

Effect of Industrial Pollution on Crop Productivity

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Abstract Industrial effluents are a major health concern for all living matter on Earth. The components of these effluents are adversely affecting the environment, causing an imbalance in nature and as a result, in the natural processes going on in the ecosystems. When disturbed, the balance among these ecosystems causes the living organisms in it to adapt to these changes by acting out alternately at various metabolic and biochemical levels. Plants being the foundation of the food chain, and not being able to move, are the major concern at this point in as much as they uptake the harmful substances from the environment and accumulate them in their system, affecting their own health as well the health of all the consumers directly or indirectly depending on them for their food. Several crop plants cultivated as a major food source for humans worldwide need to be paid attention for adverse effects on developmental processes and yield as the agricultural soils are irrigated by water polluted with industrial wastes. As the title indicates, in this chapter we are concerned with the types of substances industrial wastes can contain, their uptake by the plant influencing the uptake, transfer, and movement of other nutrients, and the effect they cause on the growth and biomass of crop plants.

Keywords Industrial pollution • Crop productivity • Heavy metals • Ammonia

1 Introduction

Any product or by-product that is due to an industrial activity and is useless turns out to be industrial waste. It includes all the products that are useless and may harm the environment on an individual or global level. For example, burning of woods or coal for cooking purposes at restaurants may produce CO (carbon monoxide; Anne Elizabeth 2010). A few of the industrial wastes are paper products, sandpaper, metals, paints, chemical solvents, radioactive wastes, and other industrial by-products.

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Table 1 Permissible limits of various elements in industrial pollutants for soils of crop fields; typical concentrations of these elements in soil and crops under normal conditions (European Union 2002; Allaway 1968)

Element	Safe limit ($\mu\text{g/g}$)	Soil concentration (ppm d.wt)	Concentration in crops (ppm d.wt)
Cu	140	2–100	4–15 2.5 mg/kg (WHO/FAO)
Fe	—	7000–55,000	400–500 mg/kg (WHO/FAO)
Zn	300	10–300	15–200 20–100 mg/kg (WHO/FAO)
Mn	—	100–4000	15–100
Ni	75	10–00	1.0 0.02–50 (WHO/FAO)
Co	—	1–40	0.05–0.5
Pb	300	2–200	0.1–10 0.05–30 mg/kg (WHO/FAO)
Cd	3	0.01–0.7	0.2–0.8 <2.4 mg/kg (WHO/FAO)
Cr	150	5–3000	0.2–1.0

Carbonates, bicarbonates, municipal solid waste, industrial solid waste, toxic waste, chemical waste, heavy metals, and surfactants, all come under the umbrella of industrial wastes and contribute to environmental pollution and the hazards caused as a result. Now there are laws and authorities who regulate these laws to treat the wastewater that before dumping should be tested for the amount of harmful wastes. Certain limits have been defined for the pollutants having adverse effects on the environment. These limits, known as permissible limits (Table 1), define the safety range in which the pollutant isn't lethal or highly toxic to the environment and the living organisms residing in it.

Soil consists of various compositions of naturally occurring elements. These elements, including carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, and chlorine, among others, are the basis of the life form being the major constituents of the molecules that build up macromolecules including DNA and proteins. These are taken up by the plant from the soil it inhabits as vital nutrients for its growth, development, and flourishing. Since their identification, different studies have been carried out on the requirement and functions of these nutrients within the plant. As excess of everything is bad, similar is the case with mineral nutrients in the soil; excessive amounts of these nutrients pose danger to the survival and well-being of the plant. In excessive amounts, they can cause nutrient imbalance, disturbance in uptake by roots, altered translocation patterns, changes in enzymatic activity, affected growth rates and patterns, various visually noticeable symptoms, and reductions in overall yield of the plant. In this chapter, we are mostly concerned with the metals released into the environment in industrial wastes and their effects, mainly harmful, on the productivity of crops.

In nature, many metals exist in their different physicochemical forms. Metal ions with water molecules attached are believed to be very toxic. Metallic ions that are commonly presumed to be less toxic, are strong complexes and species associated with colloidal particles. Tin, mercury, and lead in their organometallic forms have higher toxicity compared to the imitating inorganic species.

The enrichment of soil with metals and heavy metals is a result of elevated industrial emission of pollutants and discharge, sewage wastewater, mining, and the heavy and uncontrolled use of fertilizers (Arora et al. 2008; Wuana and Okieimen 2011). In the case of enrichment of agricultural land, the food crops grown on it uptake and accumulate high levels of these pollutants in their tissues from where they are introduced into the food chain because plants form its base (Wuana and Okieimen 2011). Although some of these elements are helpful in plant growth, they become toxic at higher levels and have a negative impact on plant growth and yield. From plants, they are easily transferred to any animals or humans that consume them as food and hence they start to accumulate in the food chain, rendering an imbalance and causing unexpected circumstances.

2 Industrial Pollutants

Industrial waste, containing toxic material, released into the environment is a major concern for plant growth and health. This waste contains several different types of elements and compounds that may affect the crops in different ways. Depending upon the type of crop and its characteristics, the effect may either be harmful or beneficial. Either way, these elements start accumulating in the plant with a definite impact on its metabolic pathways and processes, leading to differential growth and development. The pollutants may vary in the nature of their effect depending on their type; these include inorganic as well as organic compounds, nonmetals, metals, metalloids as well as heavy metals, and nanoparticles, among others. Some of the elements discussed in this chapter are essential nutrients, macro and micro, and trace elements at optimal level; however, as their concentration in the soil rises to a certain level, the same elements become toxic to the plant.

Industries may discharge their waste as effluents into water bodies or into the atmosphere while several industrial processes are carried out. Thus these pollutants might get into the plant by uptake from soil affecting the plant or the atmospheric pollutants may have a foliar effect on various crop plants. In this chapter, we adhere to the inorganic pollutant uptake from the soil by the plant.

