Chapter 8
Impact of Pollutants on Paddy Soil and Crop Quality

Iftikhar Ali, Muhammad Jamil Khan, Mumtaz Khan, Farah Deeba, Haziq Hussain, Muhammad Abbas, and Muhammad Daud Khan

8.1 Introduction

The word "paddy" is derived from the Malay word *padi*, "the rice plant" (Crawford and Lee 2003). Paddy soils can be defined as soil portion which is flooded/submerged for cultivation of rice. This process may include flooding, puddling, ponding, and making water layer on soil surface. In more convenient way, paddy soils term is used for those soils, which are submerged for a long period of time especially in rainfed and irrigated system of rice cultivation. Nearly/almost 90% of paddy soils are contributed by Asian soils. These soils flooded for rice cultivation are subjected to various processes like nutrient cycling, carbon storage, and availability of nutrients to rice crops. After the crop harvest, the soils are then drained off naturally or artificially, and this characteristic makes paddy soils differentiated from other soils (Kyuma 2004). The important changes caused due to the submergence of soils are oxygen deficiency and ultimately decrease in soil Eh (redox

I. Ali
Department of Biotechnology and Genetic Engineering, Kohat University of Science and Technology, Kohat, Pakistan

Department of Soil and Environmental Sciences, Gomal University, D.I. Khan, Pakistan

M. J. Khan · M. Khan
Department of Soil and Environmental Sciences, Gomal University, D.I. Khan, Pakistan

F. Deeba · H. Hussain · M. Abbas
Department of Biotechnology and Genetic Engineering, Kohat University of Science and Technology, Kohat, Pakistan

M. D. Khan (✉)
Department of Biotechnology and Genetic Engineering, Kohat University of Science and Technology, Kohat, Pakistan

Department of Environmental Sciences, Kohat University of Science and Technology, Kohat, Pakistan

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potential), i.e., O_2, H_2O, NO_3-N, $Fe^{3+,2+}$, SO_4^-, S_2, CO_2, CH_4, etc., and increased soil pH and variation in soil aerobic and anaerobic microbial population. All these affect soil nitrogen availability, fixation, and also phosphate solubility. Among these changes occurring at flooding conditions, some changes may be recovered/reclaimed, while others are non-recoverable like ferrolysis that may cause destruction of smectite clay lattice.

According to an estimate, 24–30% of freshwater resource is used for soil submergence to raise the rice (Bouman and Van Laar 2006). Mostly rice is grown in developing countries, and with the rapid growth of economics of these countries, more water is needed for industrial and household use as compared to agriculture activities. Therefore, the issue of paddy soil management and rice production is becoming a challenge as a result of lowering ground water table and increased demand of freshwater.

8.2 Characteristics of Paddy Soils

Paddy soils exhibit their own specific properties as a result of variant use of soil and cultivation practices. This makes them significant from other agriculture soils. A brief description of these characteristics is given as under.

8.2.1 Paddy Soil Redox Potential (Eh)

Paddy soil redox potential changes as a result of flooding conditions. Normally soils have a redox potential (Eh) value of 200 to 300 mV to +500 to +700 mV (Li 1992c), and after flooding, this may decrease/drop to nearly 250 mV. This fluctuation clearly indicates the variation in oxidation-reduction reactions of constituents/components of soils like oxygen (O_2), iron (Fe), manganese (Mn), nitrogen (N), sulfur (S), and carbon (C). During flooding, the soil pores which are initially filled with air are then filled up with water, and thus soil air/oxygen gets reduced. The soil microorganisms use the available oxygen and ultimately redox reactions occur. Among the redox reactions, soils containing high content of Fe^{2+} exhibit higher redox potential (Eh) buffering capacity.

8.2.2 Paddy Soils pH

Paddy soils have variations in pH which results mainly from alternate wetting and drying of soils. This change is mainly caused by water content of soil, amount of neutral salts, and type of cations in soil solution and on exchange complex. Generally soil pH increases with water content and decreases with sodium chloride (NaCl) concentration (Li 1992a). Similarly, soil having high organic matter show instant/

temporary rise in pH after flooding up to 3 days and then slowly fall down and become stabilized on half month of flooding period, while soils low in organic matter content increase their pH gradually after flooding, and this becomes stable till the half month of flooding. Soil pH also changes with the reduction dissolution of iron oxides by consuming H^+ ions in soil. These periodic changes in soil Eh and pH highly favor the iron redox cycling in paddy soils (Li et al. 2006).

