Chapter 12
Arsenic in Untreated and Treated Manure: Sources, Biotransformation, and Environmental Risk in Application on Soils: A Review

Muhammad Zaffar Hashmi, Aatika Kanwal, Rabbia Murtaza, Sunbal Siddique, Xiaomei Su, Xianjin Tang, and Muhammad Afzaal

12.1 Introduction

Over the past two decades, the livestock industry (swine in particular) has grown rapidly all over the world, especially in China, where livestock manure is used as an organic fertilizer for agricultural lands and is produced in excessive amounts. Organic arsenic compounds utilized as feed additives can control swine disease and improve weight. However, environmental excellence and food safety may be compromised by As, if excessive additives are released into the surroundings.

In the past three decades, additives have been used in swine feed to increase the rate of weight gain and to obtain hybrid variety. The accumulation of additives in animal wastes, and their emission levels, as well as their ultimate influence in the environment have been considered of great concern (Li and Chen 2005). Since the

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M. Z. Hashmi (✉) · A. Kanwal · S. Siddique
Department of Meteorology, COMSATS University, Islamabad, Pakistan

R. Murtaza
Center for Climate Change and Research Development, COMSATS University, Islamabad, Pakistan

X. Su
College of Geography and Environmental Science, Zhejiang Normal University, Jinhua, People's Republic of China

X. Tang
Department of Environmental Engineering, College of Environmental & Resource Sciences, Zhejiang University, Hangzhou, People's Republic of China

M. Afzaal
Sustainable Development Study Center, GC University, Lahore, Pakistan

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early 1950s, As, in the form of either sodium arsanilate or arsanilic acid (paraaminophenylarsonic acid; ASA), has been used as a preservative in growing-finishing pig feed to stop dysentery.

To cope with the unlimited demand for high-quality poultry and livestock products, the producers of livestock and poultry have to use modern and advanced technologies. To increase supply and attain this goal, the general approach is to use feed additives. For instance, since the mid 1940s, for improvement in weight and to control poultry and swine diseases, some trace elements, as well as As (100 mg As/kg), have been used in animal food as feed additives (Akhtar et al. 1992; Frost 1967; Inborr 2000; Lindemann et al. 1995). Despite its valuable applications, As in organic form not only contaminates the meat through animal fodder and feeds (Lasky et al. 2004), but is also excreted as organic As in animal manure, thus being released into soil or sediments. Where As can be transformed into its inorganic form, it eventually becomes water-soluble and this allows it to seep down into the subsurface layer and into the groundwater. Because of its harmful nature, the use of As for animal feed additives has ceased in European countries; however, in some countries, such as the United States, Pakistan, and China, As species are still in use.

In China, As use as a swine feed additive is dependent not only on nutritional and veterinary considerations but also on prehistoric practices. Several hundred years ago, As was used cosmetically by Chinese women for coloring their cheeks and lips. It is thought that such practices can explain some present-day pig agronomists' use of various As compounds as feed additives for coloring the meat of poultry and pigs. Consumers in the market were desirous of red-colored pork as they believed that this red color was a guarantee of high-quality meat, and they had little awareness of the presence of toxins. Hence, the use of As preparations in swine farms had both commercial and traditional benefits. Previous studies have reported that over a period of 5–8 years, 1000 kg As was excreted into the surrounding environment from a swine farm that reared 10,000 head. The application of pig manure could lead to a doubling of the level of As in the soil environment after 16 years. Scientists are progressively emphasizing the hazardous condition of As in the environment owing to its use in animal fodder and feed. A ban on its use in animal production has been strongly suggested by scientists.

In the history of Chinese agricultural practices, animal manure has been used for thousands of years as a source of soil nutrients (Li and Chen 2005; Li et al. 2007; Zhang et al. 1994). As animal manure has been used for such a long period of time as an organic source of nutrients in soil, people never thought to compare the risks and benefits of such use. However, because of significant changes in the amounts of swine fertilizer used and in its treatment, the question arises whether this fertilizer is still as safe and secure for land application or ecological disposal as it was earlier. Consequently, studies relevant to As content in pig feed and in pig manure, as well as the assessment of the potential hazardous consequences of As from pig waste are of interest to both scientists and the lay community.

12.2 Treated and Untreated Manure

Treated manure is free of chemical contamination as it has undergone different treatments, such as digestion and composting, before it is used as a fertilizer for cropland. Treated manure is beneficial for soil microbial communities and enhances the fertility of the soil. Untreated manure, which does not undergo a treatment process and contains significant amounts of chemicals, can be harmful to soil and microbial diversity in the soil.

