14 Endosulfan
Unveiling Sources, Toxicity, Risks, and Remediation Strategies

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14.1 INTRODUCTION

Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,3,4-benzo-dioxathiepin-3-oxide, CAS No. 115–29–7), an organochlorine pesticide, is a 70:30 mixture of α- and β-isomers of endosulfan. Endosulfan was extensively used worldwide until it was banned during 6th meeting of Persistent Organic Pollutants Review Committee (POPRC) to the Stockholm Convention (2011) at Geneva (Li, 2018). The decision to ban it was mainly governed by its acute toxicity, potential for bioaccumulation, highly persistent nature, and ability to disrupt the endocrine system (Milesi et al., 2017).

Endosulfan shows significant environmental contamination and adverse effects on human health and wildlife. Accidental and unintentional exposure of endosulfan leads to human fatalities and environmental tragedies throughout the world. The worst cases were reported from the Kasaragod district in Kerala, India; the Borgou province in Benin, West Africa; the western province of Matanzas, Cuba; the Latin American countries Colombia, Ecuador, and Costa Rica; Queensland, Australia; and California, United States. Exposure has been linked to congenital physical disorders,

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mental disabilities, and deaths in exposed communities across the globe. More than 80 countries across the world have banned production and consumption of endosulfan.

Humans become exposed to endosulfan through different ways such as accidental exposure, dietary exposure, and occupational exposure, the major exposure path being accidental exposure. Acute and chronic toxicity results in seizures, gastro-intestinal disorders, neurotoxicity, reproductive disorders, and carcinogenic effects in humans (Nawaz et al., 2014; Syed et al., 2014). Persistence of endosulfan in soil is affected by its physico-chemical characteristics like pH and organic matter content, etc., as well as environmental conditions (Harikumar et al., 2014). Endosulfan isomers (α and β) vary in their persistence and β-endosulfan is easily converted to α-endosulfan (Schmidt et al., 1997). Endosulfan undergoes oxidation resulting in the formation of endosulfan sulphate, which is a persistent metabolite and considered more toxic than the parent endosulfan. Hydrolysis of endosulfan results in the formation of endosulfan diol, endosulfan lactone, endosulfan ether, etc., which are less toxic than the parent molecule (Zaffar et al., 2018). Photo, chemical, and biological degradation are mainly responsible for endosulfan degradation in soil and water.

The persistent nature of endosulfan and endosulfan sulfate results in their frequent detection in water bodies and the environment. The maximum permissible limit of endosulfan in lakes, rivers, and streams is 74 μg L^{-1} (USEPA, 2002). Different techniques for endosulfan/metabolites remediation have been reported. Physico-chemical methods like adsorption, photolysis, membrane filtration, and biological methods involving bacteria, fungi, and plants have been successfully demonstrated for endosulfan removal/degradation (Jesitha et al., 2015; Mukherjee et al., 2020; Zieliński et al., 2022; Kalsoom et al., 2023). This chapter gives an overview of endosulfan contamination, fate, regulatory aspects, exposure, toxicity, risks, and remediation.

14.2 SOURCES OF ENDOSULFAN AND ENVIRONMENTAL CONTAMINATION

Endosulfan, an organochlorine insecticide and acaricide, was widely used in agriculture to control pests on crops. Its acute toxicity, potential for bioaccumulation, and ability to disrupt the endocrine system have made it a highly controversial agrichemical (Forero, 2011). Recognizing the significant risks posed by endosulfan, international efforts have been made to eliminate its use and ban it worldwide. The main sources of endosulfan contamination in the environment are as follows:

a) ***Agricultural use:*** The primary cause of endosulfan contamination is its use in agriculture. It has been extensively utilized in many countries for pest control on crops, particularly in regions with weaker regulations and enforcement.
b) ***Spray drift:*** During the application of endosulfan on crops, spray drift can occur, resulting in the unintended dispersion of the pesticide beyond the targeted area. This drift can contaminate nearby surface waters, soil, and vegetation.
c) ***Soil residues:*** Endosulfan can persist in soil for extended periods due to its high stability. Residual endosulfan from previous applications can remain in the soil and leach into water bodies, leading to long-term contamination.
d) ***Runoff:*** Runoff from endosulfan treated agricultural fields can carry insecticide into surface water bodies such as rivers, lakes, and ponds. Endosulfan is poorly soluble in water and highly sorbed on soil particles and can be easily carried away with running water to contaminate aquatic ecosystems.
e) ***Atmospheric transport:*** Endosulfan can undergo long-range atmospheric transport. It volatilizes from treated fields or evaporates from contaminated water bodies and can be transported over long distances by wind currents.
f) ***Illegal use and dumping:*** Despite being banned or restricted in many countries, illegal use and dumping of endosulfan still occur. Improper disposal of unused or expired endosulfan products can lead to contamination of soil and water.

Widespread use of endosulfan during 1980s and 1990s resulted in widespread contamination in the environment as well as exposure to humans.

Endosulfan poisoning in humans: Most of the reported cases of endosulfan poisoning occurred in the developing countries. Quijano (2000) reported that endosulfan barrels washing in irrigation canals in Sudan in 1988 and drinking of contaminated water led to the death of three people as well as fish. Most pesticide poisoning deaths in 1991 in the Philippines involved endosulfan (Quijano, 2000) and the highest number of human poisoning cases with fatalities following improper usage of endosulfan to kill snails was observed in 1996 (Anonymous, 2002a). During 1990–1993, 32 cases of endosulfan poisoning were documented on the Indonesian island of Sulawesi (Anonymous, 2002b). Similarly, 60 and 155 cases of endosulfan poisoning in Columbia were reported in 1993 and 1994, respectively (Anonymous, 2002b). Endosulfan use increased the number of poisoning deaths in Sri Lanka from 1994–1998 (Roberts et al., 2003). Turkey has also documented cases of poisoning due to eating food tainted with endosulfan (Oktay et al., 2003). Numerous incidents of endosulfan poisoning death have been reported in Guatemala, Costa Rica, and other Central American nations (Anonymous, 2002c). Two South African boys, who lived close to Ntabamhlophe, Kwa-Zulu Natal, died as a result of endosulfan exposure (Anonymous, 2003a). Eighteen cases of endosulfan toxicity, caused by unintentional overexposure during spraying, were reported in northern India between 1995 and 1997 (Chugh et al., 1998). Many people were accidently exposed to endosulfan due to eating contaminated food (Campoy et al., 2001; Dewan et al., 2004).

Contamination in water bodies and fish kills: Endosulfan (30 kg) release into the Rhine River, Federal Republic of Germany, caused a widespread fish kill (Anonymous, 1984; Sang et al., 1999). Similarly, an accidental spill of endosulfan in 1975 caused a major fish kill in a tributary of the Dunk River on Prince Edward Island, and the brook trout population was reduced from 2,227–4,147 to 45–246 (Sang et al., 1999). More than 24,000 fish in a river in Alabama perished as a result of mixing of runoff from endosulfan-treated cotton fields (Quijano, 2000).

Contentious cases of endosulfan poisoning/contamination: The broad environmental pollution brought on by endosulfan use in various agricultural settings is highlighted by these case studies.

(a) ***Kasaragod, India:*** The district of Kasaragod in the Indian state of Kerala saw one of the most well-known and worst pesticide disasters in recorded history involving endosulfan (James and Emmanuel, 2021). The Plantation Corporation of Kerala (PCK) had been recommending endosulfan spray, three times a year, on cashew plantations for the control of tea mosquito bugs since 1980 on roughly 4,696 acres land (Satheesh, 2017; Kumar and Jayakumar, 2019; Melangadi, 2017). Insecticide was used on tea plantations, paddy fields, and fruit orchards using manual pumps or aerial spraying (Gupta, 2021). Stunted growth and malformed limbs were noted in newborn calves as early as 1979 while health issues of a very serious nature, affecting human population, came to light by the 1990s. There have been reports of high rates of congenital abnormalities, physical deformities, mental impairments, cerebral palsy, epilepsy, hydrocephalus, delays in boys' sexual maturation, and other health issues among the locals (Patočka et al., 2016; Melangadi, 2017; Anonymous, 2019). Affected residents were presumed to have either dietary exposure (by eating food sprayed with endosulfan or drinking water tainted with endosulfan), occupational exposure (via topical or inhalation routes during mixing, loading, and/or applying endosulfan or by immediately re-entering the endosulfan-treated areas), or accidental exposure (via topical or inhalation routes as a result of proximity to endosulfan use) (Anonymous, 2011a). Reports suggested that plantation employees were not provided with the necessary safety equipment (Anonymous, 2003b). Extremely high levels of endosulfan residues were detected in human blood, human milk, soil, water, fruits, vegetables, cows' milk, cows' skin tissue, fish, and frogs (Anonymous, 2001). Harikumar et al. (2014) reported that endosulfan residues persisted for 1.5–2 years in soil and it depended on climate conditions and soil physico-chemical properties. The Kerala government banned endosulfan usage

in 2005 (Pradyumna, 2009). Its production and use were banned worldwide in 2011 (Anonymous, 2011c). A Supreme Court-appointed panel recommended phasing out the usage of endosulfan over a 2-year period.