8.2.3 *Nitrogen Fertilizer*

Elemental nitrogen is the 1st most important primary macronutrient for various crops and second most important for rice growth. Its application has largely increased worldwide with the aim to increase rice yields, but its utilization efficiency is approximately 37% (Shaobing and Jianliang 2002). This level of utilization efficiency clearly indicates the losses of applied nitrogenous fertilizers. There are two major pathways of applied N fertilizers, i.e., ammonia (NH_3) emission/volatilization (ammonification) and denitrification (Li 1992b). Approximately 12% of N losses occur due to NH_3 (Zhao et al. 2009). Ammonification is the conversion of organic nitrogen (N) to inorganic, and this mainly occurs by fixation of NH_3 to NH^{4+}, a most important transformation process in paddy soils. Zhang and Scherer (2000) reported that NH^{4+} depends upon the amount exchangeable NH^{4+} ions and lower value of redox potential (Eh). The reduction and dissolution of iron oxides due to low redox potential (Eh) value enhances the NH^{4+} fixation into interlayer minerals (Zhang and Scherer 2000). Also nitrification is the transformation process of NH^{4+} to nitrite NO_2 and ultimately nitrates NO_3 encouraging nitrogen cycle in nature (Jiang et al. 2015). This oxidation of ammonia may lead to substantial/partial loss of N fertilizer either by leaching or by denitrification. Denitrification process involves the change of nitrate NO_3 to nitrite NO_2 to nitric oxide NO to nitrous oxide N_2O and ultimately to N_2 gas. Li and Lang (2014) and Xing and Zhu (2000) reported that denitrification of NH_3 through gaseous emission is a main pathway of N fertilizer loss resulting in low fertilizer efficiency in paddy soils. However, various factors influence the process of denitrification such as soil pH, temperature, soil organic matter, NO_3 concentration, reductants concentration, and oxygen partial pressure (Lan et al. 2015; Rahman et al. 2014). Ding et al. (2014) concluded that NH^{4+} oxidation may be the major mechanism of nitrogen fertilizer loss through N_2 gas emission, which is mainly caused due to the alternate wetting and drying of soil that fluctuate the soil redox potential Eh.

8.2.4 *Paddy Soil Rhizosphere Environment*

Rhizospheric soil is found in the vicinity of roots and is influenced by roots secretions. In paddy soils, rhizosphere parenchyma cells are responsible for translocation of molecular oxygen (O_2) to roots, and therefore, redox potential around the roots is comparatively higher than surroundings (Kögel-Knabner et al. 2010). This higher redox potential may oxidize redox active substances such as $Mn^{4+}$and Fe^{2+} and as a result of these oxides formation causing plaque on root surface (Kögel-Knabner et al. 2010). This plaque plays an important bioenvironmental role in the immobilization of heavy metals near root surface (Du et al. 2013). During rice growth, various developmental stages influence soil redox potential (Eh) near the root surface, i.e., tillering stage significantly reduces redox potential due to the formation of nodes as it inhibits the transport of O_2 from stem to roots. Similarly, in heading stage, the formation of roots occurs during which O_2 is transported to roots and thus increasing redox potential Eh of rhizosphere soil. However, pH of the rhizosphere soil is inversely affected as a result of growth and development stages. This mainly causes the secretions of various organic acids, proteins, carbohydrates, mucilage, alcohols, vitamins, and hormones, thus contributing changes in various soil biogeochemical processes. Normally difference of 0.4 to 1.5 unit of pH was found between rhizosphere and neutral soils (Li 1992d). All these materials produced by root caps act as media or substrate for various soil microbes and also immobilize toxic heavy metals (Bacilio-Jiménez et al. 2003). Jia et al. (2014) reported the oxidation of As^{3+} to As^{4+} as a result of enhanced microbial activity and As^{4+} sequestration by iron oxides and hydroxides by iron plaque in root caps, thus contributing in the reduction of low bioavailability and uptake of arsenic.