Increasing numbers of swine are being raised in confinement, resulting in large volumes of untreated waste materials/manure that must be collected, stored, and utilized. Before the deposited swine waste is finally disposed of, it undergoes some treatments and processes to make it beneficial for cropland. This processing may be reflexive; for instance, anaerobic disintegration that occurs in storage services, or intentional, as occurs in oxidation channels, lagoons and creeks, or anaerobic digesters. Also, in other cases, the waste undergoes different actions and treatments whereby microbes can break down complex organic products into simpler forms and elements (Brumm et al. 1980).

The consequence of the use of feed additives on waste biodegradation has received little consideration. Taiganides (1963) proposed that the organic decay of hog manure would be lessened by adding as little as 36 ppm copper to the diet. Fischer et al. (1974) reported that the failure of a model anaerobic hog waste digester was caused by the presence of defecated antibiotics. In a review of swine producers who used tylosin to enhance the animals' growth it was reported that coastal areas at high risk. Brumm et al. (1977a) reported that at 100 or 200 ppm, ASA in the diet reduced the dehydrated content of As in hog waste kept in experimental anaerobic pits, while enhancing the proportion of overall nitrogen (dry weight basis) compared with a control. In another study, Brumm et al. (1977b) found that dietary ASA increased ammonium nitrogen and total nitrogen in the waste material of typical anaerobic lagoons. Arsanilic acid did not transform the dehydrated stock, as it had done in the anaerobic pits.

Anaerobic ingestion is considered to be an effective and significant method for treating organic matter (mainly biodegradable matter), and it is also of great worth for the reduction of greenhouse gas emissions (Kunz et al. 2009; Tauseef et al. 2013; Zaman 2013). As organic carbon cannot be removed from manure, similarly, metallic species that are found in manure cannot be removed. These species will be available in the digestate, and can be concentrated in the soil when the digestate is used as a chemical fertilizer (Achiba et al. 2010; Montoneri et al. 2014). The accessibility of metal uptake by microbes depends on the metal speciation, which is regulated by the reactor conditions (e.g., hydraulic retention time, pH, temperature, and redox potential). Anaerobic digestion is a beneficial and effective method for manure treatment. Microorganisms that function without oxygen reduce essential organic substances in poultry and livestock waste. These bacteria are sensitive to both temperature and oxygen. Therefore, design criteria for the application of anaerobic procedures will vary regionally (Whiteley et al. 2003). Agronomists and governments are challenged by growing commercial and ecological fears; consequently, manure management in poultry and livestock industries is now of much concern, and anaerobic digestion is the treatment of choice (Demirer and Chen 2005). Sung and Santha (2001) reported the dual role of anaerobic digestion in dealing with the waste; namely, the conversion of biological waste into solid organic soil conditioners or liquid manures, and the reduction of the ecological influence of organic waste products before the waste products are dumped.

12.3 Arsenic in Untreated and Treated Manure

Methylation is the process through which As and its compounds are metabolized in the environment; the process is activated by microbes. The process, which includes oxidation, reduction, and methylation, is commonly activated by microorganisms that convert As species in soils (Bentley and Chasteen 2002; Huang et al. 2012; Liao et al. 2011; Rhine et al. 2005). Arsenic cannot be removed from soil by conversion to the more toxic As(III) or the less toxic As(V). Nevertheless, for As elimination from soils and sediments, arsenite methylation and subsequent volatilization is a significant technique (Huang et al. 2012; Woolson 1977). Arsenic in organic form is considered to be less toxic than inorganic As (As in arsenite [As(III)] and arsenate [As(V)]). Arsenic can be broken down, through microbial processes, into three main species: As(CH3)3, AsH(CH3)2, and AsH2 (CH3), by the calibration of anaerobic conditions in organic matter (Mestrot et al. 2009, 2013b).

12.3.1 Arsenic Levels in Swine Manure

The levels of As in swine manure differ with respect to time and geographical location. On the whole, the concentration of total As in poultry manure ranged from 1 to 70 mg kg^{-1} (Jackson et al. 2003) and from 1 to 7 mg kg^{-1} in swine manure (Makris et al. 2008). Owing to the use of animal feed supplements for their nutritional and antibacterial effects, the levels of As in swine and dairy manure slurries are higher now than previously (Jondreville et al. 2003; Silbergeld and Nachman 2008). For instance, in intensive hog farms in southern China, the concentration of As in manure was 4–78 mg kg^{-1}, much higher as compared with findings in hog farms in other regions of China (Cang 2004; Chao et al. 2009; Dong et al. 2008) and in other countries (Chao et al. 2009; Dong et al. 2008). Moreover, because of the greater use of As-supplemented dietary products and lower efficiency of As use in pigs, the As content was higher in the raw pig manure as compared with the raw dairy manure (Cang 2004; Chao et al. 2009).

