic role in atmosphere for secondary pollutant formation. Therefore, the emission of heavy metals should be treated at the point of discharge, and it is far better than treating them at various dispersed points.

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Conflicts of interest

All author listed here declare no conflict of interest exists.

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