ANALYTICAL APPROACH FOR DETERMINATION OF ENVIRONMENTAL POLLUTANTS

Abstract

Environmental pollution of hazardous heavy metals, antibiotics, persistent organic pollutants (POPs), volatile organic compounds (VOCs) and pesticides is gradually more becoming a problem and has become of great concern due to the harmful effects around the world. These environmental pollutants are being superfluous in waters, soils and into the atmosphere due to the rapidly rising agriculture and metal industries, improper waste disposal, fertilizers and pesticides. This analysis demonstrates how contaminants enter the ecosystem as well as their eventual fate. While environmental pollutants cause major disorders like cancer, others have an adverse effect on biological processes and growth. This chapter summarises the biochemical and physiological impacts of environmental pollutants bioaccumulation in living things as well as the seriousness and alarming aspect of the condition and analytical methods.

Keywords: Environmental pollutants, toxicity, analytical methods, pollution.

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I. INTRODUCTION

Higher consumer demands and rising living standards have increased environmental pollutants in air, water, soil and foods. Globally, there is substantial worry over the regulated or uncontrolled release of environmental pollutants, such as hazardous heavy metals, antibiotics, persistent organic pollutants (POPs), volatile organic compounds (VOCs) and pesticides. Pesticides, cosmetics, personal care items, household cleaners, and medications, which are used globally and are essential to contemporary life, add pollutants to the environment. The environmental pollutants like heavy metals distributed in food chain by various processes such as combustion, extraction, industrial manufacturing process, which accumulated by human and plants. POPs & VOCs are released by various activities like agricultural sprays, power plants, heating facilities and incinerating plants. Pesticides are used in agriculture. All environmental pollutants are released in soil, water and air, which distributed in food chain and accumulated in human body and plants. Various health issues such as nephrotoxicity, cancer, birth deformities, learning difficulties, neurological issues, chromosomal breakage, miscarriage, irritation, changes in vision and hearing are caused by environmental pollutants. Therefore different analytical approaches have been used for monitoring environmental pollutants in various samples. Simple, specific, sensitive, rapid and portable methods such as atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS), laser-induced breakdown spectrometry (LIBS), electrochemical detection & chromatography have been discussed (Nigam et al., 2015, Yang et al., 2021).

II. SOURCES OF ENVIRONMENTAL POLLUTANTS

Different industrial manufacturing processes result in the production of several heavy metals; among them, it is believed that Cr, Cd, Ni, Cu, Zn, As, and Pb are the most hazardous. Aquatic organisms consume these metals because of how easily soluble they are in water. The food chain may cause the high levels of these metals to accumulate in humans. Many different activities release heavy metals into the environment, including as combustion, extraction, processing and surface water discharge from storage and transportation, which then affects the soil, groundwater and crops. The meteorological synthesis centre is to blame for the release of cadmium, lead, and mercury into the environment. The primary sources of metal contamination in the environment are a variety of human activities and the processing of various applications. One of the biggest users of water is the dying industries. Their effluent contains a variety of chemicals and coloring compound; it is released into any aquatic body. The main industries that produce heavy metal pollution include those that process metals, make leather, manufacture drugs, make chemicals, mining, use pesticides, make plastics, rubber, wood and lumber goods. Heavy metals are transported by runoff and contaminated water sources. Environmental contamination by pollutants like heavy metals mainly is due to anthropogenic activities (Babel et al. 2004, Diarra et al. 2020, Deepali et al. 2010). Persistent organic pollutants (POPs) are released into the atmosphere through a variety of industrial sources, including power plants, heating facilities, incinerating plants, furnaces in homes, vehicles, agricultural sprays, evaporation from water surfaces, soil and landfills. Other sources of POPs compounds, such as accidental creation, include chemical plants and various combustions. This category of wastes can be found in many places and result from a variety of activities, such as the use of obsolete oil, equipment upkeep and repair, building demolition, evaporation, cement production, animal carcass incineration, coal

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combustion, lixiviation of dumps and recycling activities. It also includes municipal, hazardous, medical, and sewage sludge incineration as well as waste from chlor-alkali plants, aluminium secondary plants, organ chlorine pesticide plants and cock production (Ying et al. 2005, Wenzl et al. 2006). Pesticides from point and nonpoint sources, including runoff, the atmosphere, agricultural use, home and urban trash, and industrial discharges, penetrate into the ground. Pesticide concentration and distribution in the environment are becoming increasingly common due to rapid industrialisation, urbanisation, and agricultural inputs (Yousefi et al. 2023). Consumer products contain biogenic volatile organic compounds (VOCs) and their emission can be the precursor to the emission of ozone and secondary organic aerosols. Consumer goods that are used indoors have a more immediate impact on human inhalation than industrial operations, facilities, and VOC emissions do on ambient air quality and the risk to human health. When used, household cleaners emit a lot of VOCs and have an impact on the respiratory system (Lin et al. 2022).