The contamination of animal food wastes by organoarsenic compounds is associated with the addition of arsenicals to animal feeds, and the use of these compounds has not been subject to any rules or regulations. Arsenicals in animal waste are eliminated in proportion to the concentrations used in fodder, as first described by Overby and Frost (1962). The Alpharma Animal Health company (East Bridgewater, NJ, USA), which manufactures the roxarsone (ROX) brand 3-nitro™, used for poultry production, notes that 43 mg As (150 mg of ROX) is ejected in the life duration (42 days) of a broiler bird or a chick on dietary ROX. Li and Chen investigated the concentrations of As in pig manure in China, and found a range of 0.4 to 119 mg kg^{-1}. Li and Chen reported that, as a result of the marked increment in swine production in China throughout the past decade, the environmental exposure to As in swine manure (which is managed by land application, proposed to be done for recycling organic matter) is predicted to increase, given data for the year 1999, which is based on approximations for waste production in the province of Beijing (China) (averaging 77.3 g/ha/year). Thus, China and the United States play a huge part in the environmental burden of As resulting from animal production. It has been noted that the As concentration in swine manure from China was higher than that in cattle manure (Wang et al. 2014a).

The scientists concluded that significant amounts of As were found in pig and poultry manure during the period 1990–2003, but during the period 2003–2010, the percentages of As in pig manure and in poultry manure were 53 and 87%, respectively, has been increased which show that before 2003, As was mainly suggested as feed additives. In the Chaoyang district, Beijing, pig waste had As concentrations of 0.42 to 119.0 mg kg^{-1} (Li and Chen 2005). Nicholson et al. (1999) reported on As concentrations in swine manure collected in England and Wales; the As level in the pig waste samples ranged from 0.52 to 1.34 mg kg^{-1} (dry matter basis). McBride and Spiers (2001) found that the concentration of As in dairy manure ranged from 1.0 mg kg^{-1} to 2.0 mg kg^{-1} (dry matter basis). In the study by Kpomblekou et al. (2002), As levels in 39 broiler litter samples from 12 Alabama counties were investigated, showing a significant variation in As concentrations, which ranged from 2.0 to 70.4 mg kg^{-1}. Similarly, many years ago high levels of As (40–76 mg kg^{-1}) were observed in broiler litters (Edwards and Daniel 1992; Harmon et al. 1975). It was confirmed that As deposition from pig litter collected in Chaoyang's pig farms was comparable to the results for poultry manure (Berger et al. 1981; Harmon et al. 1975). In the Chaoyang district, China, 29 pig feed and compost samples from eight pig farms revealed As levels of 0.15–37.8 mg kg^{-1} and 0.42–119.0 mg kg^{-1}, respectively (Li et al. 2007).

Similarly, Sager reported that the concentrations of As in cattle manure, pig manure, and poultry dung were 0.33, 0.88, 0.51, and 0.12 (mg kg^{-1}), respectively. In China, a countrywide survey of 212 samples of animal dung-based composts reported on the levels of nine heavy metals and on As methylation. The concentrations of As (dry weight), ranged from 0.4 to 72 mg kg^{-1}, and 2.4% of the samples exceeded the limits for As (15 mg kg^{-1}). Further research found that As in manure was generally present as the minor species monomethyl arsenite (MMA), dimethyl arsenate (DMA), and arsenate (AsV). This analysis focused on the need to reduce the concentrations of As in animal composts in order to certify their safe reprocessing for farm soils.

12.3.2 Arsenic Levels in Poultry Manure

Arsenic is used in animal feeds to promote growth and is excreted from the animals in manure. The concentrations of As measured in the body parts of broiler chickens were 2.19–5.28 mg g^{-1} in legs, 2.15–5.92 mg g^{-1} in breast, 3.07–7.17 mg g^{-1} in liver, and 2.11–6.36 mg g^{-1} in heart muscles. The highest levels of As were found in most porcine (0.26 mg g^{-1}) and avian (0.36 mg g^{-1}) samples of liver, and were 7–12 times higher than those of the other species tested. A total of 0.13 mg g^{-1} As in the muscle tissues of broiler chickens has been reported by the United States Department of Agriculture's Food Safety Inspection Service and Combined Research of the National Institutes of Health (Lasky et al. 2004).

Organoarsenics, such as ROX and ASA, and their potential metabolites, were studied in 146 animal feed samples collected from animal meal products. The study indicated that 25.4% of the samples contained organoarsenics, with the mean content of ROX being 7.0 mg kg^{-1} and that of ASA, 21.2 mg kg^{-1}. Surprisingly, AsIII and MMA mostly existed as As impurities in organoarsenic products in the meal products, with increased contents than organoarsenics. Arsenic and ROX impurities in feeds and ROX additives remained unaffected throughout the lifespan of the feeds.