Cuba: Endosulfan poisoning in February 1999 led to the deaths of 15 people in the western province of Matanzas. Authorities in Cuba claim that a total of 63 people fell ill after eating food tainted with endosulfan (Dinham and Malik, 2003).

The Benin Tragedy: During the 1999–2000 cotton season, at least 37 deaths and 36 critically ill patients due to endosulfan poisoning were reported in the Borgou province, Benin, West Africa (Ton et al., 2000).

Queensland, Australia: Endosulfan has long been used to manage pests on a variety of crops, including cotton, in the Lockyer Valley, Queensland, Australia that led to contamination of surrounding creeks, waterways, and surface water (Anonymous, 2002d). Concerns about the potential effects on the ecosystem and public health were raised due to presence of endosulfan residues in fish and other aquatic organisms because endosulfan isomers can have half-life of 30 (aerobic) and 34–47 weeks (submerged) in Australian soils (Ghadiri and Rose, 2001).

California, United States: Due to its previous use on cotton, tomatoes, and melons, endosulfan was detected in surface water, groundwater, and sediment, endangering aquatic ecosystems (May, 2011). Endosulfan concentration in downstream was 28 times greater than the level necessary to kill an average freshwater fish after a normal endosulfan application on tomatoes. The US Fish and Wildlife Service reported that the Wyoming toad, Nashville crayfish, piping plover, wood stork, and other federally protected fish and mussel species were among the numerous endangered species due to risk from endosulfan use (Anonymous, 2012) and advised the EPA to stop using endosulfan in 2002 (Rossi, 2002). Endosulfan poisoning is linked to demise of the mountain yellow-legged frog in the Sierra Nevada, San Joaquin Valley (Jeff, 2004).

Latin America: The Latin American countries Colombia, Ecuador, and Costa Rica widely employed endosulfan on banana farms. Water bodies and soils close by were contaminated as a result of runoff from the plants (Stover and Simmonds, 1987; Mansour, 2018). Endosulfan exposure extended beyond the areas immediately surrounding banana fields (Shunthirasingham et al., 2011) and higher quantities of endosulfan sulfate were detected (Bruehl et al., 2023).

Bangladesh: Joint US-Bangla research reported death of 13 children in Dinajpur in 2012 due to consumption of endosulfan-contaminated litchi (Anonymous, 2018).

14.3 ENDOSULFAN REGULATORY POLICY IN DIFFERENT COUNTRIES

Endosulfan is an isomer combination of α- and β-endosulfan; between them, α-endosulfan is more toxic in nature (Anonymous, 2015). The molecule was first made public in 1956 and 12,800 tons of endosulfan were produced globally each year (Li and Macdonald, 2005) and on a cumulative basis, ~308,000 tons of endosulfan was used during the first 50 years of its introduction. India was thought to be the greatest producer of insecticide with ~5,400 tons annual production (Ayres and Ayres, 2000). The United States consumed ~26,000 tons of endosulfan until 2000 (Li and Macdonald, 2005) while during 1998–2004, China used ~2,800 tons of endosulfan annually (Jia et al., 2009).

At the 6th meeting of the Persistent Organic Pollutants Review Committee (POPRC) to the Stockholm Convention (2011) at Geneva, 24 member countries supported an endosulfan ban. Four members (Germany, Ghana, Nigeria, and China) abstained while India opposed; even then, the committee recommended the ban (Misra, 2010). More than 80 countries including the European Union, Australia (Anonymous, 2009), New Zealand, several West African nations, the United States (Anonymous, 2010a), Brazil (Anonymous, 2010b), and Canada (Anonymous, 2011b) had already banned it or announced phase-outs by the time the Stockholm Convention ban was agreed upon. May 13, 2011, India's Supreme Court prohibited the production and sale of endosulfan in

India (Anonymous, 2011c, 2023). The status of regulatory policies in different countries is as follows:

European Union (EU): The EU banned the use, sale, and production of endosulfan inside the member nations in 2008. Endosulfan is not approved for use under EC 1107/2009 in any of the EU states nor in the European Economic Area (EEA) nations of Iceland and Norway (Lewis et al., 2016).

United States (US): An endosulfan phase-out strategy was announced by the US Environmental Protection Agency (US EPA) in 2010 since it could pose unacceptable health hazards to farmworkers, wildlife, and the environment. Before the complete ban, a phase-out period allowed for a steady decrease in usage (Anonymous, 2010a).

Australia: Endosulfan was phased out and a full ban was enforced in December 2012. All active constituent endosulfan licenses were cancelled by the Australian Pesticides and Veterinary Medicines Authority (APVMA) on October 11, 2010, while endosulfan product registrations were cancelled on October 12, 2010 (Anonymous, 2024).

India: Due to the Kasargod, Kerala tragedy highlighting endosulfan's negative effects on human health and the environment, the Honorable Supreme Court of India passed an ad-interim decision for prohibiting the manufacture, distribution, and use of endosulfan on May 13, 2011. The Joint Expert Committee on endosulfan permitted the export of endosulfan formulation (2698.056 KL) and existing stocks of technical endosulfan (1090.596 MT) produced prior to the endosulfan ban on May 13, 2011 (Anonymous, 2011c).

Brazil: Based on the decision of the Brazilian Institute of Environment (IBAMA), Ministry of Agriculture (MAP), and National Agency for Sanitary Surveillance (ANVISA), import of endosulfan was prohibited on July 31, 2011. Domestic manufacturing was reduced until endosulfan production and use was altogether prohibited in July 2013 (Birkett, 2010).

Canada: Canada banned the majority of uses for endosulfan in 2007. Restricted uses (ornamentals in greenhouses) were permitted and completely phased out by December 31, 2016, when the registrations for all endosulfan pesticide products in Canada expired (Anonymous, 2011b).

South Africa: Endosulfan was banned in 2012 after a phase-out period in accordance with Government Notice No. 853 of the Republic of South Africa's Department of Agriculture, Forestry, and Fisheries on October 26, 2012. (Anonymous, 2017).

New Zealand: The Environmental Risk Management Authority (ERMA), Government of New Zealand, phased out and banned endosulfan use on January 16, 2009 (Anonymous, 2008).

China: Endosulfan registration in China was cancelled on July 1, 2018. All endosulfan products were prohibited to be used on agricultural crops on March 27, 2019 (Anonymous, 2018).

Japan: Japan has added the brominated flame retardant HBCD and "technical endosulfan and its related isomers" to its list of class I specified substances in 2013. Manufacturers and importers of the class I substances must obtain a permit before their manufacture or import (Anonymous, 2013).

Bangladesh: Endosulfan is still listed among the approved pesticides in Bangladesh despite being banned in more than 80 nations. Joint US-Bangla research reported death of 13 children in Dinajpur in 2012 due to endosulfan poisoning from litchi (Hossain, 2018).

Countries that have banned endosulfan: Austria, Australia, Bahrain, Belgium, Belize, Benin, Brazil, Bulgaria, Burkina Faso, Cambodia, Canada, Cape Verde, Chad, China, Colombia, Cote d'Ivoire, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Gambia, Germany, Greece, Guinea-Bissau, Hungary, India, Indonesia, Iran, Ireland, Italy, Japan, Jordan, Korea, Kuwait, Latvia, Lithuania, Luxembourg, Malaysia, Mali, Malta, Mauritania, Mauritius, Netherlands, New Zealand, Niger, Nigeria, Norway, Oman,

Philippines, Poland, Portugal, Qatar, Romania, Saudi Arabia, Senegal, Singapore, Slovakia, Slovenia, Spain, Sri Lanka, St. Lucia, Sweden, Syria, United Arab Emirates, United Kingdom, United States of America

Countries that have restricted endosulfan use: Bangladesh, Honduras, Iceland, Madagascar, Panama, Russia, Thailand

Countries still manufacturing endosulfan: Israel

14.4 EXPOSURE, TOXICITY, AND RISKS TO THE ENVIRONMENT AND HUMANS

14.4.1 Exposure to Endosulfan

Humans become exposed to endosulfan through different ways (EJF, 2009). The different types of exposures are discussed in this section:

(a) **Dietary exposure:** Dietary exposure can result from the ingestion of endosulfan-contaminated food or water. There are reports of the transfer of endosulfan present in soil to the agricultural products (Jung et al., 2023). The rate of transfer and accumulation in different agricultural commodities is different and depend on the nature of the soil, its physicochemical properties, the type of crop, etc. Reports suggested that compared to endosulfan concentration in soil, concentration up to <0.1% in grains, 1.3–4.7% in leafy vegetables, and 0.1–13.6% in fruits and vegetables (Choi et al., 2018, 2018a; Hwang et al., 2018) can be detected. With increase in contact period, absorption by the plant as well as the transfer of endosulfan residues to edible parts increases (Sathishkumar et al., 2021).

(b) **Occupational exposure:** Occupational exposure can occur via skin exposure or inhalation during the mixing, loading, or applying of the pesticides. It can also happen when a person enters a pesticide-treated field. This type of exposure is unavoidable for people engaged in pesticide field applications (farm workers). The exposure is aggravated if adequate protective equipment is not used during the spray operations. The US EPA has stated that "the endosulfan handlers are at short to intermediate risk even with the use of maximum use of personal protective equipments" (US EPA, 2007).