III. TOXICITY OF ENVIRONMENTAL POLLUTANTS

The formation of reactive oxygen species, which results in oxidative damage and subsequently has an impact on health, is thought to be the general mechanism of heavy metal toxicity. Harmful non-essential metal called cadmium affects cellular enzymes, causes oxidative stress, and deprives plants of vital nutrients. Hepatotoxicity is a liver condition brought on by cadmium binding to cysteine-rich proteins like metallothionein. Cysteine-metallothionein complexes produce hepatotoxicity before moving on to the kidney, where they accumulate in the renal tissue and cause nephrotoxicity. Iron shortage resulted from its propensity to combine with glutamate, histamine, and aspartate ligands (Fu et al. 2020, Jaishankar et al. 2014). The toxicity of chromium depends on its valence state since tetravalent chromium is more hazardous than trivalent chromium. Changes in germination procedure and other effects on the development of leaves, stems, and roots are part of the plant's growth and development. Additionally, it has an impact on nutrition, water and photosynthesis. The contaminant in drinking water is chromium, which exists in the oxidation states +3 to +6. Tumours in the digestive tract are brought on by animals that consume water that contains Cr (VI). The chromosomal breakage and mutation caused by Cr (VI) on the DNA result in the formation of Cr-DNA adducts (Shanker et al. 2005, Zhitkovich et al. 2011). Lead is a potential human carcinogen, according to Environmental Protection Agency (EPA). Every organ and system in the body is affected to lead. High levels of lead exposure can seriously harm the brain and kidneys and finally result in death. Lead exposure at high levels during pregnancy might result in miscarriage. The Regulatory limits of arsenic is 15 parts per billion (ppb) in drinking water by EPA. Methyl mercury and mercuric chloride have been identified by the EPA as potential human carcinogens. All types of mercury are particularly toxic to the nervous system. High levels of exposure can harm growing foetuses, the kidneys, and the brain permanently. Irritability, shyness, changes in vision or hearing, and memory issues can all be signs of effects on brain function. The Regulatory limits of arsenic is 2 parts per billion (ppb) in drinking water by EPA (Martin et al. 2009). When POPs are released into the environment, they persist in the body for years and cause issues in both human and other animal species, including cancer, birth deformities, learning difficulties, immune, behavioural, and neurological issues (Sweetman et al. 2005). In children with early sexual development, immunological, reproductive, endocrine, and nervous system abnormalities, pesticides can have detrimental effects on their health, including liver cancer, nephrotoxicity, and renal cancer (Yousefi et al. 2023). Terpenes and terpenoids are found in

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household cleaners that are utilised in a variety of consumer goods. These terpenes are carried indoors and released following photochemical processes that encourage ozone production (Lin et al. 2022).

IV. ANALYTICAL APPROACH FOR THE ENVIRONMENTAL POLLUTANTS

On the basis of analytical and physicochemical techniques, many methods are used for environmental pollutants such as inductively coupled plasma-mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), voltametry, atomic fluorescence spectrometry (AFS), inductively coupled plasma mass spectrometry/atomic emission spectrometer (ICP-MS/AES), Laser-induced breakdown spectrometry (LIBS), electrochemical detection three-dimensional porous high boron-nitrogen-doped carbon-electrochemical detection, chromatography and X-ray fluorescence techniques. These analytical techniques provide complete information of selectivity and sensitivity of environmental pollutants determination.

1. **Atomic absorption spectrometry (AAS):** Atomic absorption spectrometry (AAS) is frequently used to detect heavy metals in a range of samples. In AAS, a light beam passes across the sample. Depending on the concentration of the element, a particular portion of the light is absorbed. By comparing the intensity of the starting beam with the beam after passing the sample, it is possible to estimate the element's concentration. The AAS instruments contain separate light sources for each element since each element absorbs light of a certain wavelength. M'hamdi et al. determined heavy metals such as Cd, Fe, Zn, Cu, Ni and Pb in aromatic and medicinal plant (Urtica Dioica L.) (M'hamdi et al., 2023). Depending on the mass concentration range and different atomization system analysis can be carried out flame AAS (FAAS), graphite furnace (GF-AAS) or hydride generation AAS (HG-AAS). Among them, FAAS can determine more than 30 elements and the LOD can reach μg cm-3 with a relative error of less than 1%. However, flame atomic absorption spectrometry can only measure the total concentration of chromium. It is always not possible to directly measure Cr (III) and Cr (VI) at lacking concentrations due to deficient sensitivity of the method and matrix effect of impurity ions in water samples. So, Yilmaz et al. used preliminary species separation and preconcentration steps before detection by FAAS and established an ultrasound assisted-deep eutectic solvent-based emulsification liquid-phase microextraction method (UA-DESELPME) combined with micro-sample injection flame atomic absorption spectrometry was developed for speciation, preconcentration, and determination of chromium (Yilmaz et al., 2016). GF-AAS is more sensitive than FAAS, which can be evaluated more than 70 elements and deliver energy via electricity (Rashid et al., 2016). As, Sb, Bi, Ge, Sn, Pb, Se, Te and other elements was determined by HG-AAS. Arsenic was analysed by FI-HG-AAS in groundwater in Bihar State, India (Chakraborti et al., 2016).