Arsenic added to poultry meal as ROX ends up in poultry litter. Fresh litter predominantly contains ROX, whereas mature litter predominantly contains inorganic As. Owing to the continuous soil accumulation process, As-containing litter used as compost is assumed to be unsustainable. Carboxylic and amide functional groups are responsible for ROX sorption to soils. ROX sorption capacity decreases in the presence of As(III) and As(V); the mobility of ROX in soils was revealed to be increased by competing anions and dissolved organic matter.

ROX, an organic As compound, used as an antibiotic additive to chicken feed, continues to cause concern over its potentially negative ecological effects. Total As concentration in poultry litter can reach >40 mg kg^{-1}; likewise, both ROX and its mineralization product As(V) have been recognized in poultry litters (Jackson et al. 2003).

In the categorization of 40 poultry litter samples from the Southeastern United States, total As absorptions ranged from 1 to 39 mg kg^{-1} dry weight, with an average of 16 mg kg^{-1} (Jackson et al. 2003) and As was quickly soluble, at a range of 70 to 90%, from the poultry litter (Jackson et al. 2003). Cabrera and Sims observed that in the United States in 1996, 11.4 million tons (US) of poultry litter was produced; 90% of this total amount was applied to land as fertilizer. Reports have also shown that ROX is partly transformed to As(V) and other unknown As species in organic fertilizers in poultry litter (Jackson et al. 2003). In soil, ROX is partially degraded into As(V) and is present as a suspension in water. Further, in poultry litter leachates, ROX undergoes a process of photodegradation. Field surveys in the Shenandoah Valley, in Virginia, United States, have reported increasingly lower trends of As in soils treated with litter.

12.4 Potential Sources and Production of Arsenic in Manure

Arsenic is found in both organic and inorganic forms in the environment. Arsenic is the 53rd most common element in the Earth's crust and comprises about 1.5 ppm (0.00015%) of the crust volume. Commercial sources of As are native As, As sulfide mineral (realgar), and minerals with the formula MAs2 (M = Fe, Ni, Co) and MAsS. Arsenopyrite (FeAsS) is a mineral that is structurally related to iron pyrite. The United States Geological Survey and the British Geological Survey in 2014 categorized the top producers of white arsenic in the following order: China, Morocco, Russia, and Belgium. Arsenic is recovered from copper refinement dust and in dust from lead, gold, and copper smelters.

Organic As compounds have been used as feed additives in swine to control disease and to improve weight gain. The accumulation of additives and their emission levels in animal wastes, as well as their ultimate influence in the environment have been considered of great concern (Li and Chen 2005). Since the early 1950s, As, in the form of either sodium arsanilate or arsanilic acid (ASA), has been used as a feed preservative in growing-finishing pig diets to stop pig dysentery.

12.5 Transformation of Arsenic During Treatment of Manure (Composting and Anaerobic Digestion)

With treatment on a large scale, different species of As are obtained through a methylation process. The resultant species are trimethylarsine oxide (TMAs(V)O), dimethylarsenate (DMAs(V)), and monmethylarsenate (MAs(V)) , which are found at low concentrations in certain types of soil (Huang et al. 2011). DMAs(V), and periodically, compounds of tetramethylarsonium (CH 3) 4 As+ and MAs(V) are found in rice grains (Hansen et al. 2011; Meharg and Zhao 2012). Arsenic methylation can increase the amounts of methylarsines, chiefly trimethylarsine and mono- and dimethylarsine (Mestrot et al. 2011a).

The arsine (AsH3) gases react in the atmosphere with ultraviolet light and form nonvolatile types of As (Mestrot et al. 2011b); moreover, such As species are deposited on land and sea surfaces. Some microbes have developed mechanisms to methylate As, while others have evolved pathways to perform the reverse reaction, i.e., the demethylation of methylated arsenical herbicides. These mechanisms are not limited to methylated arsenicals but also cause the disintegration of several aromatic arsenicals, such as growth promoters in feed supplements, as well as chemical weapon agents. These processes are presented below.

Various approaches, both chemical and biological, have been widely utilized for the remediation of arsenic-contaminated atmospheres (Wang et al. 2014b). Chemical remediation can lead to secondary pollution and this approach is often costly. If the bioremediation technique is delineated adequately, it can be more beneficial. Because the end product, TMAs(III), of the biomethylation reaction is volatile, the reaction can be advantageous for the removal of As from contaminated water and soil (Ye et al. 2012). Methylation and volatilization are natural processes, which are often considered as rather slow, and cannot be used for an industrial level of bioremediation. The production of volatile arsenicals may be accelerated by the expression of *arsM* genes in soil organisms (Chen et al. 2013; Mestrot et al. 2013a; Wang et al. 2014c).