(c) **Accidental exposure:** Accidental exposure is very common and countless incidents can be cited (Menezes et al., 2017). It can occur due to the exposure of skin or due to inhalation of endosulfan. This type of exposure, apart from pesticide handlers, can happen to non-handlers as well as animals. Many individuals have been affected due to the long-range transport of endosulfan (Patočka et al., 2016).

14.4.2 Toxicological Effects

Endosulfan is a highly toxic molecule and it can enter in the body by absorption through skin, mouth, or inhalation. After a pesticide enters in human body, it eventually enters the blood stream and is distributed to all organs. Pesticide poisoning symptoms vary with the type of pesticide and include headaches, dizziness, nausea, vomiting, mental confusion, convulsions, hyperactivity, seizures, coma, and respiratory depression, and even death at severe conditions. The acute symptoms arise due to a single exposure to a high dose of a chemical while the chronic poisoning symptoms can result from repeated intake of low levels of the chemical for a long period of time (EJF, 2009). The toxicological effects of endosulfan on aquatic and terrestrial animals including mammals are reported.

(a) **Acute toxicity:** The primary acute effect of endosulfan is on the nervous system. It can cause hyperexcitation and convulsions, and nervous system-mediated effects on respiration

and heart. Low levels of exposure can also result in death of animals (Annex, 2008). Oral LD_{50} value of endosulfan varies with the species, sex, formulation, and the nutritional status of the test animal. Among the different species, mice appear to be more susceptible to endosulfan toxicity: the males have an LD_{50} value of 7.36 mg kg^{-1} and there were reported deaths of 2 out of 10 male mice after consuming a 7.5 mg technical endosulfan kg^{-1} diet for 7 days (Wilson and LeBlanc, 1998). The oral LD_{50} for rats is reported to be 10–23 mg kg^{-1} (female) and 48–160 mg kg^{-1} (male). However, the dermal LD_{50} values for rats are reported to be 500 mg kg^{-1} (female) and >4,000 mg kg^{-1} (male). The inhalation toxicity values for rats are 0.0126 mg L^{-1} for female and 0.0345 mg L^{-1} for male (Annex, 2008). The α- and β-isomers of endosulfan have different LD_{50} values in rats. Between the two, the α-isomer is more toxic in female rats. Both endosulfan sulfate (oxidative metabolite of endosulfan) and α-endosulfan's lethal doses for mice are comparable (~8 mg kg^{-1}) (ATSDR, 2015).

(b) **Chronic toxicity:** It is reported that the exposure of laboratory mice to endosulfan results in compromised fertility in both sexes (Sharma et al., 2022). The exposure of endosulfan can lead to tenacious higher levels of DNA damage resulting in compromised DNA repair. Researchers have reported an increase in the occurrence of tumor development in the endosulfan-exposed mice in their later life (Sharma et al., 2022). The sub-acute and chronic toxicity of endosulfan targets different organs such as liver, kidneys, immune system, and testes. An oral dose of 10 mg kg^{-1} d^{-1} in rats can cause high rates of mortality within 15 days, but the lower doses (5 mg kg^{-1} d^{-1}) can cause liver enlargement and some other effects within the same time period (EXTOXNET, 1996).

(c) **Reproductive effects:** The effects of endosulfan on the reproductive system in experimental animals depend on species, age at exposure, dose, duration of exposure, and study end points. The experimental studies suggest that the human male reproductive system can be affected by endosulfan and prominent effects are likely to occur if exposure occurs during the developmental phase (Saiyed et al., 2003). Exposure to endosulfan may delay sexual maturity and interfere with hormone synthesis in male children.

(d) **Teratogenic effects:** No conclusive study is available which confirms the role of endosulfan in inducing teratogenic effects (ATSDR, 2015). However, a few studies indicated that transplacental exposure can result in neurochemical alterations in the brains of animals.

(e) **Neurotoxicity:** Endosulfan is reported to have neurotoxic effects in laboratory animals. The expected mechanism of neurotoxicity includes:
- Variation of neurotransmitter levels in brain areas by affecting synthesis, degradation, and/or rates of release and reuptake
- Interfering with the binding of neurotransmitters to their receptors

Alterations in behavioral responses have been recorded when the animals are repeatedly exposed to tolerated doses of endosulfan (Paul and Balasubramaniam, 1997). It is believed that a serotonergic mechanism is involved in endosulfan-induced learning impairment. Gross impairment of visual-motor coordination was also reported (Anonymous, 2011a).

14.4.3 Risk to the Environment and Humans/Mammals

(a) **Risk to humans/mammals:** The exposure concentration and exposure duration determine the possible health effects of endosulfan in humans. Based on monitoring data of endosulfan in the environmental matrices, it is proposed that the environmentally relevant concentrations are much less than the concentrations at which the animal studies are conducted. Higher levels of exposure result in tremors and seizures; only at extreme levels, death happened. In general, endosulfan readily degrades into hydrophilic compounds and is removed with the least absorption in the gastrointestinal tract of mammals. The β-endosulfan was readily removed as compared to α-endosulfan from rabbit blood plasma

with half-life in blood of 6 h and 10 days, respectively. Most of the endosulfan is eliminated from the body within days to weeks (EXTOXNET, 1996).

Some studies indicated the effect of endosulfan on the alteration of thyroid and sex hormones in humans. An Indian study found that exposure to endosulfan was not associated with increased risk of Alzheimer's disease (Singh et al., 2013). A recent study by Sharma et al. (2023) indicated the role of β-endosulfan as an endocrine disruptor for thyroxine II leading to breast cancer. However, the US Department of Health and Human Services (HHS), the US Environmental Protection Agency (EPA), and the International Agency for Research on Cancer (IARC) have not classified endosulfan as carcinogenic (ATSDR, 2015).

(b) **Risk to the environment:** Endosulfan, being hydrophobic in nature, accumulates in the fatty tissues of living organisms. Da Cuña et al. (2020) conducted a study to evaluate the bioaccumulation and organ distribution of waterborne endosulfan in the freshwater fish *Cichlasoma dimerus*. They found that endosulfan is rapidly metabolized into endosulfan sulfate in the tissues. Endosulfan sulfate levels correlated with the tissue fat content in fish. Cerrillo et al. (2005) studied the occurrence of α- and β-endosulfan and their metabolites in fatty and non-fatty tissues and fluids in women in their reproductive age and the children in southern Spain. They found that the maximum concentration of commercial endosulfan isomers was found in adipose tissue (~17.72 ng g^{-1} lipids), followed by human milk (~11.38 ng mL^{-1}). These conclusions support the hydrophobicity of endosulfan and its removal by milk secretion. Botella et al. (2004) studied the levels of 15 organochlorine pesticides in the fat tissue and blood of 200 women in southern Spain. Endosulfan was found both in fat tissue and serum samples. Among the different endosulfan metabolites, the most predominant compound was endosulfan ether both in fat tissue (68%) and serum (86%) samples. Their results suggested that endosulfan exposure to a child via the mother is common, both in utero and via breastfeeding, due to the high rate of exposure to women at reproductive age (Cerrillo et al., 2005; Amizadeh and Saryazdi, 2011).

14.5 FATE AND DYNAMICS IN THE ENVIRONMENT

Once released into the environment, endosulfan undergoes various transfer and transport processes. The fate of endosulfan in the environment is determined by its physico chemical properties. Endosulfan is reported to be present in almost all environmental matrices, even though it is released in the environment during pesticide application on crops. The commercial product of endosulfan is a mixture of two isomers, α and β, in a 2:1 ratio. Between the two isomers, the α-isomer is considered to be more volatile and dissipative, whereas the β-isomer is considered to be more adsorptive and persistent (US EPA, 2007). The volatile nature of the compound enables it to be transported as vapor and spray drift to different environmental media, whereas its adsorptive and persistent nature helps it to stay in the environment for a long period of time. Endosulfan can also be transported via runoff to surface water bodies or via dust dispersion in the atmosphere and redeposition in diverse areas. The overall fate of endosulfan in the environment is depicted in Figure 14.1.