2. **Inductively coupled plasma-mass spectrometry (ICP-MS):** ICP-MS is another leading analytical technique, which is used for the determination of heavy metals in different samples. In this technique samples are pretreated by acidification digestion or microwave digestion. After the sample aqueous solution is atomized into the aerosol, the aerosol is introduced into the inductively coupled plasma (ICP) with an inert gas and then evaporates, atomizes, and ionise as a result of plasma at a high temperature. The ionised materials enter the vacuum mass spectrometer. In order to distinguish between one

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another, mass spectrometers employ the difference in the mass-to-charge ratio (m/z) of ionised atoms or molecules. The element ion separation is completed by the separator. Atoms or molecules can be quantified using mass spectrometry. ICP-MS may be used to evaluate practically all of the periodic system's elements in a single analysis step with high sensitivity, a broad linear range, excellent anti-interference, outstanding repeatability and a very low detection limits (LOD) (Zheng et al. 2007). Lagerstron et al. determined Mn, Fe, Co, Ni, Cu & Zn by automated online extraction flow-injection ICP-MS method in seawater samples (Lagerstrom et al., 2013). For the improving of the sensitivity of trace heavy metal determination, preconcentration and separation are used. Solid phase extraction (Rahmi et al., 2007), Solid phase microextraction (Kaur et al., 2007) and dispersion liquid liquid microextraction (Garcia et al., 2013) are mainly used for preconcentration and separation of trace heavy metals in various samples. The advantages of using the on-line analysis technologies of laser ablation (LA) and ICP-MS for the direct analysis of solid samples include easy sample preparation, no requirement for sample digestion, and minimal contamination. Figure 1(a) shows the simple schematic of a LA-ICP-MS system and (b) presentation of nanosecond laser interaction with a solid (Shaheen et al., 2012).

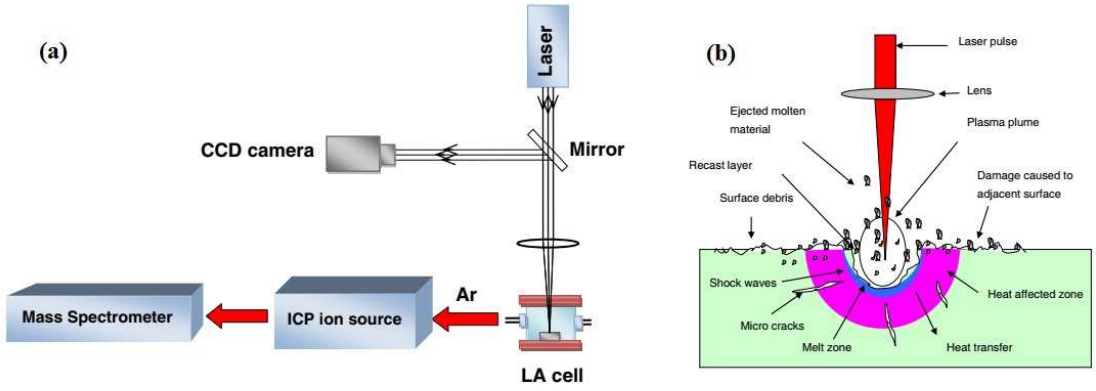

Figure 1: (a) A simple schematic of a LA-ICP-MS system and (b) Schematic presentation of nanosecond laser interaction with a solid. (Shaheen et al., 2012)