In the soil environment, As and its species are complex and they are very susceptible to redox conditions. As(III) predominates under anaerobic circumstances, and its solubility increases owing to dramatic changes in its geochemistry. It may even be volatilized in the presence of organic matter from rice paddies or in the presence of soils treated with mine waste (Mestrot et al. 2009, 2011a, b). P-arsanilic acid (ASA) is used in large industrial farms and operations. ASA is an emerging but less concerning toxin that is used for animal feed, but it can be degraded into more contaminating metabolites after being passed through the animal gut. Therefore, the use of ASA and the dumping of animal dung need more detailed consideration. Arsanilic acid (ASA), an organic As compound, has also been widely used as an additive in animal feed. Organoarsenic compounds and their degradation products, such as arsenite (As(III)) and arsenate (As (V)), are present in the products of anaerobic reactors that process organic waste enriched with ROX and ASA; these products consist of phosphate ($PO_4 3--P$) and ammonium ($NH_4 +-N$). In this scenario, As species in the soil environment can be modified by the application of organic As, thus exerting influence on the environmental hazards of application of organic material.

Concentrations of As that ranged from 3.07 $\mu g\ g^{-1}$ to 7.17 $\mu g\ g^{-1}$ and 2.15 $\mu g\ g^{-1}$ to 5 $\mu g\ g^{-1}$, respectively, were found in the tissues of various body organs, such as liver, muscles, and heart, of broiler chickens. Moreover, concentrations of As in the range of 21.3–43.7 $\mu g\ g^{-1}$ were found in many poultry feeds. It is probable that the high As concentration reached with the disposal of excretory products may add toxicity to the ecosystem on a large scale.

Composting, vermicomposting (with *Eisenia fetida*), and the combined process of composting and vermicomposting performed on industrial sludge (subsurface water treatment waste) contaminated by As (396 ± 1 $mg\ kg^{-1}$) indicated reductions of As bioavailability and mobility in all the samples of vermicomposts and composts. The combined approach revealed a much greater impact than composting or vermicomposting alone.

12.6 Application of Organic Modifications to Arsenic Management

The application of organic modifications, along with volatile iron salts, is an appropriate method for the remediation of lands contaminated by As. Iron oxides naturally present in soils are well known to be important scavengers of As and thus the addition of iron oxides to soils has been shown to efficiently immobilize As in short and long time periods. The use of Fe(0) as a iron oxides results in a decrease in As mobility, but commonly the application of Fe(II) and Fe(III) salts is proposed as a better option than iron oxides for treating As-contaminated soils, as these salts have shown As fixation, through inducing chemical reactions in soil (e.g., co-precipitation), and this is more efficient than the fixation achieved by iron oxides adsorption. Among the iron salts, agricultural grade $FeSO_4$ is recommended over $FeCl_3$ owing to its salient features of cost-effectiveness and ease of application.

Another approach, a pot experiment, following the modification of a heavily contaminated mine soil with biochar and compost fertilizers (10% v:v), revealed that, individually, the two modifications induced great solubilization of As in pore water (>2500 mg l), associated with soil pH and soluble phosphate; however, combining both modifications led to markedly reduced toxicity, owing to simultaneous reductions in extractable metals and increases in soluble nutrients (such as phosphorus). Thus, using the two modifications was most effective at mitigating the attendant toxicity risk.

Organoarsenical compounds such as 3-nitro-4-hydroxyphenylarsonic acid, also termed roxarsone (ROX), are used extensively in poultry feeds for growth promotion and efficient feed utilization, and are referred to as biological agents for disease control. ROX ingested by broilers is excreted unchanged in the excretory product or compost (PE). It was observed that ROX was found even in fresh PE, but after composting ROX was transformed to As(V) and As(III). When PE is used as an organic fertilizer in farmed lands, it raises soil As loads. Soil bacteria convert organic As to the most toxic inorganic forms, which leach into the nearest water tables and subsequently pollute the environment. The As also easily percolates from the PE during precipitation, when the PE is either accumulated in windrows or has only been applied to the soil surface. Reduction of the ROX level is possible through both biotic and abiotic activities, and, certainly, As finds its way into and penetrates water bodies such as rivers and streams, and even finds its way into the crops that are later ingested by humans via the food chain (Jackson et al. 2003).