8.3 Pollutants in Paddy Soils

8.3.1 Excess Use of Chemical Fertilizers

Application of chemical fertilizer has become an integral part of modern agriculture, and nearly 25% yield production of crops is accredited to the use of organic and inorganic fertilizers. Soil needs various plant nutrients in different concentrations for normal growth and development of crops. Among these, N, P, K, Ca, Mg, and S are needed in large quantities called as macronutrients, while others like B, Fe, Zn, Cu, Mo, Mn, Ni, and Cl are needed in small amounts known as micronutrients. These nutrients are essential for various normal functions of crops. At maturity level when the crops are harvested, some amounts of nutrients are exhausted and therefore soil becomes deficit in nutrients, thus resulting in low fertility. Resultantly, there occur low crop yields and biomass production. Hence rehabilitation of soil fertility status is necessary for normal crop growth and yield. Rice needs greater amount of nutrients result in reduced soil fertility and net return per unit area (Anonymous 2001). Rice crop needs 15 kg N, 4 kg P_2O_5, and 24 kg K_2O per ton production of rice grain with equal amount of straw from the soils (Hegde 1992). Normally, high-yielding varieties of rice take up more nutrients than applied amount of fertilizers. This imbalanced application of fertilizers cause low soil fertility and decreased/low crop yields (Nambiar et al. 1992). Similarly overdose of fertilizers also causes severe hazards not only to plants but also contaminates soil water environment like eutrophication, etc. Therefore, proper and balanced use of fertilizer is necessary for nutrient supply and maximum fertilizer use efficiency (Tiwari 2001).

8.3.2 Lead and Cadmium in Fertilizers

According to Donald Worster "soil is natural resource which cannot be recreated by application of chemical fertilizers"; therefore, we need integrated farming system for sustaining soil health and degrading soil environment pollution. Reckless use of fertilizer for intended rice crop yields has raised a problem of heavy metal pollution especially lead and cadmium in soil environment. The whole amount of the fertilizers applied is not taken up by the crops, some of its part lost in the air through volatilization while some is leached down in soil profile which ultimately results in the pollution of natural resources.

8.3.3 Nitrogen as Pollutant

Excess use of nitrogen fertilizer also poses a threat in paddy soil especially when they are either flushed out with runoff water or leached down in groundwater and converted to nitrite. Nitrogen fertilizer is added to soil in various forms like organic and inorganic nitrogen which are rapidly mineralized to ammonia and nitrate through various chemical and biological processes in tropical and subtropical areas. The nitrate formed become prone to leaching if not taken up by plants or denitrified. Nitrate-rich groundwater is commonly subjected to impervious layer in paddy soils resulting in shallow water table (Misra and Mani 1994). However, runoff losses are very rare and nitrate is mainly harmful in nitrite form.

8.3.4 Potash as Pollutant

Potassium the third most required macronutrient by plant is also considered as pollutant if it is present in excess amount in soil. Mahalanobis (1971) reported 15.94 kg/ha loss of potassium in irrigated lowland rice soils. Similarly, Naidu (1974) also reported an average loss of 21.10 kg/ha in submerged rice soils which is comparatively greater than that of unsaturated soils ranging from 5 to 8 g/ha.

8.3.5 Pesticides in Paddy Soils

Pesticide application has become an essential component of modern farming system. However, their use may cause a severe hazard not only to soil environment but also to human beings and all living organisms. Commonly pesticides are applied to plant foliage, and nearly 99% of which ultimately comes into soil subjecting to various fates/processes in soil. Generally per hectare use of pesticide might be low than developed countries, but most of them are highly persistent and nondegradable. The agriculture sector uses 250 pesticides, 100 of which are insecticides. Pesticides are used against pests, they may also affect other soil beneficial organisms which use soil as a harbor for their survival and have important role in soil fertility and health. Only 1% of the applied pesticides reach their target, and the entire remaining amount may adversely affect soil flora and fauna (Misra and Mani 1994). Irrigated rice is more prone to pest attack and generally above 100 species of pests and pathogens may attack on rice. This results in a loss of 5–15% of yield, and therefore, greater amount of pesticides and fungicides are used to get desired yields. Almost 17% of total pesticides used is applied to rice crop (Subbaiah 2006). The high-yielding varieties of rice and other cereals are easily attacked by pests and diseases; thus, it has increased the use of chemicals. The persistence and degradation of pesticides/insecticides depend upon various factors like nature of chemical and soil (type, moisture, temperature, aeration, fauna, etc.). The persistent chemicals tend to accumulate in soil, plants, and living organism through food chain. For example, DDT is a synthetic insecticide and was considered very effective in its initial era/stage of application, but after some time, it was found very injurious/toxic as its half-life in temperate areas goes on from 10 to 15 years and that is in tropical areas 6 months. Pesticides also get attached to soil particles which are translocated by various agents, and thus they may accumulate everywhere in soil.