3. **Atomic fluorescence spectrometry (AFS):** A fast-evolving technique called atomic fluorescence spectroscopy (AFS) uses radiation at a certain wavelength to excite atoms in the element's vapour state, resulting in the creation of atomic fluorescence. Atomic fluorescence's intensity and concentration are mutually exclusive. The elements in the soil determined efficiently based on fluorescence intensity. Dispersive and nondispersive AFS are the two categories. AFS is identical to AAS, except the light source and other parts are at a 90° right angle instead of in a straight line to prevent the radiation from the excitation light source from interfering with the atomic fluorescence detection signal. It benefits from atomic emission as well as atomic absorption (Li et al., 2020). The development and use of AFS in heavy metal detection studies is a popular area of study for analysts. The detection of trace elements in soil, coal, rock, stream sediments, and different minerals is the first application field for AFS. Researchers have conducted more thorough research on AFS as a result of the continued development of this technology. Agriculture, food, medicine, health and epidemic prevention, the environment, etc. are currently applicable fields (Lancaster et al., 2019). Figure 2 shows the simple

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representation of a UV digital micromirror spectrometer for dispersive AFS (Tao et al., 2018).

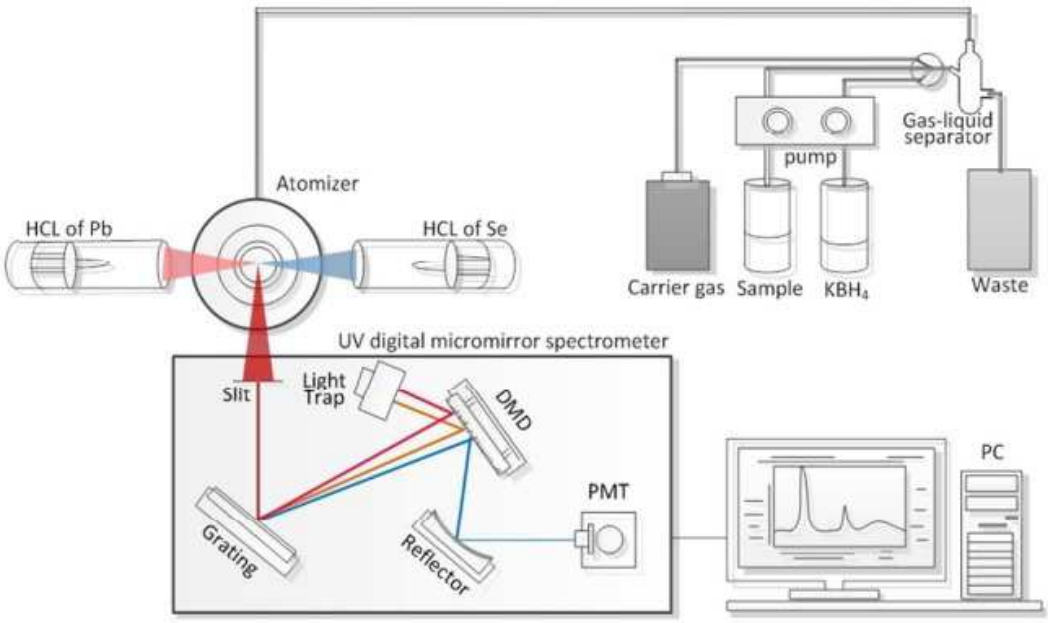

Figure 2: A simple schematic of a UV Digital micromirror Spectrometer for dispersive AFS (Tao et al., 2018).

4. **Laser-induced breakdown spectrometry (LIBS):** The qualitative and quantitative analytical information using the quick, ubiquitous, and non-contact atomic spectroscopy technique known as LIBS, with little to no sample preparation required (Galbacs et al., 2015). However, compared to solid or gas analysis, direct liquid analysis with LIBS has worse LODs and less accuracy. This is because the laser-induced plasma that is created in the centre of the bulk liquid has a propensity to erupt (Lee et al., 2012). In order to cause the sample to produce transitory plasma, the method employs a laser to emit a high-energy laser that is focused directly onto the surface of the sample through a focusing lens. By examining the distribution intensity and emission line wavelength of the plasma, it is possible to determine the amount and make-up of the elements in the sample. A powerful analytical tool is LIBS. It has shown exceptional results when used to find heavy metals in the air, water, and soil (Li et al., 2015).

Aerosols, particles, and pollutants are monitored and analysed using LIBS technology for air quality monitoring. There are two different ways to detect compounds in aerosols: either focus the laser on the enrichment filter, which can detect substances at lower concentrations in the aerosol, or directly on the aerosol itself, which has a larger detection limit than the former (Gallou et al., 2011).