14.5.1 Fate in Soil

Oxidation and hydrolysis are two major pathways of endosulfan degradation in soil. The major degradation product of endosulfan is its oxidation to endosulfan sulfate which is more persistent than its parent isomers (Fan, 2008; Romero-Aguilar et al., 2014; Fang et al., 2016; ATSDR, 2015). Parent (α- and β-isomers) and endosulfan sulfate are not expected to be highly mobile in soil and cause groundwater pollution (US EPA, 2007). Further, they can enter the water bodies through soil erosion, runoff, spray drift, and atmospheric depositions. Endosulfan sulfate further undergoes degradation and results in the formation of endosulfan lactone. The endosulfan molecule is quite stable to photodegradation, but its degradation product endosulfan sulfate is susceptible to photodegradation

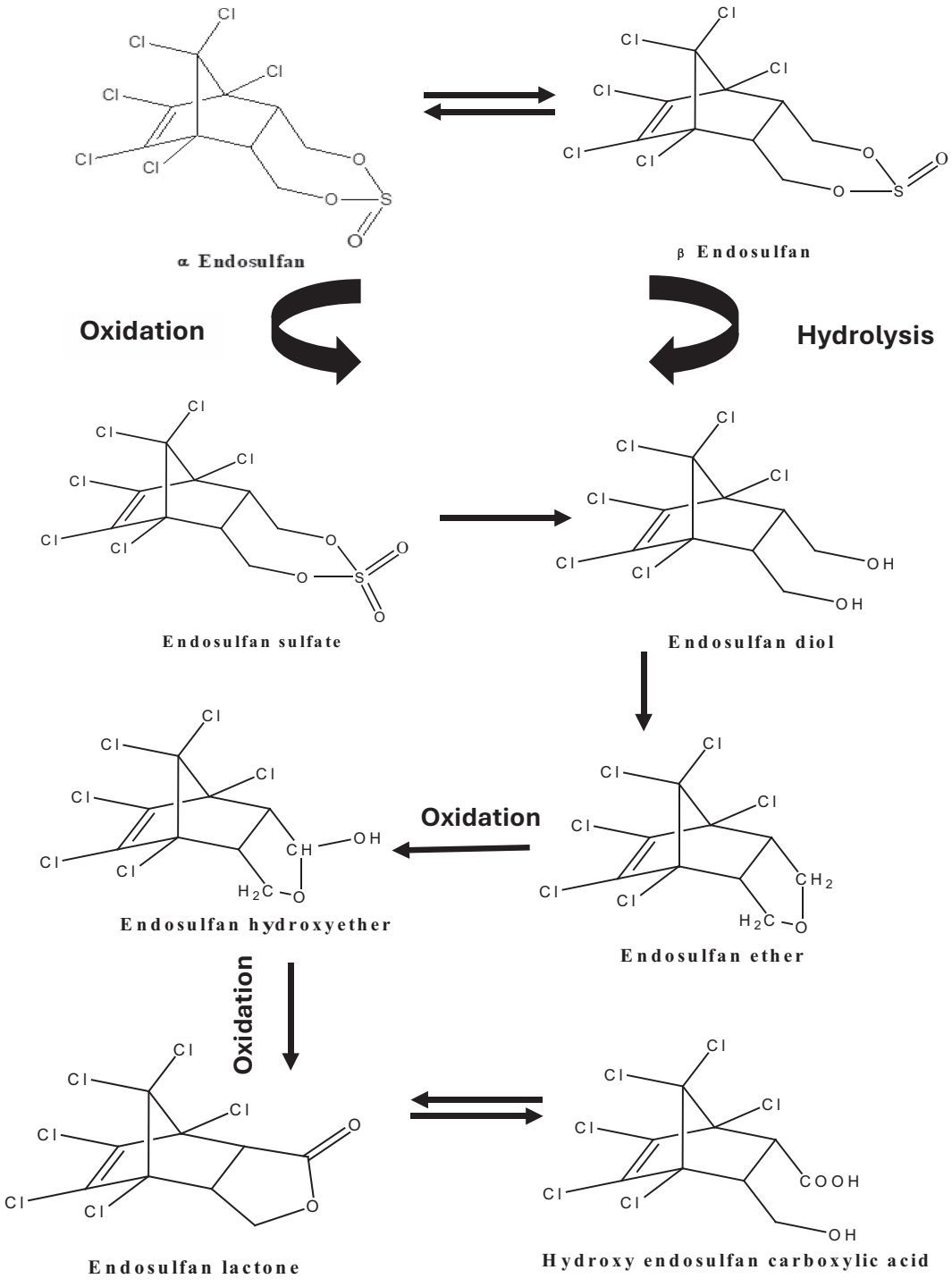

FIGURE 14.1 The fate of endosulfan in the environment.

under favorable conditions. The adsorption of endosulfan to soil particles results in increased persistence of insecticide. Endosulfan adsorbs onto soil colloids when applied in aqueous solution. It exhibits moderate affinity to soil colloids as evidenced from its average adsorption coefficient Koc = 12,000 $cm^3\ g^{-1}$. The mobility of the compound is reduced by its adsorption. However, the adsorbed endosulfan-soil colloid complex can also be transported via runoff to surface water bodies or via dust dispersion to the atmosphere and redeposit to off-target areas. Endosulfan persists in acidic soil for weeks to months after application because of unfavorable conditions for hydrolysis. The US EPA reports that "the potential for endosulfan to reach ground water is limited to acidic to neutral soils and aquifers, where preferential flow may be a prevalent pathway to ground water or where the ground water is shallow and is overlain by highly permeable soils" (US EPA, 2007). The loss of endosulfan from agricultural land via runoff and leaching is affected by many factors, such as soil texture, organic matter content, rainfall intensity, water table level, etc. Endosulfan is degraded in soil by both abiotic and biotic processes. The rate of degradation depends upon the conditions such as soil type, organic carbon content, pH, temperature, moisture content, microbial population and biomass, etc. Abiotic hydrolysis is considered to be the major mechanism of degradation. Half-lives of endosulfan vary with the soil pH.

14.5.2 Fate in Water

The contamination of surface water bodies by endosulfan is mainly due to spray drift and runoff. Spray drift carries both α- and β-isomers of endosulfan and deposits them into water bodies. Horizontal transport of endosulfan is caused by runoff and it can carry both the isomers of endosulfan and its degradation product, endosulfan sulfate. Endosulfan can undergo hydrolysis both by abiotic and biotic processes. The half-lives of endosulfan in natural waters depends on redox potential, pH, microbial population, organic matter content, etc. (Fan, 2008). The major transformation pathway of endosulfan in water is the formation of endosulfan diol, which is a less toxic metabolite of endosulfan (ATSDR, 2015). Endosulfan reactivity towards oxidation in water varies between the two isomers of endosulfan: the α-isomer is readily converted to endosulfan sulfate as opposed to the β-isomer (Landeros et al., 2018). However, the rate of conversion of endosulfan sulfate to endosulfan diol is slower as compared to the direct conversion of α-endosulfan to diol by hydrolysis. Rapid degradation of endosulfan-to-endosulfan sulfate is also reported in seawater because of base-mediated hydrolysis (Landeros et al., 2018). Alkaline pH favors hydrolysis and endosulfan diol is obtained as the major degradation product. The degradation of endosulfan sulfate is considered to be the slowest. Endosulfan volatilization from water to atmosphere is another process which results in a decrease in its concentration; weather conditions affect the volatilization of endosulfan.

14.5.3 Fate in Air

The entry routes for endosulfan into atmosphere are volatilization and vapor transportation. When it is applied on crops, volatilization from the crop surface results in vapor transport. Dust transportation can contribute to atmospheric endosulfan activities besides volatilization and spray drift. Regional weather, geography, and topography conditions, and anthropogenic activities affect the dust transportation. All three forms of endosulfan, α-isomer, β-isomer, and endosulfan sulpfate, are carried away by dust transport (Fan, 2008). A study by Hapeman et al. (2013) suggested that heavy agricultural use of endosulfan led to high atmospheric concentrations of endosulfan, especially the α-isomer. Endosulfan is not liable to atmospheric degradation. Abiotic hydrolysis and photolysis do not contribute significantly to endosulfan degradation in the troposphere. Endosulfan reacts with hydroxyl (OH)-radical in the atmosphere and is considered to be an effective atmospheric removal process for gaseous endosulfan (Fan, 2008).

14.5.4 Fate in Biota

Endosulfan is not found to be persistent in biota. It is metabolized very easily in terrestrial animals and in most aquatic organisms. However, endosulfan is found to be very toxic to some aquatic species, especially fish. Fish exhibit extreme sensitivity to endosulfan. There are reports of the killing of fish due to the discharge of endosulfan into rivers. A study on the acute toxicity of endosulfan on two fish species (*Hyphessobrycon bifasciatus* and *Brachydanio rerio*) indicated behavioral changes including hyperactivity, erratic swimming, and convulsions at the highest exposure levels. The half-life was found to be around 24 hours for both α- and β-isomers of endosulfan (Jonsson and Toledo, 1993). Endosulfan is found to have moderate toxicity for honey bees. Toxicity for birds is high in lab conditions, but no poisonings have been reported under field conditions (Fan, 2008). The bioaccumulation for endosulfan was found to be significant in mussels (*Mytelus edulis*) with 600 times accumulation as compared to the ambient concentration (EXTOXNET, 1996).

14.5.5 Regional Transport

There are reports of the presence of endosulfan all over the world – even in the Arctic. This could be attributed to its long-distance travel. This transportation involves different processes and routes occurring at the same time. The main routes for endosulfan's long-range and regional transportation include volatilization, vapor transportation, and runoff transportation (Fan, 2008).