The release of various types of pollutants from different industries is interlinked and some of the common industries and the kind of pollutants they discharge into the environment are shown in Fig. 1. These include the dyes and pigment industry releasing arsenic, aluminum, iron, cadmium, copper, and lead; the textile industry releasing aluminum, arsenic, iron, nickel, copper, mercury, and cadmium; the chemical industry releasing arsenic, silver, gold, zinc, chloride, aluminum, chromium, lead, cadmium, copper, mercury, and iron; tanneries releasing zinc, arsenic, aluminum,

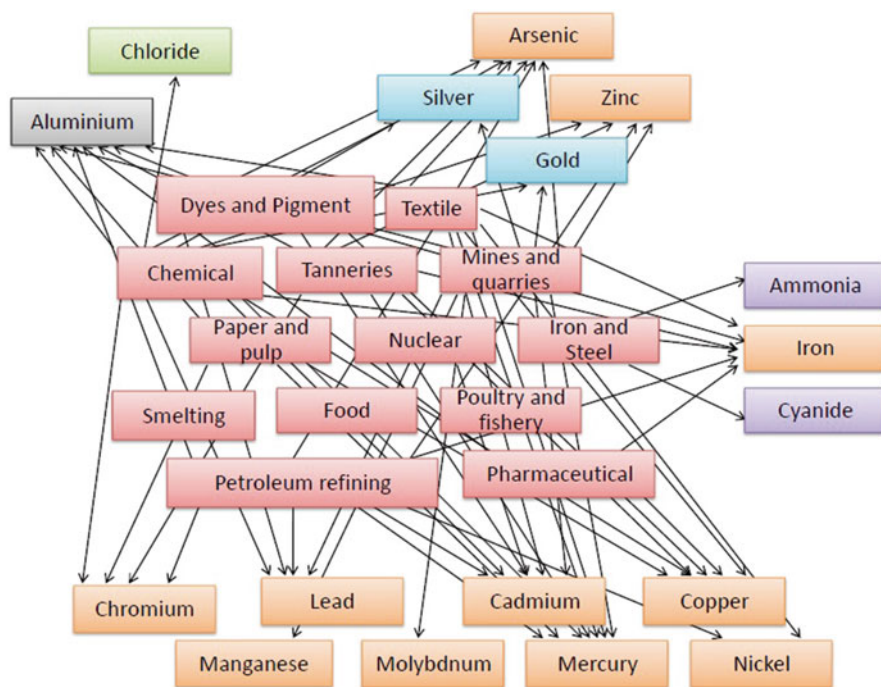


Fig. 1 Types of industries and most common elements released by them as pollutants. *Pink*, industries; *orange*, heavy metals; *purple*, inorganic compounds; *cyan*, metals/nanoparticles; *grey*, metals; *green*, nonmetals

iron, chromium, copper, and mercury; mines and quarries releasing aluminium, silver, gold, zinc, arsenic, mercury, cadmium, molybdenum, lead, and manganese; the paper and pulp industry releasing aluminium, chromium, copper, and mercury; the nuclear industry releasing cadmium; the iron and steel industry releasing ammonia and cyanide; the petroleum refining industry releasing aluminium, arsenic, zinc, iron, chromium, lead, mercury, cadmium, and nickel; and the pharmaceutical industry releasing aluminium, iron, and copper.

The effect of these pollutants in crop plants is described here with some examples focusing more on the harm caused by them.

3 Effect on Crop Productivity of Various Pollutants

Crop productivity is the growth of the cultivated crop plant achieved after it has reached its full grown state. In addition to the seed quality and genetic characteristics of the crop, its productivity depends on several environmental factors. The soil

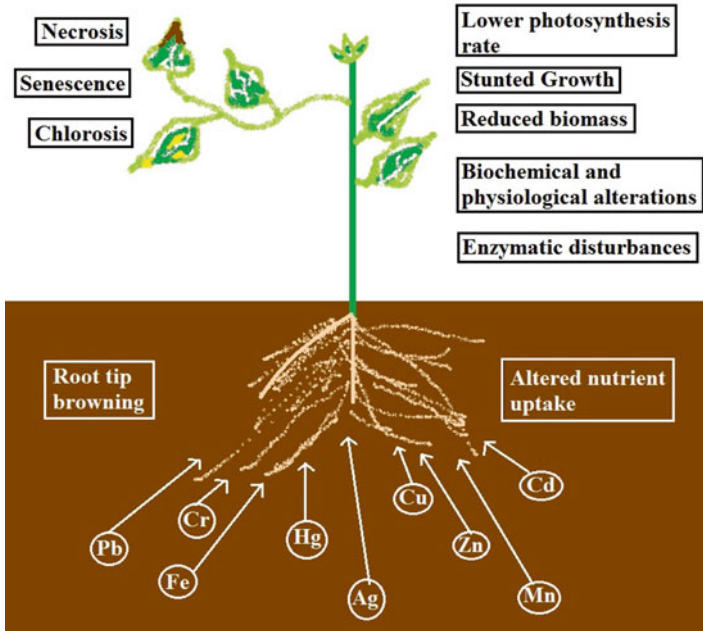


Fig. 2 Major types of effects on plants caused by industrial pollutant uptake from soil

composition of the field in which the crop is cultivated contributes a great deal to the proper growth of the plant. This composition varies from field to field and changes with natural processes, ecosystem composition, crop cultivation, and so on. The dumping of industrial waste near agricultural land contributes to drastic shifts in soil composition and balance from the original.

As described earlier in the chapter, the composition of industrial pollutants varies widely and ranges from simple elements such as metals and heavy metals to inorganic compounds to complex organic compounds. These cause a wide range of effects on the plants and are overviewed in Fig. 2. These effects include, but are not limited to, reduced growth, lowered levels of photosynthetic rates, biomass reductions, altered biochemical and metabolic pathways, different enzymatic compositions, silencing of some genes and overexpression of some others, reduced chlorophyll levels, visual symptoms including chlorosis, necrosis, root browning, wilting, senescence, and plant death.

Various crops follow different nutrient uptake patterns according to their needs and genetic makeup. Disturbances in the soil composition also cause adverse alterations in these patterns. Once taken up from the roots, the nutrients are stored there, according to the requirements, and then translocated farther upwards to various plant parts as per need. Roots release various exudates and other secretions to create charges and attract the required nutrients near roots. The uptake occurs at the exchange sites, however, the rise in levels of certain nutrients that are more reactive

than others make them able to replace the less reactive ones from the exchange sites. These elements are then taken up by the plant in larger amounts, despite being needed just as trace elements. Increase in uptake rates leads to accumulation and alterations in the normal processes in the plant.

Various nutrients under the categories of inorganic compounds, metals, metalloids, and heavy metals are described here with the effect of their toxicity in crop plants and their production patterns.