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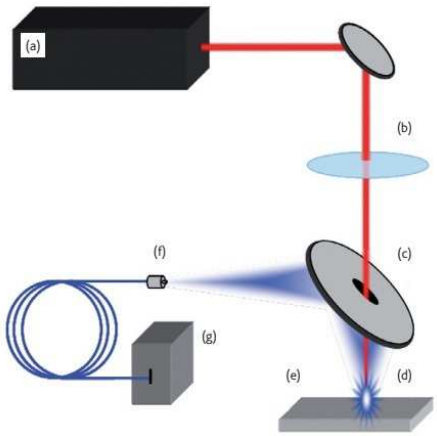

Figure : LIBS experimental setup (Lucia et al., 2011)

5. **Electrochemical detection:** Huang et al. determined Cd(II) and Pb(II) in food sample, which developed novel electrochemical sensors based on the novel type of carbon and nitrogen co-doped carbon (BCN) material. Applying optimum environment, BCN-modified glassy carbon electrode was applied using square wave anodic stripping voltametry, which showed LOD 0.41µg/L and 0.93 µg/L for Cd(II) and Pb(II), respectively (Huang et al., 2023). Table 1 shows the various determination techniques for the environmental pollutants.

Table 1: Environmntal pollutants determination by various techniques

S.No.	Analytial Technique	Sample type	Analyzed elements	Remarks	Reference
1	AAS	Plant	Cd, Fe, Pb, Cu, Zn and Ni	Contains in the plants (µg/g) Cd (42.62), Fe (13.10), Zn(2.90), Cu(1.2), Ni(0.21) and Pb(0.14)	M'hamdi et al., 2023
2	ICP-MS	Sea water	Mn, Fe, Co, Ni, Cu and Zn	Limit of detection range (0.3 to 16 pmol/kg)	Lagerström et al., 2013
3	AFS	Plant	Hg and As	Limit of detection 0.021 µg/L (Hg) and 0.069 µg/L (As)	Li et al., 2020
4	LIBS	Water	Ca, Mg, K, Cu, Sr, Pb and Cr	Limit of detection 2.70 ppm (Pb) and 0.36 ppm (Cr)	Lee et al., 2012
5	BCN-modifide Carbon elctrode	Food	Cd and Pb	0.41 µg/L (Cd) and 0.93 µg/L (Pb)	Huang et al., 2023
6	Chromatography	Aquatic environment	persistent organic pollutants	-	Leeuwen et al., 2008

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6. **Chromatography:**Chromatography has been used for the accurate quantification of POPs. Liquid chromatography has been used for POPs with various advantages such as short run times and complementary nature of potential ionization techniques. Gas chromatography (GC) has been performed with good separation potential and multidimensional gas chromatography has been used with excellent separation potential. Because of its excellent resolution, gas chromatography (GC) frequently proved to be the best method. Recent advancements in comprehensive two-dimensional GC (GC GC) demonstrate that this technique can offer far more information than traditional (single-column) GC. Tens of microliters of sample extract can be injected in large volumes, greatly enhancing the detection limits (e.g., via programmable temperature vaporiser, or on-column injection). Although electron-capture detection (ECD) is a sensitive detection technique, it cannot be used for unambiguous identification. Mass spectrometric (MS) detection significantly enhances identification and the lower the likelihood of misidentification, as with MS/MS, time-of-flight (TOF) MS and high-resolution (HR) MS. While several chromatographic techniques have the potential to be helpful, gas chromatography (GC) and high performance liquid chromatography (HPLC) are without a doubt the most common methods for environmentally relevant separations. Since the early 2000s, a range of environmental separations have been successfully accomplished using ultra-high performance liquid chromatography (UHPLC) (Leeuwen et al., 2008; Megson et al., 2016). Various pesticides were determined by GC with electron capture detection (ECD) and tandem mass spectrometry (MS-MS) detection mode. It was also demonstrated that MS-MS is preferable to ECD for identifying endocrine disruptive substances in complex matrixes (Frenich et al. 2003).

V. CONCLUSION

Environmental pollutants and other inorganic pollutant contamination of soil, sediments, and marine resources is undoubtedly an increasing problem. The region's livelihood and sustainable growth are currently in danger due to environmental degradation brought on by human activity, in addition to climate change. A analysis of the existing literature identifies a variety of anthropogenic activities as significant point sources of hazardous metal pollution, including industrial processes, the use of pesticides in agriculture, leachate from inadequately built landfills, and unregulated mining operations. However, there is a dearth of information and study regarding the level of pollution and related human risk factors in the area. As a result, there is a need for ongoing research on the extent of environmental contamination, as well as for the development of clear rules and regulations for the use and disposal of environmental pollutants. Many analytical methods such as atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS), laser-induced breakdown spectrometry (LIBS), electrochemical detection and chromatography have been used for monitoring environmental pollutants in various samples. Simple, specific, sensitive, rapid and portable methods have been discussed in this chapter.

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