14.6 REMEDIATION

Degradation of endosulfan in contaminated soil and water samples is highly desirable because endosulfan residues can pose threats to living organisms, especially because insecticide is poorly soluble in water, is highly lipophilic in nature, and can easily be transferred from one tropic level to another with ease and might result in bioconcentration and biomagnification. Remediation of endosulfan-/metabolite-contaminated soil and water can be mediated by physico-chemical and biological methods. Among physico-chemical methods, adsorption, photo-chemical, oxidation/advance oxidation process (AOP), and membrane filtration methods are more common; while in biological methods, microbial degradation mediated by bacteria and fungi and phytoremediation using plants are common methods (Pradeep and Subbaiah, 2012; Mudhoo et al., 2019). Each remediation method has its advantages and disadvantages. Adsorption of contaminants from water using adsorbents is a low-cost process, is nonspecific in nature, and can be used for all types of contaminants. Generally, activated carbon is the most preferred adsorbent, although recently, agricultural biomass, natural and modified clays, clay composites, zeolites, and molecularly imprinted polymers have been used and recommended as adsorbents for pesticide removal from water (De Smedt et al., 2015; Huong et al., 2016; Wen et al., 2016; Zieliński et al., 2022). Although adsorption is the most preferred method for contaminants' removal, this process involves transfer of the contaminant from one matrix to another matrix where contaminants are concentrated; this residual toxic sludge generated poses a threat to the environment, and its incineration is the only option for disposal. Photo-chemical degradation of pesticides also results in removal of pesticides from water, but sometimes, photo-chemically produced degradation products are toxic in nature, so this process might not be applicable to all pesticides. Moreover, the process requires a special setup and the cost of the energy required is relatively high. Similarly, the chlorine-mediated oxidation process is highly effective for microbial contaminants, but its efficiency to remove pesticides not well studied. AOPs are potent oxidizing agents of the hydroxyl group formed by the combination of free radicals and are more effective than single oxidation processes. Therefore, the combination of UV radiation with ozone, hydrogen peroxide, and ferrous and titanium oxide are used for micro-pollutant removal. These systems are used for treating drinking water containing organic pollutants and for wastewater treatment.

14.6.1 Photocatalysis and Oxidation Processes

Photocatalytic process is considered to be a green technology and is used to remove organic pollutants from aqueous solution. Among several catalysts, titanium oxide (TiO_2) is considered to be the best photocatalyst due to its stability, minimal toxicity, and high efficiency in the degradation of pollutants (Sood et al., 2015; Yu et al., 2010). However, inefficient harnessing of visible light, low adsorption capacity, homogeneity of photocatalyst particles, and less recovery after the first treatment are limiting its use at commercial levels. Therefore, approaches like doping and replacement of UV light with solar photocatalysis processes have been used to enhance the efficiency of TiO_2 (Kalsoom et al., 2023). The application of TiO_2 along with a semiconductor in visible range and TiO_2 along with metal/non-metals in UV light showed promising result for degradation of endosulfan. Turkyilmaz and Kucukcongar (2023) demonstrated the removal efficiency of $Ag/TiO_2/Fe_3O_4$ photocatalyst for endosulfan and its metabolites (endosulfan sulfate, endosulfan ether, and endosulfan lactone) that varied from 84.8–94.2% in synthetic, raw, and spring water samples. Further, 77.23% removal efficiency was achieved after five consecutive uses of the catalyst. Similarly, graphitic-carbon nitride/copper/titanium oxide ($g\text{-}C_3N_4/Cu/TiO_2$) removed 60% endosulfan from aqueous solution (Nekooie et al., 2022). Endosulfan removal efficiency of >95% was achieved when the photocatalytic reactor was coated with TiO_2 (Begum and Gautam, 2011). Use of a solar photocatalyst (Ag-doped nano TiO_2 crystal) showed better removal efficacy than TiO_2 and Degussa P25, commercially available photocatalysts. Solar light-driven photocatalytic degradation of endosulfan was achieved by $Cu:Cu_2O$ core-shell based nanoparticles via oxidation, reduction, and hydrolysis reaction (Goel and Arora, 2022). Iron molybdate photocatalyst ($Fe_2(MoO_4)_3$) was also effective in degrading 77% endosulfan (Parveen et al., 2020). Metal ferrite-loaded guar gum nanomaterials ($GG\text{-}CdMgFe_2O_4@TiO_2$) exhibited adsorption as well as photocatalytic degradation of endosulfan and 20 mg adsorbent degraded 94% endosulfan at neutral pH under sunlight (Rani and Shanker, 2023).

Generation of hydroxyl radical and degradation of pollutant in the environment can be achieved by ozonization, although it is very successful technique for microbial contaminants. Mitra and Varshney (2013) reported that endosulfan ozonization resulted into the formation of endosulfan diol that is 1,000 times less toxic than endosulfan. The combined use of electro-fenton/electro-oxidation/ozonization (EF/EO/O3) resulted in 92% degradation of endosulfan in 1 h as compared to the ozonization process alone which removed 62% endosulfan in 2 h (Rodriguez-Peña et al., 2020). The use of 57 mg min^{-1} ozone application resulted in 89% endosulfan degradation (Begum and Gautam, 2011). Yazgan and Kinaci (2004) reported 97% β-endosulfan degradation using a 16 mg min^{-1} ozone dose, pH 4, 60-min ozonization period.

Dechlorination processes and use of metallic/bimetallic compounds can be used for removal of endosulfan. Removal of endosulfan is achieved due to reductive transformation by zero valent magnesium (70% removal at 10 mg L^{-1}) and bimetallic system, Mg^0/Pd^0-carbon (90% removal at 10 mg L^{-1}) after 30 min reaction (Suresh and Thangadurai, 2019). Pillai and Kottekottil (2016) showed the use of nano zero valent iron (1,000 mg kg^{-1}) in soil, which reduced the endosulfan concentration in crops due to hydrogenolysis and reductive dechlorination. More than 99% degradation was observed and use of immobilized palladium was recommended due to the possibility of recovery and reuse of the materials (Thangadurai and Suresh, 2013). Abbas et al. (2019) demonstrated that zero valent iron (Fe^0) and iron oxide removed 85% endosulfan following oxidation and dechlorination in a batch experiment. Hwang and Kim (2021) demonstrated the application of 1% commercial zero valent iron (mZVI) along with 0.01 M ascorbic acid (AA) and 0.1 M hydrogen peroxide (H_2O_2) removed 98–100% endosulfan within 24 h from aqueous solution, 65–73% from soil slurry, and 64–66.2% from soil.

14.6.2 Adsorption Process

Materials with superior specific surface area, highly porous structure, conducive pore size distribution, high variability in surface chemistry, and significant degree of surface reactivity have

exhibited significant adsorption capacity for contaminant removal from contaminated/polluted water. Adsorption, in general, is a non-specific process and can be applicable for different types of contaminants, although capacity of a particular adsorbent will vary with the nature of the contaminant. Researchers have used several adsorbents primarily made from organic and inorganic sources. Zeolite, activated carbon, nano particles, nanocomposites, biopolymers, etc. are mainly used as adsorbents. Carbon slurry-based adsorbent was found to be effective for removal of endosulfan and adsorption capacity of 34.11 and 32.62 mg g^{-1} in batch and column operation, respectively (Gupta and Ali, 2008). Lu et al. (2011) demonstrated that adsorption capacity of chitosan beads was higher (6.7–10 μg) than crab shell powder (0.1–0.15 μg) and more than 99% removal of endosulfan was achieved. Researchers have used oil shale ash (Al-Qodah et al., 2007) and wood charcoal (Sudhakar and Dikshit, 1999) as adsorbents for endosulfan removal. The use of nanocomposites for contaminant removal is increasing due to their high adsorption capacity. Memon et al. (2022) synthesized diallylcalix[4]arene incorporated polystyrene nanofibers (PS-CLX NFs) and reported 22.12 and 20.11 mg g^{-1} α- and β-endosulfan removal at 120 rpm, 60-min incubation period, and 7.5 mg adsorbent. Alkali activated municipal waste fly ash and their polymers showed 1.87–20.01 mg g^{-1} endosufan adsorption and alkylation-enhanced adsorption capacity by ~8–10 times and affinity by ~30 times (Luttah et al., 2023). Carbon-based adsorbent (powdered activated carbon, granular activated carbon, oak charcoal, rice husk charcoal) were more effective (60–100%) than inorganic adsorbent (silica and alumina) for α- and β-endosulfan removal from water (Eun et al., 2021). Biopolymer Ɛ-caprolactone (Mourabit and Boulaid, 2019), sucrose derived activated graphene clay composite (Mathanakeerthi et al., 2021), magnetite diatomite (Alacabey, 2022), and activated carbon and biochar-based adsorbents (Kalsoom et al., 2023) have been successfully employed for adsorption of endosulfan.

14.6.3 Membrane Separation Process

The use of an ion exchange membrane and surface functionalization of the membrane increases retention of pollutants on the membrane. However, foul odor and blocking of pores due to cake formation reduces the retention capacity during prolonged use (Jhaveri and Murthy, 2016). Despite limitations, due to high retention capacity, research using membranes has attracted researchers to work on the different aspects of the process. Banasiak et al. (2011) demonstrated that ion exchange resin works better for endosulfan adsorption at pH 7 than at pH 11, and that the pH of the medium and the molecular weight of the membrane are important factors controlling the retention of the endosulfan on the surface (De Munari et al., 2013). Mukherjee et al. (2020) developed an asymmetric polysulfone-based low-pressure thin film composite membrane that was efficient in rejecting organochlorine pesticides including endosulfan (100%). A hydrogen-based membrane biofilm (H_2-MBfR) reactor effectively removed more than 99% endosulfan from water (Cuci and Taşkın, 2020).