8.3.6 Excess Salt Water in Paddy Soils

Like other problems of soil, excess amount of salts and water also negatively affect paddy soils, as most of irrigation water contains higher amount of salts and large amount of this water is lost through evaporation. As a result salts make layer on soil surface. This causes low growth, low yield, and ultimately plant death, and soil becomes degraded and unfit for agriculture. The removal of these salts is costly and also makes downstream water salty. Excess water in soil is a major issue that causes waterlogging (a condition in which all the soil pores become filled with water and anaerobic condition is developed). This mostly occurs in poor drained saline soils where large amount of water is applied for leaching salts in water, and water table is raised to root zone enveloping plant roots that ultimately result in crop failure.

8.3.7 Arsenic

Arsenic is a bioactive toxic metalloid which is accumulated in rice. Long-term exposure to arsenic (As) causes various diseases like hypopigmentation; melanesia;

keratosis; skin, bladder, and lung cancer; etc. (Naujokas et al. 2013; Smith et al. 2003). The food and drinking water are the sole pathways of arsenic (As) to human and animals. Besides other heavy metals like cadmium, rice is an efficient accumulator of arsenic (As), making its consumption a major source of arsenic (As) exposure to humans (Sohn 2014). Arsenic is almost present every part/ubiquitous of the world. In aerobic condition, it occurs in oxidized form, i.e., As(V), where in anaerobic condition it is present in reduced form, i.e., As(III) (Huang et al. 2011). Arsenic (As) is more efficiently accumulated in rice as compared to others cereals as a result of dominant anaerobic conditions causing As^{3+} which is mobile form of As (Xu et al. 2008; Sohn 2014; Williams et al. 2007). Rice is also a Si accumulator and needs large amount of Si for optimal growth. Due to the resemblance with silicon (Si), rice accumulates larger amount of As (Ma and Yamaji 2006). Rice grain contains inorganic As^{3+} and As^{5+} and also considerable amount of organic arsenic (As) as dimethyl arsenic acid (DMAV) (Williams et al. 2005). Rice nodes are the most crucial place for As storage, serving as a filter restricting arsenic (As) transfer/movement/translocation to the shoots and rice grains (Song et al. 2014; Yamaji and Ma 2014; Chen et al. 2015).

8.3.8 Fluorine

Fluorine is thirteenth most abundant element in earth crust, but its uptake by plant from the substrate is low as it occurs mostly in unavailable form (Ochoa-Herrera et al. 2009). However, in polluted soils, plants may take up large amount of fluorine (Smolik et al. 2011). It is a common phytotoxic element in air and soil pollutants (Zhang et al. 2013). Soils contaminated with greater amount of fluorine accumulate it, and plants grown on such soils exhibit chlorosis and necrosis eventually decreasing chlorophyll content of plants resulting in decreased biomass and low growth (Gupta et al. 2009). Kumar and Singh (2015) demonstrated a 73% decline in the amounts of roots biomass harvested from *Gossypium hirsutum* L. under the irrigation water contaminated with fluorine in a dose of 1000 ppm.

8.3.9 Methane Emission

Methane (CH_4) is a potent greenhouse gas produced by anaerobic archaea by anoxic conditions. According to an estimate, rice contributes 11% to the total anthropogenic emission of greenhouse gas (Smartt et al. 2016). Methane emission from rice soils is an end product of complex anaerobic process in which a group of microorganism (bacteria) decomposes soil organic matter to acetate H_2 and CO_2. The acetate produced is further degraded by methanogenic archaea to CH_4 and CO_2 (Conrad et al. 2006; Nazaries et al. 2013). The process involved in methane production consists of two steps, i.e., methane production by methanogen bacteria and methane oxidation by methanotrophs and vertical transport of gas from soil to atmosphere. Methane production mainly depends on available methanogenic substrate and environmental factors. Sources of methanogenic substrates as an organic carbon are mainly rice plants, i.e., roots exudates, root senescence, plant litter, and organic fertilizer added (Lu et al. 1999). The environmental factors influencing methane emission from rice soils are soil texture, climate, and agricultural practices (Wassmann et al. 2000).