3.1 Inorganic Compounds

Inorganic compounds, naturally occurring in the environment as well as synthesized or released due to industrial activities, are a main cause of nutrition imbalance for plants growing in soil affected by the wastes. This group ranges from simple compounds such as oxides of carbon in the air with foliar effects on plants to more complex inorganic compounds, even toxins in the soil causing toxicity in the rhizosphere of the plant and accumulating in the plant parts, adversely affecting its growth and development.

Salt pollution caused as a result of higher salt concentrations in agricultural soil causes salinity which is a major addressed problem for crop productivity. High salt concentrations in the soil cause salinity and sodicity leading to a harmful impact on plant growth as well as yield, such as in wheat (Nuttall et al. 2003). However, we do not discuss the effects of salinity in this chapter as there is vast information on it and there are plenty of examples from which a whole new chapter can be formulated on the consequences of salinity on crop productivity. Ammonia and cyanide are the major concern from industrial pollutants, but we just stick to ammonia in this chapter.

3.1.1 Ammonia

Ammonium and nitrate, as nitrogen sources together, help in improving the growth of the plants; however, independently neither can cause this growth enhancement effect (Haynes and Goh 1978; Cox and Reisenauer 1973). Nitrogen being among the most important mineral nutrients for the plant, small quantities of ammonia as basic sources of nitrogen availability to the plant are beneficial for its growth and have a positive impact on the health of the plant; yield and flavor are known to be enhanced in fruits by relatively small amounts of ammonia (Siddiqi et al. 2002). In the presence of ammonia, the growth of tomato seedlings becomes restricted and limited. Ammonia disturbs ion uptake balance by the roots leading to retarded root and shoot growth eventually leading to growth inhibition due to the acidity of the external environment as cation uptake rises (Raven and Smith 1976; Magalhães and Huber 1989).

The uptake pattern of certain essential nutrients is known to be affected by the presence of ammonia, and with increases in its concentration, this pattern appears to

have drastic effects on mineral nutrient uptake of the plants grown in that contaminated soil. Ca, Mg, and K uptake decrease significantly in tomatoes when ammonia is the only N source (Siddiqi et al. 2002).

Ammonia concentrations higher than normal cause ammonia accumulation in certain crop plants without affecting growth and development, for example, rice and spruce (Wang et al. 1993; Kronzucker et al. 1998). However, it is reported to accumulate more in tomato which is known to be a lot more sensitive to ammonia and hence is affected by higher ammonia concentrations (Britto et al. 2001). High ammonia levels are also known to result in Ca deficiency leading to a significant yield reduction (Siddiqi et al. 2002).

High ammonia levels in constructing wetlands threaten and inhibit plant growth (Surrency 1993). Many types of plants have been studied and are known to be affected by ammonia toxicity caused as a result of various concentrations (Hageman 1984; Wang 1991; Dijk and Eck 1995; Magalhães et al. 1995)

Growth of common cattail and Indian potato noticeably reduces along with a significant reduction in total biomass at ammonia levels higher than 200 mg per liter (Clarke and Baldwin 2002).

3.2 *Metalloids*

Metalloids are a group of elements that can act both as metals as well as nonmetals depending upon their properties and associations. Among metalloids, arsenic is the most important element affecting various plant activities, most importantly nutrient uptake.

3.2.1 **Arsenic**

Arsenic is a metalloid that, when discharged into the environment, produces toxicity of utmost concern (American Agency for Toxic substances and Disease Registry (ATSDR), 2007; Tu and Ma 2003; Hasanuzzaman et al. 2014). In some environments, it is present in high values that can be very toxic to all levels of life. As (V) and As (III) are found to be a predominant inorganic form of the arsenic. (Tripathi et al. 2007). As III and AsV, depending on the redox conditions, are known to interconvert. They also exert numerous toxicity effects on plant health. (Carbonell-Barrachina et al. 1998; Marin et al. 1992).

As can enter aquatic as well as terrestrial environments via anthropogenic activities alongside natural formations (Tu and Ma 2003). Plants mainly take up arsenic in the former form, that is, AS (V), which causes a lot of stress including growth suppression (Stoeva et al. 2003) and deformed body (Stoeva et al. 2005) and can be fatal. Under greenhouse conditions phytotoxicity of As has also been reported; As when in excess produces stresses such as reduction in plant height, stem length, suppression of seed germination, decrease in shoot growth, wilting of leaf, necrosis of leaf blades, and

lower fruit and grain yield (Liu et al. 2005; Abedin and Meharg 2002; Burló et al. 1999). This is because of the similarity of the phosphorus to the arsenic, and the system flaws due to which it is taken up by the plant (Meharg and Macnair 1992). Research has shown that it resembles the phosphorus analogues which are transported by the phosphorus transporters to the cell plasma. (Stoeva and Bineva 2003). As and P have analogous activities exhibiting comparable physicochemical behavior in soil and they tend to compete in soil particle surfaces for the sorption sites (Hingston et al. 1971). Research has shown the evidence for P nutrition to be closely related to As sensitivity in plants, and P fertilizers, when applied, raise soil availability of As and enrich As uptake in plants (Pigna et al. 2010; Wang and Duan 2009; Geng et al. 2006). On the other hand, availability of P can also be affected by AS concentration in different soil. It is a big concern that when P is applied at a normal pace the effects of different As concentrations in the ground for the increase of plants is investigated. After getting into the cell plasma, it interferes with the metabolic pathways; moreover, it is rarely seen that the As (v) reduces to As (III). (Stoeva et al. 2003; Meharg and Hartley-Whitaker 2002;). As (III) inhibits cellular function even causing death by inhibiting, combining with sulfhydryl groups and inhibiting cellular enzyme and tissue proteins. (Ullrich-Eberius et al. 1989). Also, there is sufficient evidence that plants, when exposed to an inorganic form of As, although As is not a redox metal, result in the generation of reactive oxygen.

Most importantly the potential uptake by food crop plants and transfer of soil As into them is hazardous to not only humans, but to other consumers too. Many cases have shown clear evidence of arsenic-related toxicity that can be related to the uptake of As by the food crop and later by the humans who mainly consume them. The nature of As in water stored underground from Asian countries is essentially inorganic and several investigators have shown the presence of equal quantities of As III and AsV species (Samanta et al. 1999). The presence of As in soil and the effects of toxicity to plants and animals are major concerns. It can cause skin, bladder, lung, and prostate cancer if exposed to long term at low concentrations. Other than cancer, it can cause cardiovascular disease, diabetes, and anemia at low-level exposure (Zhang et al. 2002).