14.6.4 Biological Remediation

Biological methods can be classified into two major categories: (i) microbial degradation and (ii) phytoremediation. Microbial degradation is the phenomenon of biological transformation of organic compounds by living organisms, particularly bacteria and fungi. Phytoremediation is the use of living green plants for risk reduction and/or removal of contaminants from contaminated soil, water, and sediments. There are many advantages of biological degradation: (i) it can be conducted *in situ* as well as *ex situ*; (ii) it is an environmentally friendly technique; (iii) it is low cost and low maintenance. These techniques have some disadvantages like (i) the time required for complete remediation is variable and relatively long; (ii) biological processes are often highly pesticide-specific; and (iii) the presence of metabolically capable microbial populations, suitable environmental growth conditions, and appropriate levels of nutrients required for success.

Biological degradation of endosufan can be mediated by primarily two prominent pathways (i) hydrolysis which leads to the formation of endosulfan diol, endosulfan ether, endosulfan lactone as major degradation metabolites which are non-toxic in nature, (ii) oxidation results in the formation of endosulfan sulphate which is a toxic and persistent metabolite.

14.6.4.1 Bacterial Degradation

Microbial remediation might utilize native microbes for degrading any contaminant, because when exposed to any contaminant, microbes develop enzyme systems to degrade that contaminant. Bacteria from genuses *Pseudomonas*, *Bacillus*, *Klebsiella*, *Mortierella*, *Stenotrophomonas*, and *Achromobacter* have shown endosulfan degradation potential (Seralathan et al., 2015; Singh and Singh, 2014a; Mir et al., 2017; Ozdal et al., 2017; Zaffar et al., 2018). Addition of microbes having capability to degrade a particular contaminant enhances the process of remediation and is known as bioaugmentation. Success of bioaugmentation depends on the survival and proliferation of added microbes. Bioaugmentation can be coupled with biostimulation, a process which involves adding nutrients or introducing oxygen in contaminated soil/water so that microbes' survival and activity can be enhanced. A few studies reported that microbes used endosulfan as their sole source of carbon or sulfur (Castillo et al., 2011; Singh and Singh, 2011; Seralathan et al., 2015).

Pseudomonas sp. is the most studied bacterial species that has been isolated from the contaminated soil or endosulfan-seasoned soil (Harikumar et al., 2013; Zaffar et al., 2018). Degradation of α-endosulfan and its oxidative metabolite endosulfan sulfate followed a hydrolytic pathway and resulted in the formation of endosulfan diol, endosulfan ether, and endosulfan lactone (Bajaj et al., 2010; Mir et al., 2017; Zaffar et al., 2018). Similarly, *Alcaligenes faecalis* strain JBW4, isolated from activated sludge, degraded α- and β-endosulfan following a hydrolytic pathway; endosulfan ether and endosulfan lactone were the major metabolites (Kong et al., 2013, 2014). The bacterium was able to colonize in endosulfan-contaminated soils, confirmed by PCR-DGGE assay.

Bacteria of the genus *Bacillus* have shown endosulfan degradation potential. *Bacillus* sp. KF984414 and *Bacillus* sp. LN849696 isolated from endosulfan-stressed soil showed plant growth promoting effect and could degrade 70–74% endosulfan in medium and 63–67% in soil (Rani and Kumar, 2017). Seralathan et al. (2015) reported that *Bacillus megaterium* converted endosulfan into the toxic metabolite endosulfan sulfate, while *Pseudomonas aeruginosa*, *Ochrobactrum* sp., and *Achromobacter xylosoxidans* followed the hydrolytic pathways with formation of endosulfan diol and their consortium could degrade 94% of endosulfan as their sole source of sulfur. Similarly, *Achromobacter xylosoxidans* strain C8B (Singh and Singh, 2011) and *Azotobacter* sp. (Castillo et al., 2011) utilized endosulfan as their sole source of sulfur. Mostly, bacteria used endosulfan as their source of sulfur; however, Verma et al. (2006, 2011) isolated an endosulfan-degrading bacterial strain from earthworm gut that used endosulfan as its sole carbon source.

Silambarasan and Abraham (2014) reported that *Halophilic* bacterium JAS4 from the *Gossypium herbaceum* rhizosphere had remarkable potential to degrade α-endosulfan (1,000 mg L^{-1}) and endosulfan sulfate in the aqueous medium with a half-life (DT_{50}) of 0.01 d and 1.07 d, respectively. *Klebsiella* sp. M3 could tolerate and degrade 50 mg L^{-1} (medium) and 100 mg L^{-1} (soil) of endosulfan and was more effective in degrading α-endosulfan (Singh and Singh, 2014a). Ozdal et al. (2017) and Zaffar et al. (2018) reported that α-endosulfan-degrading potential of *Stenotrophomonas maltophilia* OG2 was greatly influenced by many factors and optimum (81.53%) degradation was observed at concentration of 100 mg L^{-1}, temperature 30°C, and pH 8.0.

In general, most of the bacteria used for endosulfan degradation were more effective in degrading α-endosulfan. However, Odukkathil and Vasudevan (2015) reported that *Bordetella petrii* I GV 34 and *Bordetella petrii* II GV 36 degraded both endosulfan isomers with equal ease. Contrary to this, Jimenez-Torres et al. (2016) reported that *Enterobacter cloacae* PMM16 was more efficient at degrading β-endosulfan (100%) than α-endosulfan (71.32%).

Most of the studies on microbial breakdown of endosulfan were conducted in an aerobic environment. But, a few researchers have studied anaerobic microbial breakdown of endosulfan (Sutherland et al., 2002; Kwon et al., 2005). Endosulfan degradation under anaerobic conditions can follow a hydrolysis pathway and result in the formation of endosulfan diol (Guerin, 1999), which can be metabolized further to endosulfan lactone, endosulfan hydroxyether, and endosulfan monoaldehyde and dialdehyde by anaerobic bacterial and fungal cultures (Sutherland et al., 2000; Awasthi et al., 2003). Sadiq et al. (2019) reported that *Pleurotus ostreatus*-mediated degradation of α-endosulfan was higher under solid-state fermentation than submerged fermentation, while the inverse was true for β-isomer. The calculated DT_{50} of α- and β-endosulfan under solid-state fermentation was 3.99 and 44 days, respectively, while respective values were 10 and 20 days under submerged fermentation. Rapid reduction in endosulfan sulfate metabolite under submerged fermentation revealed its ascendancy in degradation over solid-state fermentation.

Immobilization of the pure cultures may help to improve the bioremediation potential, since immobilized cells have prolonged microbial cell viability and improved capacity to tolerate higher concentrations of pollutants and repeated use (Richins et al., 2000; Chen and Georgiou, 2002). Jesitha et al. (2015) compared endosulfan degradation in batch and column reactor using free and immobilized *Pseudomonas fluorescens*. The bacterium was able to utilize both α- and β-endosulfan as its sole source of carbon and energy and tolerated 550 mg L^{-1} concentration. Degradation was relatively faster when the bacterium was immobilized in calcium alginate beads. Degradation was mediated by a hydrolytic pathway and the formation of endosulfan diol, endosulfan ether, and endosulfan lactone metabolites was confirmed. Pradeep and Subbaiah (2016) used Ca-alginate immobilized cells of *Pseudomonas aeruginosa* for endosulfan degradation using a repeated continuous batch. Immobilized bacteria were highly effective in degrading 2% endosulfan solution at 100 mL h^{-1}; endosulfan lactone and endosulfan ether were the products of degradation.

14.6.4.2 Fungal Biodegradation

There are very few reports that fungi have shown an ability to degrade endosulfan. The filamentous nature of fungal growth offers a major advantage over bacteria because it helps fungi to effectively permeate the soil environment. Fungi can degrade a wide variety of pesticides by introducing minor structural changes in the molecule to convert them into a less or nontoxic form; the biotransformed pesticide is then released into the soil, where it is further degraded by bacteria (Kumar and Philip, 2017). Fungal enzymes like laccase, dehydrogenase, peroxidase, hydrolases, lignin peroxidase, and manganese peroxidase have shown an ability to degrade endosulfan by hydrolysis, oxidation, chlorination, dehydrochlorination, and esterification mechanisms (Maqbool et al., 2016). *Aspergillus niger* showed very high capability to degrade endosulfan (95%) (Goswami et al., 2009; Mukherjee and Gopal, 1994). Silambarasan and Abraham (2013) isolated *Botryosphaeria laricina* JAS6 and *Aspergillus tamarii* JAS9 that could degrade endosulfan and endosulfan sulfate from endosulfan-spiked soil. Both strains were able to tolerate elevated levels of endosulfan (1,300 mg L^{-1}) and grew well up to 1,000 mg L^{-1}.