A pot experiment with *Amaranthus tricolor Linn* and *Ipomoea aquatica Forsk* (water spinach) grown in a paddy soil (PS) and a lateritic red soil (LRS) treated with 2% and 4% (w/w) As-containing chicken and pig manure increased the biomass of both vegetables, and increased the As ratio in water spinach but reduced the As ratio in amaranth. The As content was positively correlated with biomass in water spinach, but a negative correlation with biomass was observed in amaranth. Manure application significantly decreased the total As content in amaranth; however, the As content was significantly increased in water spinach in both soils, PS as well as LRS. Hence, the application of As-containing livestock wastes should be avoided in the cultivation of water spinach.

Fenton reagent can remarkably accelerate ROX reduction and produce arsenite. Further, the use of this reagent led to the reduced uptake of soil-borne As. Livestock manure from concentrated animal feeding operations (CAFOs) can cause soil As pollution owing to the widespread use of organoarsenic feed additives. Although, experimentally, the potential environmental hazards posed by the As in surface soils in the CAFO zone was comparatively low, the continuous excretion of organoarsenic feed additives could cause increases of As in the soil, and hence, the use of these feed additives deserves significant attention.

High quantities of cow dung can decrease As levels in soils. For example, short-term (up to 6 weeks) experimental studies from Bangladesh agrarian lands revealed that fresh cow slurry activated biochemical (e.g., bio-methylation) processes, which may decrease the levels of As.

Organic materials from natural organic matter, as well as clay, aluminum, manganese, sulfide minerals, and iron hydroxides, are constituents of land deposits, and play vital roles in significant As adsorption. Sites contaminated due to geochemical conditions (co-occurring ions, redox potential and pH) and As species have an impact on the level of As sorption. Furthermore, As mobility is influenced by bacterial activities that mediate redox reactions or catalyze the conversion of As species.

12.7 Environmental Risks of Arsenic Application

The results given above suggest that untreated manure has greater quantities of As than treated manure and application of the untreated manure could pose a greater risk to the environment . Other research found considerable amounts of As (15–30 ppm) in poultry litter, although the As content in soil and crops was not changed by the use of poultry litter as compost. Artificial and human sources of As exposure arise from the daily use of arsenical products in animal feeds in the United States and the Peoples Republic of China, among various countries. This results in contamination owing to the use of these dietary products and environmental pollution related to the disposal of the animals' manure. The discharge of hazardous and solid wastes can contaminate the surface as well as the groundwater; the transformation of animal manure into fertilizer for domestic purposes, as well as the application and management of animal manure, may increase the probability of As exposure.

Exposure to As is an environmental and health hazard in many countries. Arsenic is a human toxin 1 and is associated with numerous risks of several noncancerous endpoints, including cardiac disease, diabetes, neuropathy, and neurocognitive deficits in children.

Roxarsone in poultry feces is degraded by chemical and biological activities to arsenite (AsIII) and AsV, both in animal litter and in soil. Furthermore, these As compounds have been found in poultry-barn litter; the compounds are capable of being dissolved and can percolate from broiler litter-treated soil, where they become available for downward migration into the subsurface water (Overby and Frost 1962). Jackson et al. (2003) investigated broiler litter from poultry barns in Georgia, Alabama, and South Carolina, and reported that 71% of the As was water-soluble; owing to the presence of inorganic As and the high absorption of phosphorus, As in broiler waste is extremely leachable. Rutherford et al. found that the percolation rate for As was slow, leading to a high concentration of As in soil, while As residues were soluble in water. Jain and Loeppert reported that phosphate increased the adsorption of arsenate and arsenite on ferrihydrite over a pH range of 3 to 10, which suggests that arsenate in broiler litter-treated soil may be more freely available than As in soils treated by other means, with lower arsenate-to-phosphate proportions. Exposure to waste-borne As occurred primarily in workers at chicken and swine intensive animal production facilities, ranchers, farm managers, and people living near such facilities. However, with the application of pelletization and incineration, the risk of exposure to manure- and animal litter-borne As may be increased in the general public as well. Paradoxically, workers in animal production facilities are likely to have reached the peak of the toxic effects of As. These livestock production workers and managers are also likely to be exposed to ROX in air and dust, preceding its adaptation to inorganic As. Basu et al. found that, in cultured human epidermal cells, ROX showed higher angigenic potential and lower cytotoxicity as compared with arsenite, suggesting that ROX-induced vascular changes may precede cancers and vascular diseases.

In several developing countries, p-arsanilic acid (p-ASA) is extensively used as an animal feed additive, and it is often applied to farmlands with animal manure. A common soil metal oxide, birnessite (δ-MnO_2), was launched to mediate the decay of p-ASA; it showed faster rates under acidic conditions and was highly pH-dependent. Subsequently, the p-ASA radicals underwent cleavage of the arsenite group (which was oxidized to arsenate) or radical–radical self-coupling. Rather than showing full mineralization (with respect to As only), about one-fifth of the p-ASA "couples" formed an As-bearing azo compound that bound strongly to δ-MnO2. The fast conversion of p-ASA to arsenite and arsenate mediated by δ-MnO2 significantly increases the risk of As pollution in soil.