Many developing countries such as China are now taking steps and have great concern controlling environmentally hazardous compounds. There was an epidemic that caused 40 ha of agricultural soil polluted in Hunan province due to irrigation of As-contaminated water by local farmers (Liao et al. 2004). Now there are standards by which the government regulates agricultural activity in the areas where they suspect As in soil. For instance, if soil arsenic concentrations exceed the limit of 40 mg/kg, the area is banned for agriculture purposes. The Chinese government, in 2005, constituted the maximum limitations of inorganic arsenic in some crop products as less than 0.2 mg/kg, although some heavy metals concentrations in soil exceeded the limitations.

The main winter crops in Asian countries are winter wheat and rape. In the grains of these two crops or the stalk which is employed as cattle feed, high arsenic concentrations in land or water may contribute to elevated As accumulation. The permissible level of the inorganic form of As intake from all external sources, including water and food is 15 µg/kg body mass (WHO 1989). Therefore the evaluation of the potential

health hazard to humans or animals through the consumption of crop plants that have been grown under high As levels in soils is urgently called for.

3.3 Metals

Metals play an important role as part of the nutrients required by the plant for normal biochemical functioning of the metabolic pathways. Some, in their ionic form, play roles in ion flux and maintaining the balance of nutrients across the membranes. Imbalance of nutrients is caused by improper functioning as a result of disturbed levels in the plants.

3.3.1 Aluminum

Being among the most abundant metals on earth, Al comprises approximately 7 % of the Earth's crust. It is highly toxic for plants and causes considerable harmful effects on plant growth and yield. However, its presence in the form of precipitates or complexes with silicates or aluminosilicates isn't toxic to the plants. Under acidic conditions, it gets solubilized and hence crop growth depends on soil acidity as it's a limiting factor. That is why it is commonly linked to higher grades of aluminum.

Soil pH is maintained by the balance among cations and anions. This balance, however, can be disturbed as a result of various natural factors, including acid rain that can bring down acidic molecules from the atmosphere to the soil and leaching down of basic cations that proceeds steadily and can be enhanced depending upon various farming procedures in the crop fields (Kennedy 1986).

Root growth in maize gets completely inhibited as its apex comes in contact with the Al toxic region in soil (Ryan et al. 1993). Initially, root growth is inhibited by aluminum concentration, which results in lower consumption of water and nutrients and lower exploration of bulk soil. Nitrogen fixing may be seriously affected by Al toxic in the subsoil mainly for leguminous plants. At toxic levels, Al is known to alter other minerals' uptake and translocation in plants such as that of calcium by significantly lowering its uptake from soil (Huang et al. 1992; Rengel 1992). In a nutshell, these results may decrease carbon separation, biomass formation, and erosion and protect soil against elevated temperature, nitrogen incorporation (Debarba and Amado 1997), and weed control, and the addition of organic carbon to the soil.

3.4 Heavy Metals

Heavy metal refers to a group of elements that may be metallic in nature with a high density. These are naturally found in the environment but industrial activities have resulted in an increase in the levels of these heavy metals. As a result of higher

levels, they are disturbing the natural processes in the ecosystem. For plants, some of these are essential micronutrients and trace elements as part of vital molecules whereas others are nonessential. The nonessential ones are more toxic to the plants especially in higher concentrations causing toxicity conditions. These include lead (Pb), mercury (Hg), and silver (Ag) (Nieboer and Richardson 1980).

The essential elements among the heavy metals, necessary for the plant in trace amounts as micronutrients, include copper (Cu), iron (Fe), zinc (Zn), manganese (Mn), nickel (Ni), cobalt (Co), and molybdenum (Mo) (Wintz et al. 2002; Reeves and Baker 2000). The effect of these on crop productivity is discussed here in detail.

3.4.1 Copper (Cu)

An essential micronutrient for the plant, Cu functions in assimilating carbon dioxide, being a part of proteins involved in the electron transport chain of respiration as well as photosynthesis and in turn ATP synthesis (Demirevska-kepova et al. 2004).

Mining and smelting of Cu ores results in excessive Cu in soil, affecting plant growth and productivity. High Cu concentrations represent stress conditions for the plant causing chlorosis on leaves and a decrease in plant growth (Lewis et al. 2001). Cu toxicity has been reported to have a highly negative impact on the growth of cauliflower, accompanied by severe chlorosis in young leaves of the plant (Chatterjee and Chatterjee 2000). Reductions in chlorophyll content are a result of disturbed electron transport during photosynthesis and degradation of the thylakoid membranes under high Cu concentrations (Bohner et al. 1980; Sandmann and Boger 1980).

The plant roots take up Cu in ionic as well as chelated forms from the soil. Due to its high reactivity and bonding with the exchange sites at roots, it is known to displace a variety of ions occupying the free spaces in the root regions. As a result of this activity, its concentration in the root regions rises up significantly as compared to other parts (Mengel and Kirkby 1987).

Oxidative stress in plants resulting in the formation of reactive oxygen species occurs as a result of Cd toxicity (Stadtman and Oliver 1991) causing alteration in metabolic pathways (Hegedus et al. 2001). Higher Cu concentrations affect plant growth by altering the Cd movement and levels in cucumber (Moreno-Caselles et al. 2000) and Indian mustard (Singh and Tewari 2003). Cu toxicity causes harmful effects on plant growth starting from germination of seed, length of the seedling, and amount of lateral roots, for example, in aubergine (Neelima and Reddy 2002). Higher Cu concentrations cause significant biomass reduction in cauliflower along with disturbances in the metabolism of nitrogen within the plant (Chatterjee and Chatterjee 2000). At enzymatic levels, Cu toxicity has inhibitory effects on the activity of catalase in barley and cauliflower (Chatterjee and Chatterjee 2000; Agarwala et al. 1977).

3.4.2 Iron (Fe)

Iron is a vital constituent of many important proteins in the plant involved in some crucial processes such as photosynthesis, which is responsible for all food produced, and the major constituents of the photosynthetic system such as the chlorophyll and the chloroplast (Marschner 1995). For optimum growth of the plant, it requires an adequate amount of Fe being available to the plant constantly at all times (Wiersma 2005).