Similarly, white rot fungi *Trametes hirsuta*, *Trametes versicolor*, *Pleurotus ostreatus*, *Bjerkandera adusta*, and *Phanerochaete chrysosporium* harbor lignin degrading enzyme systems which have been reported for endosulfan degradation (Kullman and Matsumura, 1996; Bisht et al., 2019). *Trametes hirsuta* showed complete degradation of both α- and β-endosulfan isomers (Bisht et al., 2019) and endosulfan sulfate was the major degradation product recovered. Wang et al. (2018) suggested that *Pleurotus eryngii* and *Coprinus comatus*, alone or in combination, resulted in endosulfan removal exceeding 87%. There is a need to isolate and identify endosulfan-degrading fungal strains since fungi are more tolerant to environmental stress.

14.6.4.3 Phytoremediation

Plants can be used for removal and degradation of contaminants and have been widely reported for both organic and inorganic contaminants. Plants facilitate remediation of soil and water by different

mechanisms: rhizofiltration is used for contaminated water while rhizodegradation, phytodegradation, phytostabilization, etc. can be used for contaminated soils. Success of phytoremediation is mainly dependent on the ability of plants to survive in contaminated soil (Prasad et al., 2011; Mitton et al., 2016) and efficiency of plant roots and rhizosphere microbes to uptake and degrade contaminants. A robust root system is the key to successful phytoremediation because it helps in better uptake of contaminants from soil and promotes proliferation and habitation of rhizosphere microbes that can degrade contaminants by metabolism (using them as source of energy) or co-metabolism. Efficiency of phytoremediation varies with type of plant, soil type, weather, stage of plant, etc. Mersie et al. (2003) evaluated ability of plant buffer strips to remove endosulfan from runoff water and reported over 98% endosulfan removal. Ramirez-Sandoval et al. (2011) reported that *Ocimum* sp. is a good candidate for endosulfan degradation in contaminated soils; *Ocimum basilicum* was more effective in degrading endosulfan than *Ocimum minimum*. Rose et al. (2006) reported that macrophytes and algae can reduce the persistence of endosulfan in on-farm constructed wetlands water because partitioning onto sediment acted as a sink for the insecticide. Sethunathan et al. (2004) reported that green algae, *Chlorococcum* sp. or *Scenedesmus* sp., enhanced degradation of α-endosulfan; endosulfan sulfate (major) and endosulfan ether (minor) metabolites were detected along with isomerization of α-endosulfan to β-endosulfan. Thus, coupled with a biotransformation ability, especially at a high inoculum density, the biosorption ability of algae makes them effective candidates for remediation of α-endosulfan-polluted environments.

Harikumar et al. (2013) showed that the aquatic plant *Salvinia molesta* was highly efficient in endosulfan removal (97.94 ± 0.33% in 21 days) from water. Among the terrestrial plants, tomato and spinach took 21 and 24 days, respectively, for complete removal of pesticide from soil (140 μg kg^{-1} endosulfan). Mitton et al. (2016) reported that among four plants used for endosulfan degradation, sunflower was the best phytoremediation plant for endosulfan residue uptake from contaminated soils and maximum decrease in its concentration in contaminated soil.

Abaga et al. (2014) reported effectiveness of *Vetiveria zizanioides* in degrading endosulfan because it harbored a greater number of endosulfan-degrading microorganisms. Singh and Singh (2014b) reported similar observations while evaluating uptake and accumulation of the α- and β-endosulfan and endosulfan sulfate from contaminated soil. Out of seven plants used, *V. zizanioides* accumulated 343 ng g^{-1} of endosulfan (α+β) and endosulfan sulfate (21 ng g^{-1}). The variations in the uptake of the endosulfan isomers was attributed to the morphology of the plant, type of root system, number of branches and extent of branching, types and surface area of leaves, and tolerance of the plant to the individual chemical. Singh et al. (2018) reported that out of nine locally available plant species *V. zizanioides* accumulated the highest amount of endosulfan. No significant reduction in lipid peroxidation and chlorophyll content in *V. zizanioides* supports its suitability for phytoremediation.

Earlier, wetland was evaluated for degradation of 8 priority pesticides, including endosulfan (Matamoros et al., 2007) and results suggested that wetland showed maximum degradation of endosulfan. It was attributed to biodegradation and plant uptake since retention in the sediment was negligible. Authors suggested that reductive dehalogenation was the major mechanism of endosulfan degradation. Zhao et al. (2014) evaluated vertical-flow constructed wetlands at the lab scale for bioremediation of endosulfan. After 20 days' experiment, endosulfan isomer removal efficiencies were increased to 89.24–97.62% through bioremediation. Bacteria bioaugmentation and sucrose biostimulation promoted biodegradation while KH_2PO_4 biostimulation promoted plant uptake.

14.7 CONCLUSION

Endosulfan, an organochlorine insecticide, was banned by the Persistent Organic Pollutants Review Committee (POPRC) to the Stockholm Convention in 2011. However, due to its persistent nature and long-distance transport, endosulfan is still detected in environmental components. Although the hydrolytic metabolites of endosulfan, namely endosulfan diol, endosulfan ether, and endosulfan

lactone, are less toxic than the parent molecule, the oxidized metabolite endosulfan sulfate is equally persistent and toxic in nature. Endosulfan is considered to be an endocrine disruptor and adversely affects human health by inducing seizures, cancer development, and reproductive and gastrointestinal disorders. Both physico-chemical and biological methods have been suggested for remediation of endosulfan-contaminated soil and water, but techniques that can be effectively scaled up need more research and standardization.

REFERENCES

Abaga, N.O.Z., Dousset, S., Munier-Lamy, C., Billet, D., 2014. Effectiveness of vetiver grass (*Vetiveria zizanioides* L. Nash) for phytoremediation of endosulfan in two cotton soils from Burkina Faso. *Int. J. Phytoremediation* 16, 95–108.

Abbas, T., Wadhawan, T., Khan, A., McEvoy, J., Khan, E., 2019. Iron turning waste media for treating Endosulfan and Heptachlor contaminated water. *Sci. Total Environ*. 685, 124–133.

Alacabey, İ., 2022. Endosulfan elimination using amine-modified magnetic diatomite as an adsorbent. *Front. Chem*. 10, 907302. https://doi.org/10.3389/fchem.2022.907302

Al-Qodah, Z., Shawaqfeh, A.T., Lafi, W.K., 2007. Adsorption of pesticides from aqueous solutions using oil shale ash. *Desalination*. 208, 294–305.

Amizadeh, M., Saryazdi, G.A., 2011. Effects of endosulfan on human health. *Webmed Central Toxicol*. 2(12), WMC002617. https://doi.org/10.9754/journal.wmc.2011.002617

Annex, D., 2008. *Endosulfan meets the POPs screening criteria*. http://www.indiaenvironmentportal.org.in/files/endosulfan.pdf (Accessed on 7 July 2023)

Anonymous, 1984. *Endosulfan, environmental health criteria 40*. The International Programme on Chemical Safety (IPCS), UNEP, World Health Organization, Geneva. https://wedocs.unep.org/bitstream/handle/20.500.11822/29342/EHC40Endo.pdf?sequence=1 (Accessed on 19 July 2023)

Anonymous, 2001. *Analysis of samples from Padre village in Kasaragod district of Kerala for endosulfan residues*. Centre for Science and Environment, New Delhi, India, February 21. http://www.indiaenvironmentportal.org.in/content/324991/analysis-of-samples-from-padre-village-in-kasaragod-district-of-kerala-for-endosulfan-residues (Accessed on 15 July 2023)

Anonymous, 2002a. *Regionally based assessment of persistent toxic substances: Europe regional report*. United Nations Environment Programme, Chemicals; Global Environment Facility. Europe RBA PTS regional report. https://issuu.com/pan-uk/docs/pesticide_news_131_-_March_2023 (Accessed on 19 July 2023)

Anonymous, 2002b. *End of the road for endosulfan - a call for action against a dangerous pesticide*. In: EJF, 2009. *End of the road for endosulfan: Pushing for a global ban on a deadly pesticide*. Environmental Justice Foundation, London, UK. ISBN No. 1-904523-18-8. https://ejfoundation.org/resources/downloads/end_of_the_road_for_endosulfan.pdf] (Accessed on 19 July 2023)

Anonymous, 2002c. *Regionally based assessment of persistent toxic substances: Central America and the Caribbean regional report*. United Nations Environment Programme, Chemicals; Global Environment Facility. Central America and the Caribbean RBA PTS regional report. https://digitallibrary.un.org/record/487294 (Accessed on 19 July 2023)

Anonymous, 2002d. *Pesticide use in Australia*. Australian Academy of Technological Sciences and Engineering. John C. Radcliffe. ISBN 18 756 186 94. https://www.atse.org.au/wp-content/uploads/2019/01/pesticide-use-australia.pdf (Accessed on 15 July 2023)

Anonymous, 2003a. An international perspective on the health and environmental effects of pesticides. *Pesticide News* – Issue 131. Pesticide Action Network UK, P19. https://www.pan-uk.org/pesticide-news/ (Accessed on 19 July 2023)

Anonymous, 2003b. *Endosulphan aerosol spraying health risks in Kasaragod district, Kerala*. www.indiaenvironmentportal.org.in/files/KeralaGovt_FinalReport.pdf (Accessed on 2 July 2023)