ROX is added to feed in organoarsenic additive compounds, which are excreted in livestock dung in their original form and in metabolites. Yao et al. investigated the effects of ROX and its metabolites in fertilizer from broiler dung and found that, in garland chrysanthemum, the accumulation of As species in the plants increased the risk of As exposure in the following order: crop > soil > cow manure (CM) > chicken > ROX.

Roxarsone biodegradation analysis, revealed that underground water microbes, e.g., Proteobacteria, Firmicutes, Actinobacteria, Planctomycetes, and Spirochaetes, after 15 days with nutrients, degraded 83.3% and 90%, respectively, of ROX under aerobic and anaerobic conditions. However, under anaerobic and aerobic conditions, the microbes without nutrients degraded 50% and 33.1%, respectively, of ROX. Microbes with nutrients showed higher conversion of ROX into contaminating inorganic As species. When chicken litter is used as a chemical fertilizer, ROX will be rapidly transformed into toxic derivatives that contaminate soil and underground waters. These derivatives, including 4-hydroxy-3-amino-phenylarsonic acid; dimethylarsinic acid; arsenate, and arsenite, are influenced by the redox conditions in the environment. Inorganic N composts may accidently increase the probability of As contamination from ROX in vegetation in the order of ROX→chicken→cow manure (CM)→soil→crop.

If poultry waste is used as organic compost, such degraded products can find their way into the atmosphere. The amount of ROX integrated with the soil, in the United

States alone, is approximately 1 × 10^6 kg/year. Morrison reported that when ROX was incorporated with poultry feeds, the proportion of As in poultry feces was 11.8–27.0 ppm. Morrison also observed that 88% of As present in poultry wastes was found as ROX. ROX, after contact with the topsoil, is converted into inorganic As (Jackson et al. 2003). Hancock et al. collected fresh poultry waste and found a total As concentration of 27 mg kg^{-1} in the manure. Initially, Hancock et al. found that As was in organic form; however, As in the sediment collected in the agricultural lands of districts where poultry waste was used as fertilizer was mainly found in the toxic inorganic state. From the perspective of public health, ROX being less toxic than other inorganic forms of As, such as arsenite and arsenate. However, in the topsoil, ROX may be converted into toxic inorganic species, causing a human health problem.

It has been shown that, after reaching the soil, ROX, with the availability of soil microorganisms, is easily altered into toxic forms of As, such as As(V). Through microorganisms and in a deoxygenated atmosphere, this toxic compound (As(V)), based on the moisture level of the soil, can readily be transformed into As(III) or dimethylarsenate, compounds that can be assembled simply and absorbed quickly by many types of soils.

Garbarino et al. estimated that through 2000 in the United States, 9 × 10^5 kg of ROX, which is equal to 2.5 × 10^5 kg of As, was released and that 60–250 g of As per hectare was integrated into the soil when waste from ROX-fed poultry was used as fertilizer. Nachman et al. reported that the transformation of As(V) into As(III) or dimethylarsenate is feasible depending on the moisture and oxygen level of the soil. Furthermore, it has been proven that underground water bacterial colonies can also biotransform ROX, producing As(III) and AS(V). Until now, researchers have proposed that ROX toxicity depends strongly on inorganic arsenical species, such as As(III) (Chen et al. 2013), and, because of organoarsenical biotransformation, ROX toxicity also depends on many byproducts such as MMA, dimethyl arsenate (DMA-V), dimethyl arsenite (DMA-III), and trimethyl arsine oxide (TMAO). Some organic fertilizers had high concentrations of heavy metals, including arsenic (As), cadmium (Cd), and lead (Pb). The As concentration in these fertilizers ranged from 0.50 to 24.4 mg kg^{-1}. Furthermore, pig manure contained 15.7 and 4.59 mg kg^{-1} of As and Cd, respectively, which is higher than their levels in livestock manure (1.95 and 0.16 mg kg^{-1}, respectively).