Its presence and availability in the soil is due to the presence of its ionic as well as chelated forms, however, higher concentrations sometimes lead to stressful circumstances leading to phytotoxicity in the plants grown in that soil. A large amount of Fe^{2+} is absorbed and taken up via plant roots when its concentration in the soil rises to toxic levels, causing Fe toxicity, mainly translocating it to leaves and causing damage to various plant parts at the cellular and genomic level (de Dorlodot et al. 2005; Arora et al. 2002).

Reduction in photosynthesis rates leading to a huge reduction in crop yield as a result of Fe toxicity is known to occur in several crops including soybean and canola. This is because of the inhibitory effects of the toxic conditions on chlorophyll. Induction of oxidative stress is also a common cause of Fe toxicity leading to production of several reactive oxygen species and other responses in the plant body (Sinha et al. 1997).

Fe accumulates in leaves of rice plants and causes disturbances in the normal occurrences leading to toxic conditions; this follows as a result of higher concentrations of Fe(II) in the field (Ponnamperuma et al. 1955). Higher Fe concentration leads to unbalanced nutrient uptake, especially affecting macronutrients such as potassium and phosphorus (Olaleye et al. 2001; Yoshida 1981).

Browning of leaves and roots occurs under such conditions, leaves dry out, and root growth is stunted (Sarwani et al. 1995; Jugsujinda and Patrick 1993; Yoshida 1981; Ponnamperuma et al. 1955). With a rise in the toxicity level and based on the resistance ability, yield of the rice crop reduces to about 12–100 % (Sahrawat et al. 2000; Abifarin 1988). Cultivars of rice that can resist Fe toxicity conditions have also been reported which can be grown under such conditions to avoid the adverse effects caused by the toxic conditions (Sahrawat and Sika 2002; Abifarin 1988).

3.4.3 Zinc (Zn)

Various metabolic pathways are dependent on different nutrients that the plant uptakes from various sources; zinc is one of the essential micronutrients required in the normal functioning of various metabolic processes in plants. It is a structural part of several enzymes and transcription factors, and also acts as a cofactor for enzymes such as peroxidase, dehydrogenase, oxidase, and anhydrase. It's very well known to regulate nitrogen as well as photosynthesis (Swietlik 1999; Marschner 1995).

However, an increase in its concentration up to 150–300 mg/kg (Warne et al. 2008; Devries et al. 2002) and uptake by the plant results in phytotoxicity events that can be overviewed due to the physical effects. This results in noticeably lowered or inhibited metabolism resulting in reduced growth and development in several species including the common bean (Cakmak and Marshner 1993) and mustard (Prasad et al. 1999), along with oxidative damage triggered by an increase in zinc or cadmium concentration. Senescence may also result depending upon metal concentration in the contaminated soil.

In abnormal concentrations, Zn and Cd can cause abrupt changes in enzymatic activities and their efficiency to catalyze associated pathways in bean (Somasekharaiah et al. 1992; Van Assche et al. 1988) and pea plants (Romero-Puertas et al. 2004).

Root growth as well as shoot growth has been shown in various studies to be limited in higher Zn concentrations (Fontes and Cox 1998; Ebbs and Kochian 1997; Choi et al. 1996). Leaf chlorosis may result in young leaves and extend to the older ones in the case of long-term exposure to excessive Zn (Ebbs and Kochian 1997).

High Zn concentration also results in a competitive micronutrient transfer to upper plant parts; a high Zn level causes difficulty for Mn and Cu in moving from the roots towards the shoots causing their deficiency in the shoot region and accumulation in the root region (Ebbs and Kochian 1997), disturbing the metabolic processes. Apart from the micronutrients Mn and Cu, the macronutrient P's transport has also been shown to be hindered producing reddish-purple leaf color representing a P deficiency in the plant leaf (Lee et al. 1996).

3.4.4 Manganese (Mn)

Mn has an important role in functionality of several enzymes. It also has an important role in photosynthesis and as part of the chloroplasts. Mn is basically an important nutrient for better growth of the plant (Marschner 1995; Burnell 1988). Despite its essentiality, higher concentrations of Mn compromise plant health and growth.

Photosynthesis has been observed to slow down as a result of high Mn concentrations (Kitao et al. 1997a, b). Chlorophyll synthesis gets affected due to alterations in certain vital processes (Clarimont et al. 1986). Rice accumulates Mn in its chloroplasts (Lidon et al. 2004; González and Lynch 1999) and common bean shows decreased chlorophyll levels and activity (González and Lynch 1997, 1999; Gonzalez et al. 1998). Tobacco and wheat have also been known for these effects under Mn toxicity; chlorophyll decreases significantly in wheat and its activity falls down in tobacco under such conditions (Moroni et al. 1991; Houtz et al. 1988; Nable et al. 1988).

Mn toxicity may block the availability of certain nutrients such as Fe due to its antagonistic effects on it, which is also a cause of chlorosis in such plants as a result of insufficient uptake of Fe by the plants (Lidon 2002; Horst 1988a, b). This is because Fe and Mn share the same exchange or translocation sites and thus compete

for these sites. At higher Mn concentrations, it is able to occupy these sites to enhance its uptake inhibiting Fe uptake by the plant (Alam et al. 2000).

Higher Mn concentrations than normal cause necrosis in the aerial parts of the plants (Wu 1994) leading to browning of the leaves and ultimately the leaf dies (Elamin and Wilcox 1986a, b), such as in cucumber (Crawford et al. 1989). Browning of roots and leaves may also be caused during Mn toxicity: in leaves it causes chlorosis, whereas in roots it causes cracking (Foy et al. 1995; Le Bot et al. 1990; Bachman and Miller 1995; Wu 1994). Chlorosis and necrosis of leaves is also an effect of toxicity caused at higher Mn concentrations in cowpea and common bean, due to its oxidation in the epidermal cell wall (Wissemeier and Horst 1992; Horst and Marschner 1987; Horst 1982).

Enzymatically, the plant generates peroxidase as a result of induction of oxidative stress in response to Mn toxicity (Fecht-Christoffers et al. 2003).

3.4.5 Nickel (Ni)

Ni is another micronutrient acting as a structural part of enzymes such as urease helping in normal functionality. It plays a redundant role as cofactor in some enzymes replacing Zn and Fe. Ni is a trace element; however, its concentration has been rising because of industrial activities releasing pollutants into the ecosystems, that include but aren't limited to mining, smelting, and even fertilizers (Gimeno-Garcia et al. 1996).