8.3.10 Heavy Metals

Heavy metal pollution is ubiquitous problem in most of the global soils. It is mainly due to various anthropogenic activities like mining, waste disposal and effluents, etc. in past few decades especially in agricultural soils (Liu et al. 2005; Zeng et al. 2008; Rogan et al. 2009). Among the wider list of heavy metals, some are required to plants in lower quantity as micronutrients like Fe, Mn, Zn, etc., while others are quite toxic and pose large threat to living organisms (Machender et al. 2014; Adepoju and Adekoya 2014). The major pathway of these heavy metals to human beings and other living organisms is soil-crop-food pathway where some part of plant residue as root, straw, etc., is added to soil. Their remaining portions are used as feed/fodder for cattle (Almasoud et al. 2015). Crops and vegetables can accumulate various amounts of metals. This accumulation mainly depends on the mobility and availability of these metals in soils (Sidenko et al. 2007). Yap (2009) reported that most of heavy metals get accumulated in plant roots except for Mn that is accumulated in paddy leaves and Cd evenly distributed in the whole paddy plant. However, Cu is also highly accumulated in paddy plant roots.

8.4 Management of Paddy Soils

Paddy soil management generally relates to the accumulation of soil organic matter (Urbanski et al. 2017). Rice/paddy cultivation basically depends more on the soil moisture status than on soil. Its cultivation is not so much sensitive to prior textural and nutrient status of soil except high sulfate content (Barnes 1990). Thus management practices play vital roles in the development of paddy soils (Kirk 2004). These practices include artificial submergence, plowing, puddling, leveling, organic manuring, liming, and fertilization. They induce some spatial and temporal oxic and anoxic conditions in soil causing oxidation and reduction which ultimately changes dynamics of various organic and inorganic components of soils (Cheng et al. 2009). Anoxic condition mostly prevail during rice developmental stages when the soil is saturated with water. However, when the soils are drained off before the harvest of rice crop, the reduced compounds like Fe^{2+} get oxidized and oxic condition is sustained to a length when upland crops are grown (Jäckel et al. 2001;

Ratering and Conrad 1998; Ratering and Schnell 2000; Krüger and Frenzel 2003). The decrease in redox potential my also cause flocculation and dispersion of soil particles that encourages the translocation/migration of soil particles (Li and Horikawa 1997). This migration of particles to plow layer generates a plow pan and hence increases the water holding capacity of soil. Paddy management leads to the development of pedogenatic horizon which is specific only to paddy soils.

8.5 Impact of Pollutants on Rice Crop

Access to safe food is the desire and demand of each and every individual of any population. People are warned of hidden danger in the dining table especially through unsafe rice and poisoned vegetables through food chain as harmful substances get their way into crops and human and cause severe health problems. Hence soil pollution is now given a great attention as it is a natural resource for plants growth and development.

Since rice is a staple food in most Asian countries. Many paddy soils are recklessly/carelessly contaminated by improper waste disposal that eventually results in contaminated foods. Studies in various countries showed rice containing Cd content to a toxic level. According to an estimate only in China, 12 million tons of rice grain is contaminated each year. Among the wider list of pollutants, elements like As, Pb, Cd, Hg, and Se are highly toxic. The ability of plants to uptake and translocate these metal in different plant parts depends upon various climatic factors, soil factors, plant genotypes, and agronomic practices (Banerjee and Sanyal 2011).

8.6 Remediation Techniques for Polluted Paddy Soils

Remediation of polluted soils is a global issue. Various techniques are adopted for the remediation of soil and ensuring food safety. These include excavation, attenuation by mixing, chemical stabilization, soil washing, phytoremediation, and thermal desorption. The most popular remediation techniques used are as follows:

8.6.1 Dilution/Turnover

This technique is mostly used when the concentration of pollutant is lesser in subsoil than the surface soil. Deep plowing and continuous mixing of layers decrease the metals level in soils. This technique is very suitable in terms of time, budget, rapid reduction in the total concentration of heavy metals, and high impact on crop production after treatment compared with other soil remediation techniques (Hseu et al. 2010).

8.6.2 Chemical Stabilization/Washing

This technique involves the application of various chemicals/amendments, which decrease the solubility and mobility of metals in soils, and thus plant uptake of metals is reduced. It is one of the most cost-effective techniques of soil remediation for heavy metal-contaminated sites (Chen et al. 2000).

8.6.3 Phytoremediation

In this technique, various plant species are used either to degrade or eliminate or uptake various organic and inorganic pollutants in soil. The phytoremediation is a broad term consisting of phytostabilization, phytovolatilization, phytodegradation, etc. Phytoremediation is a suitable method for treating contaminated paddy fields that have large areas and low to medium levels of heavy metal concentration (Lai and Chen 2005).

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