Investigations of heavy metal concentrations showed that the total contents of Zn, Cu, and As in digested pig slurries were <10, <5, and 0.02–0.1 mg l^{-1}, respectively; while the contents of these heavy metals were <2 and 10–30, <1, and 0.02–0.1 mg l^{-1}, respectively, in digested dairy slurries. Reducing the food supply of these metallic elements in pig and dairy products would be the most effective way to control heavy metal concentrations in the digested compost slurries. Small fractions of Zn, Cu, and As accounted for 1–74%, 1–33%, and 2–53% of the total contents, respectively, in digested pig slurries; and 18–65%, 12–58%, and 3–68% in digested dairy slurries. In China, with advances in technology and hybrid varieties of animals, the annual livestock and poultry manure slurry production has reached roughly 3 billion tons. The resulting heavy metal concentrations have become some of the most powerful toxins causing water eutrophication. For instance, in intensive pig ranching in southern China, the amounts of Zn (113.6–1505.6 mg kg^{-1}), Cu (35.7–1726.3 mg kg^{-1}), and As (4–78 mg kg^{-1}) in the wastes were considerably higher than those in other areas of China (Cang 2004; Dong et al. 2008) and those in other countries.

The contents of these metals were higher in untreated swine wastes than those in raw dairy litter (Cang 2004). Furthermore, swine manure treatment degrades organic matter and leads to salient modifications in physical and biochemical properties, such as water content, pH, oxidation-reduction potential, and bacterial actions. The organic fraction of heavy metals may be affected by these factors that is an analytical feature in estimation of their strength and eco-toxicity (particularly for As). High amounts of As may cause dysmetabolic syndromes in humans, often causing death; high As concentrations also prevent growth in most floral species. In addition, the presence of heavy metals in soils, water, and vegetation through the use of livestock waste material as compost affects the ecosystem. The use of poultry waste as a fertilizer poses high risks to human health, indirectly shifting the risk to living beings through the food web.

Long-term use of feces and wastes may increase the accretion of heavy metals in soil and pose problems for environmental health (Luo et al. 2009; Muehe and Kappler 2014; Nicholson et al. 2003). Potentially malign effects of soil contamination by heavy and trace metals are generally referred to as environmental hazards and ecological threats. In this respect, the term hazard means undesirable, unpredictable, and typically harmful consequences and resultant outcomes of the presence of the metal in soil (e.g., staple crop contamination, groundwater toxification, toxicity to plants, digestion of metal-laden particles by children). However, the statistical probability that the hazard will truly occur is uncertain (Kumar et al. 2013). Determining nontoxic parameters for As and other heavy metals is of great worth because of the toxic influence of these metals on the biotic environment, their application to the soil environment, and their extensive contamination. Accepting rules and regulations that are too rigid leads to reduced financial investment and less utilization of valuable land for remediation. In contrast, procedures that are too permissive may trigger intolerable risks from soil toxins, not only for human health but also for the ecosystem.

The introduction of As has played a significant role in the burden of avoidable diseases worldwide, because As is closely associated with increased risks and dangers of diabetes, cancer, and circulatory diseases. Exposure to soil As (Ryan and Chaney 1994) occurs predominantly through direct soil digestion by young children (United States Environmental Protection Agency; USEPA Pathway 3: soil-human). Young children are the most sensitive carriers of soil As because of their direct ingestion of soil and dust, as part of their typical behavior; excessive ingestion of As can cause neurobehavioral impairment in children's growing brains (Needleman 1990). Skin cancer, cardiovascular disorders, and internal cancers are the leading public health hazards associated with As exposure.

The concentration of As in pig manure might be larger than that in urban sewage sludge, so that the risks from As toxins related to biological waste may actually be higher than the risks associated with urban sewage sludge. Chen et al. (2013) evaluated 26 samples of Chinese urban sewage sludge and reported As concentrations ranging from 0.29 to 47.0 mg kg^{-1}, with an average value of 16.1 mg kg^{-1}, which was less than the 19.2 mg kg^{-1} in 29 swine waste samples in their survey. In addition, in agriculture, much more poultry and livestock waste than sewage sludge is usually applied to soil (Chen et al. 2013). Nicholson et al. (2003) estimated that the agriculture sector of England and Wales contributed an annual input of arsenic of 16 tons from organic manures; further, it was found that the yearly input of arsenic in the countryside of Beijing was 13 tons, which was estimated to originate from pig manure (Ryan and Chaney 1994).

12.8 Conclusions

Both natural processes and anthropogenic activities are the main causes of As pollution in the environment. Arsenic is a refractory element that cannot be destroyed in the environment. However, the biomethylation/biotransformation of As in the soil environment can change it into different species with less toxic effects. The biotransformation of As in the environment follows different pathways and is complex. To understand these biotransformation pathways, and how these pathways affect the manure/soil environment, future research endeavors will need to involve:

1. The determination of the exact mechanisms behind As speciation, the understanding of As biotransformation kinetics, and the linkage between As and microbial diversity;
2. The employment of biomitigation and bioremediation techniques for As biomethylation in microbial communities; and
3. The use of systematic approaches to spatio-temporal scales to model and manipulate As fate in different ecosystems.

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