Toxic levels of Ni in the soil can lead to severe alterations in metabolic activity of the plant, stunted growth, and ultimately reduced yield. Chlorosis is an aftereffect of high Ni concentrations and uptake by the plant (Yang et al. 1996b). Certain vegetables are known to uptake and accumulate Ni in their leaves (Sharma and Kansal 1986).

Ni toxicity caused by abnormally high levels of Ni²⁺ causes a wide variety of physiological changes that lead to abnormal physical appearances such as chlorosis and necrosis in crops such as rice (Rahman et al. 2005; Pandey and Sharma 2002; Zornoza et al. 1999; Das et al. 1997; Sabir et al. 2014). Ni toxicity is also known to affect nutrient uptake activities of the plants. With an increase in concentrations of Ni, Fe has a direct relation and increases in shoots and roots of fenugreek, whereas the opposite occurs for Zn and Cu at both sites (Parida et al. 2003) due to the competition among them for exchange sites at the roots for uptake by the plant (Narwal et al. 1994; Cataldo et al. 1978). The direct uptake relation of Ni with Fe is also known for maize plant.

Under high concentrations, Ni gets accumulated in the roots as well as shoots of the plants, for example, fenugreek (Parida et al. 2003), spinach, mustard, and chickpea (Gupta et al. 1996; Wadhawan 1995).

Shoots of crops are affected at the enzymatic levels, for example, H-ATPase in the plasma membrane of rice (Ros et al. 1992). Ni toxicity can be observed as lowered water uptake in the plants which has been studied in angiospermic species, both monocots and dicots (Gajewska et al. 2006; Pandey and Sharma 2002).

Ni toxicity is also known to cause metabolic disturbances in wheat (Pandolfini et al. 1992) and other plants depending on their sensitivity to stress and the conditions (Gonnelli et al. 2001).

3.4.6 Cobalt (Co)

Higher concentrations of Co are found in many types of soils including calcareous and acidic soils. Industrial areas including industries set up for refining metal have higher Co concentrations than normal in their surrounding regions due to their effluents being released into the environment (Freedman and Hutchinson 1981; Barceloux 1999).

Co is important as part of the vitamin B12 complex. It has an important role in the symbiosis of leguminous plants with nitrogen-fixing bacteria. It is known to influence various enzymes as well as coenzymes by making various associations with them (Marschner 1995). At higher concentrations and affected by the mineral composition of the soil, its uptake by the plant increases (Kubota 1965). However, even at higher concentrations, with a rise in the pH of soil, significant reduction in its uptake occurs (Adriano 1987). Co toxicity is known to cause alterations in the uptake and translocation of various nutrients important for plant growth and development. Chlorophyll content in the chloroplasts also is affected under such conditions and the process and rate of photosynthesis reduces to a significantly lower level in addition to affected enzymatic activity (Vanselow 1965). Iron chlorosis gets induced in barley under Co toxicity due to its inhibitory effects on the activity of catalase and decreased chlorophyll content (Agarwala et al. 1977).

Co toxicity in plants hasn't been studied much in detail, however, shoot growth is known to be retarded and adversely effected in tomato, barley, and rapeseed, along with biomass reduction of the plants (Li et al. 2009). The effects of higher Co concentration on cauliflower have also been studied and are shown to disturb the normal uptake and transport of other nutrients including P, Mn, Cu, Zn, and S from the roots of this plant. Photosynthetic activities are affected because of reduced Fe and chlorophyll amount in the leaves due to Co toxicity. On the enzymatic level, certain proteins such as the enzyme catalase become limited. The water content in leaves, however, is known to rise under higher Co concentrations than usual (Chatterjee and Chatterjee 2000).

Plant metabolism has been reported to be negatively affected by Co concentrations as low as 0.1 ppm in the medium. Retarded leaf growth accompanied by chlorosis is an effect of Co toxicity in citrus (Vanselow 1965). Concentrations of Co as much as 50 ppm cause Co toxicity and adverse effects on the leaf of oats (Vergnano and Hunter 1952).

3.4.7 Lead (Pb)

Pb has been found to be the most abundant element in soil with highly toxic effects on life especially for plants growing in the contaminated soil which are affected in terms of growth and development by alterations in their vital metabolic pathways

such as photosynthesis (such as cause of chlorosis). Due to its effects on enzymes, it can cause reduction and loss of germination in some plants (Morzck and Funicelli 1982). Effects on the enzymatic levels include activity reductions of amylase and protease to about half in the endosperm of rice (Mukherji and Maitra 1976). Photosynthetic processes are affected because of enzyme inhibition (Sinha et al. 1988a, b), for example, the enzymes involved in fixing carbon dioxide, carboxylating enzymes (Stiborova et al. 1987), and also unbalancing the mineral nutrition of the plant (Sharma and Dubey 2005).

Hazardous effects of Pb on crops have been an interest for scientists since long ago. They have been studied to reduce and even completely abolish growth of seedlings in important crops such as rice, tomato, maize, soybean, barley, and some leguminous plants (Huang et al. 1974; Miller et al. 1975; Mukherji and Maitra 1976; Stiborova et al. 1987; Sudhakar et al. 1992). Pb is known to affect radish, barley, and onion at all parts of the plant, including leaves, stem, and underground roots by interfering with the process of elongation (Juwarkar and Shende 1986; Gruenhagen and Jager 1985). Negative effects on root growth increase with rising Pb levels, for example, in sesame (Kumar et al. 1992). The degree of damage by Pb toxicity also depends upon the pH and the ionic composition (Goldbold and Hutterman 1986).

The morphological effects of Pb on pea and sugar beet have also been studied extensively at anatomical levels (Paivoke 1983). It has also been reported in vascular plants to interfere with the process of repair (Kaji et al. 1995). However, it's interesting how alfalfa doesn't show any apparent effects on its morphology even under Pb concentrations as high as 100 mg/mL (Porter and Cheridan 1981). But in the case of lettuce and carrot roots, a considerable effect occurs on growth patterns and rate (Baker 1972). Pb⁺² toxicity altering metabolic pathways highly reduces plant growth and hence its overall biomass (Van Assche and Clijsters 1990). The effects are also known to induce reactive oxygen species (ROS) under Pb toxicity (Reddy et al. 2005).

3.4.8 Cadmium (Cd)

Cd gained attention due to being the most abundant and severely toxic heavy metal; its uptake by the plants has raised concerns (Arora et al. 2008). Cd concentrations higher than 100 mg per kilogram in soil (Salt et al. 1995) can cause phytotoxicity in crop plants resulting in retarded growth, necrosis, chlorosis, root tip browning, and senescence (Guo et al. 2008; Mohanpuria et al. 2007; Wojcik and Tukiendorf 2004; Sanita di Toppi and Gabbriellini 1999). Altered nutrient uptake, for example, reduction in uptake, is known to be a cause of Cd toxicity for important mineral macronutrients and micronutrients (Mohamed et al. 2012; Yang et al. 1996a).

Cd is known to have a highly negative effect on the process of photosynthesis (Mohamed et al. 2012). In some plants, the process of photosynthesis is disturbed due to deficiency of Fe(II) caused as a result of high Cd concentrations (Alcantara et al. 1994). Gaseous exchange through stomata is known to be affected under Cd

toxicity (López-Climent et al. 2011). Higher Cd concentrations have also been known to be a cause of closed stomata in soybean and clover, resulting in reduced or no transpirational activity at all (Barcelo and Poschenrieder 1990). Alterations in the uptake and transportation of macronutrients such as K, P, and Ca, the micro-nutrient Mg, and even water occur as a result of higher Cd concentration (Das et al. 1997).

Cd has also been identified to inhibit nitrate assimilation in the shoots of some plants by affecting the enzyme nitrate reductase failing root-to-shoot transport of nitrates (Hernandez et al. 1996). Higher Cd concentrations cause a reduction in the assimilation of ammonia and fixing nitrogen in plant nodules, for example, in soybean (Balestrasse et al. 2003).

Permeability of the plasma membrane is altered by high Cd concentrations toxic to the plant resulting in reduced water content (Costa and Morel 1994) and ATPase activity, for example, in roots of sunflower as well as wheat (Fodor et al. 1995). Lipid peroxidation has also resulted because of higher Cd levels (Fodor et al. 1995). Some other consequences include effects on those enzymes responsible for carbon dioxide fixation and inhibition of chlorophyll synthesis in the chloroplast affecting metabolism (De Filippis and Ziegler 1993). Cd toxicity induces oxidative stress in plants with a huge reduction in concentrations of superoxide dismutase, catalase, and peroxidase (Mohamed et al. 2012; Milone et al. 2003; Hendy et al. 1992).

Growth and as a result yield of crop plants such as chickpea, maize, and soybean reduce to significantly lower levels at toxic Cd levels (Hasan et al. 2008; Krantev et al. 2008; Dewdy and Ham 1997). Reduced vegetative growth under such conditions has been reported in maize and mung bean (Ekmekci et al. 2008; Wahid and Ghani 2007).

3.4.9 Chromium (Cr)

Cr is known to hold the seventeenth place on the list of most abundant elements found in nature (Avudainayagam et al. 2003). Over the past years, an increase in chromium levels in the environment due to industrial activities has raised concerns regarding the risks it causes in contaminated environments (Zayed and Terry 2003).

Concentrations above 100 $\mu\text{ kg}^{-1}$ dry weight cause toxicity to plants growing in contaminated soil (Davies et al. 2002). Large quantities of Cr cause disturbances in the physiological processes of the plant and hence affect the initial seed germination negatively (Peralta et al. 2001), for example, germination of common bean reduces to half its original rate during Cr (VI) toxicity (Parr and Taylor 1982), germination of alfalfa reduces to around one fourth in Cr (VI) toxic medium (Peralta et al. 2001), and sugarcane bud germination decreases by one third to about half the percentage (Jain et al. 2000). Wheat germination has been known to be markedly reduced in high Cr(III) conditions, in contrast to oat, which is not affected at levels under 4000 mg per kilogram of soil (Lopez-Luna et al. 2009). On the enzymatic level, this reduction in germination rate is a result of the effect on the activity of protease, which is enhanced by high Cr levels, or reduced amylase activity which involves sugar transport (Zeid 2001).

A variety of crops and trees has been shown to be affected by diminished root growth due to the occurrence of heavy metals (Tang et al. 2001). Cr is one of the heavy metals with the most hazardous effects on the root length of plants (Prasad et al. 2001). It may be a result of the fact that a large portion of the chromium taken up by the plant remains in the root region and only a fraction of it moves towards the upper parts (Paiva et al. 2009; Sundaramoorthy et al. 2010). Cr (VI) has been known to cause significant reductions in root number as well as growth and later root formation in mung bean (Rout et al. 1997; Samantary 2002). Similarly, in maize, it causes reductions in size and root hair (Mallick et al. 2010).

Plant height has been reported to reduce as a negative effect of Cr(VI) on shoot growth in oat, maize, wheat, and mung bean (Mallick et al. 2010; Rout et al. 2000; Lopez-Luna et al. 2009). Leaf growth in cauliflower is affected by Cr(III) toxicity (Chatterjee and Chatterjee 2000; Pandey et al. 2007, 2009).

Photosynthesis is largely affected by Cr toxicity at various enzymatic as well as metabolic levels, such as carbon fixation and the electron transport chain (Clijsters and Van Assche 1985). Again in this case, Cr (VI) has been studied well to affect both photosystems in the chloroplasts, for example, in peas (Bishnoi et al. 1993a, b). Cr toxicity causes an imbalance in the uptake and translocation of various mineral nutrients in crops such as maize, rice, watermelon, and spinach (Mallick et al. 2010; Sundaramoorthy et al. 2010; Dube et al. 2003; Gopal et al. 2009).

Heavy metal stress is known to induce antioxidant activity as a stress response when levels rise from the normal tolerable level (Shanker et al. 2003a). This includes activation of antioxidant enzymes such as catalases and SODs (superoxide dismutases) until the concentration rises to a certain point after which the activity of SOD does not rise and that of catalase lowers (Gwozdz et al. 1997).

3.4.10 Mercury (Hg)

Living beings have been endangered by yet another pollutant, mercury, with a very high risk factor (Boening 2000). Hg toxicity in agricultural lands results from an increase in Hg^{+2} levels (Han et al. 2006). More importantly, the toxicity caused by it and the aftereffects are far more severe and worrisome than several other metals and heavy metals, including but not limited to zinc, cadmium, copper, and lead (Munzuroglu and Geckil 2002).

Hg toxicity causes adverse changes in physiological processes in various species (Zhou et al. 2007), accumulating in higher plants as well as aquatic ones (Israr et al. 2006; Wang and Greger 2004; Kamal et al. 2004). In higher plants, toxicity resulting from this heavy metal can trigger various responses, based on biochemical as well as physicochemical changes, leading to visual and noticeable changes in normal plant life (Gupta and Chandra 1998).

As the concentration of mercury increases in the medium, biomass begins to decrease as shown by many plant species (Patra and Sharma 2000); however, with

rising nutrient concentrations in the medium, the amount of mercury uptake by the plant starts to fall down considerably (Göthberg et al. 2004). It has also been reported that the mercury, when present, can cause noticeable changes in the translocation pattern and uptake amount of various nutrients required for normal functioning of the plant (Gupta and Chandra 1998).

Hg has been reported to be a cause of decreased levels of chlorophyll in higher plants as a result of the high inhibitory effects on the enzymes involved in its biosynthesis, thus affecting photosynthesis (Cho and Park 2000; Prasad and Prasad 1987). Another effect is a change in flow of water by a physical blockage due to closure of stomata (Zhang and Tyerman 1999). The ROS level is elevated as an active response to oxidative stress induced in response to high Hg levels, which also influence the mitochondrial activity leading to disrupted metabolic activities (Cargnelutti et al. 2006; Messer et al. 2005). At the enzymatic level, during oxidative stress induced as a result of Hg toxicity, an increase in the activity of peroxidase, catalase, and superoxide dismutase, as well as malondi-aldehyde and hydrogen peroxide at the molecular level have been observed (Cho and Park 2000).

As a response to toxicity caused by mercury, the plant cell wall can retain mercury as a strategic measure for its defense (Cavallini et al. 1999).

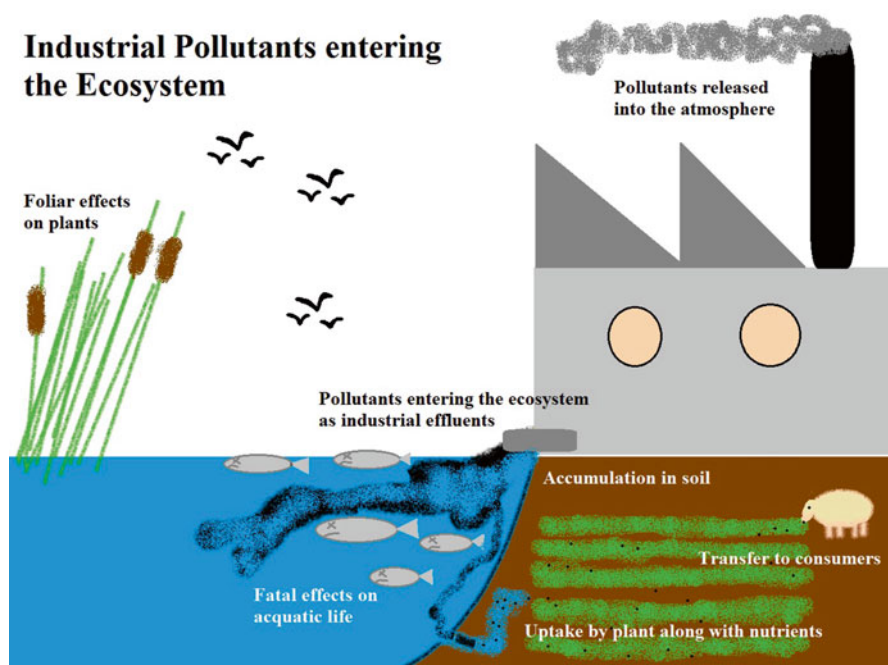


Fig. 3 Overview of industrial pollutants being released into the environment and entering the food chain

4 Long-Term Ecosystem Effects: Why Consider Pollutant Treatment before Discharging into the Environment

As a result of toxicity and accumulation in the plant, these pollutants enter the food chain as plants are at the bottom of the food chain and are a primary source of food for most living species. The end-user for crops is a human who cultivates this crop on quite large scales as a food source and its effect on them needs to be detailed to get a better understanding of how these pollutants are adversely affecting the ecosystem and all the living organisms in it. The entrance of these pollutants into the environment and the effect on the food chain is briefly represented in Fig. 3.

5 Conclusion

Industrial pollutants containing organic and inorganic compounds, metals, and heavy metals, need to be pretreated before their discharge and entrance into the ecosystem as they adversely affect plant life at all levels, including seed germination, seedling and plant growth at roots, shoots, leaves, fruit, and total biomass of the crops. Although beneficial for the plant at optimal levels causing improvement in growth and development at various stages, the same elements that act as nutrients for the plant can cause toxicity leading to harsh environmental conditions which harm plant growth considerably and raise concerns regarding the safety and balance of nature. The accumulation of these pollutants in the atmosphere and the environment as a whole disturbs the balance among various levels of the ecosystem as plant yield decreases which is the basic source of food in the ecosystem. As these elements accumulate in the soil, plants, being unable to move, having no choice but to grow and survive under these phytotoxic conditions, uptake these harmful elements, and accumulate them in various parts depending upon their translocation patterns. When these plants are consumed by various animals and humans, the toxic elements, including the heavy metals are transferred to them and can cause serious health issues. The accumulation of these industrial pollutants in agricultural soils is thus quite dangerous as the crops grown over them are affected adversely and transfer these adverse effects to humans, being the ultimate food consumer of those crops. Another aspect of the harm caused by these pollutants is the huge economic losses caused by them as a result of considerable yield reduction due to the crops being unable to cope with the polluted soil resulting initially in either lower biomass production or worse, no germination at all. Although the plants have evolved certain ways to survive these stressed conditions, including changes in translocation pattern, nutrient uptake, or altered gene expression to counteract the effect of these elements, certain crop plants are sensitive to them and are not able to keep up with the changing harsh conditions. As a result, they may be affected which is sometimes seen as visual symptoms of chlorophyll loss, chlorosis, necrosis, abnormal growth, wilting, and ultimate death of the plant. The balance of nature thus needs to be

maintained to avoid unprecedentedly adverse conditions severely affecting plant growth leading to poor human health as the final consumer level is the human for whose well-being all the research carried out is directly or indirectly focused. As these pollutants have raised concerns and endangered all life forms, there should be strict policies applied for the industrial pollutants entering the environment in any form and action should be taken to preserve the balance of nature.

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