Anonymous, 2008. *New Zealand joins others in banning endosulfan, U.S. use continues*. https://beyondpesticides.org/dailynewsblog/2008/12/new-zealand-joins-others-in-banning-endosulfan-us-use-continues (Accessed on 6 November 2024)

Anonymous, 2009. *Australia should ban endosulfan: Greens, weekly times now*. https://web.archive.org/web/20090121213637/http:/www.weeklytimesnow.com.au/article/2009/01/08/40315_horticulture.html (Accessed on 15 July 2023)

Anonymous, 2010a. *Endosulfan phase-out, 2010. Pesticides: Reregistration, U.S. EPA*. https://archive.epa.gov/pesticides/reregistration/web/html/endosulfan-agreement.html#:~:text=EPA%20has%20initiated%20action%20to,can%20persist%20in%20the%20%20environ%20ment (Accessed on 5 July 2023)

Anonymous, 2010b. Brazil cancels the registration of pesticide endosulfan. *Environmental Justice Foundation*. https://ejfoundation.org/news-media/brazil-cancels-the-registration-of-pesticide-endosulfan (Accessed on 5 July , 2023)

Anonymous, 2011a. *Health impacts and eco-toxicity of endosulfan*. https://cdn.cseindia.org/userfiles/health_impacts.pdf (Accessed on 11 November 2024)

Anonymous, 2011b. *Re-evaluation note REV2011-01, discontinuation of endosulfan, 2011. Pesticides and pest management report and publications*. Government of Canada. ISSN: 1925-0649. https://www.canada.ca/en/health-canada/services/consumer-product-safety/reports-publications/pesticides-pest-management/decisions-updates/reevaluation-note/2011/discontinuation-endosulfan-rev2011-01.html (Accessed on 5 July 2023)

Anonymous, 2011c. Endosulfan: Supreme Court to hear seeking ban on Monday. *The Hindu*. Chennai, India, 1 May. https://www.thehindu.com/news/national/Endosulfan-Supreme-Court-to-hear-seeking-ban-on-Monday/article13874099.ece (Accessed on 25 July 2023)

Anonymous, 2012. *U.S. fish and wildlife service*. https://www.fws.gov/sites/default/files/documents/Investigation%20of%20Contaminants%20in%20Feeds%20and%20Fish%20at%20FWS%20Pacific%20Region.pdf (Accessed on 19 July 2023)

Anonymous, 2013. *Japan bans HBCD and endosulfan*. https://chemicalwatch.com/15568/japan-bans-hbcd-and-endosulfan (Accessed on 27 July 2023)

Anonymous, 2015. *Health effects. Toxicological profile for endosulfan*. https://www.atsdr.cdc.gov/toxprofiles/tp41-c3.pdf (Accessed on 19 July 2023)

Anonymous, 2017. *Agricultural remedies that are banned or restricted for use in the Republic of South Africa*. http://www.thedtic.gov.za/wp-content/uploads/Agric-Remedies.pdf (Accessed on 6 July 2023)

Anonymous, 2018. Use of endosulfan and methyl bromide for agriculture to be prohibited as of 31 December in China. *AgNews*. https://news.agropages.com/News/NewsDetail-28722.htm#:~:text=Since%20July%201%252%20C%202018%2C%20the,Asian%20and%20West%20African%20countries (Accessed on 7 July 2023)

Anonymous, 2019. *Ready Reckoner, plant protection division plant protection – I section (pesticide unit)*. Government of India Ministry of Agriculture & Farmers Welfare Department of Agriculture, Cooperation & Farmers Welfare. https://agriwelfare.gov.in/sites/default/files/ready_reckoner_pp_new.pdf (Accessed on 11 November 2024)

Anonymous, 2023. *Banning of pesticides*. PIB Government of India. https://pib.gov.in/PressReleaseIframePage.aspx?PRID=1896140 (Accessed on 5 July 2023)

Anonymous, 2024. Endosulfan chemical review. *Australian Pesticides and Veterinary Medicines Authority*. https://apvma.gov.au/node/12516#:~:text=Phase%20status,-Completed&text=On%2011%20 October%202010%2C%20the,cancelled%20all%20endosulfan%20product%20registrations (Accessed on 6 November 2024)

ATSDR (Agency for Toxic Substances and Disease Registry), 2015. *Toxicological profile for endosulfan (draft for public comment)*. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA. https://www.atsdr.cdc.gov/toxprofiles/tp41.pdf (Accessed 7 July 2023)

Ayres, R.U., Ayres, L.W., 2000. The life cycle of chlorine, Part IV. *J. Ind. Ecol*. 4, 121–159.

Awasthi, N., Singh, A.K., Jain, R.K., Khangarot, B.S., Kumar, A., 2003. Degradation and detoxification of endosulfan isomers by a defined co-culture of two Bacillus strains. *Appl. Microbiol. Biotechnol*. 62, 279–283.

Bajaj, A., Pathak, A., Mudiam, M.R., Mayilraj, S., Manickam, N., 2010. Isolation and characterization of a *Pseudomonas* sp. strain IITR01 capable of degrading α-endosulfan and endosulfan sulfate. *J. Appl. Microbiol*. 109, 2135–2143.

Banasiak, L.J., Van der Bruggen, B., Schäfer, A.I., 2011. Sorption of pesticide endosulfan by electrodialysis membranes. *J. Chem. Eng*. 166, 233–239.

Begum, A., Gautam, S.K., 2011. Application of photocatalysis for the degradation of endocrine disrupting chemicals: Endosulphan and lindane. *Indian J. Environ. Prot*. 31, 658–665.

Birkett, R., 2010. *Brazil bans endosulfan*. https://www.agribusinessglobal.com/agrochemicals/insecticides/brazil-bans-endosulfan/ (Accessed on 5 July 2023)

Bisht, J., Harsh, N.S.K., Palni, L.M.S., Agnihotri, V., Kumar, A., 2019. Bioaugmentation of endosulfan contaminated soil in artificial bed treatment using selected fungal species. *Bioremed. J*. 23, 196–214.

Botella, B., Crespo, J., Rivas, A., Cerrillo, I., Olea-Serrano, M.F., Olea, N., 2004. Exposure of women to organochlorine pesticides in Southern Spain. *Environ. Res*. 96, 34–40.

Bruehl, C.A., Andres, M.A., Echeverria-Saenz, S., Bundschuh, M., Knäbel, A., Mena, F., Stehle, S., 2023. Pesticide use in banana plantations in Costa Rica – a review of environmental and human exposure, effects and potential risks. *Environ. Int*. 174, 107877. https://doi.org/10.1016/j.envint.2023.107877

Campoy, C., Jimenez, M., Olea-Serrano, M.F., Frias, M.M., Canabate, F., Olea, N., Bayes, R., Molina-Font, J.A., 2001. Analysis of organochlorine pesticides in human milk: Preliminary results. *Early Hum. Dev*. 65, S183–S190.

Castillo, J.M., Casas, J., Romero, E., 2011. Isolation of an endosulfan-degrading bacterium from a coffee farm soil: Persistence and inhibitory effect on its biological functions. *Sci. Total Environ*. 412–413, 20–27.

Cerrillo, I., Granada, A., López-Espinosa, M.J., Olmos, B., Jiménez, M., Caño, A., Olea, N., Olea-Serrano, M.F., 2005. Endosulfan and its metabolites in fertile women, placenta, cord blood, and human milk. *Environ. Res*. 98, 233–239.

Chen, W., Georgiou, G., 2002. Cell surface display of heterologous proteins: From high throughput screening to environmental applications. *Biotechnol. Bioengin*. 79, 496–503.

Choi, G.H., Lee, D.Y., Ryu, S.H., Park, B.J., Moon, B.C., Kim, J.H., 2018. Investigation of the bioconcentration factor of endosulfan for rice from soil. *Korean J. Pestic. Sci*. 22, 25–28.

Choi, G.H., Lee, D.Y., Seo, D.C., Kim, L., Lim, S.J., Ryu, S.H., Park, B.J., Kim, J.H., Kim, J.H., 2018a. Endosulfan plant uptake suppression effect on char amendment in oriental radish. *Water Air Soil Pollut*. 229, 1–7.

Chugh, S.N., Dhawan, R., Agrawal, N., Mahajan, S.K., 1998. Endosulfan poisoning in Northern India: A report of 18 cases. *Int. J. Clin. Pharmacol. Ther*. 36, 474–477.

Cuci, Y., Taşkın, E.G., 2020. Simultaneous removal of nitrate and pesticide endosulfan in groundwater using membrane biofilm reactor. *J. Environ. Biol*. 41, 351–357.

Da Cuña, R.H., Lo Nostro, F.L., Shimabukuro, V., Ondarza, P.M., Miglioranza, K.S.B., 2020. Bioaccumulation and distribution behavior of endosulfan on a cichlid fish: Differences between exposure to the active ingredient and a commercial formulation. *Environ. Toxicol. Chem*. 39, 604–611.

De Munari, A., Semiao, A.J.C., Antizar-Ladislao, B., 2013. Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter–pesticide complexation and solute–membrane interactions. *Water Res*. 47, 3484–3496.

De Smedt, C., Ferrer, F., Leus, K., Spanoghe, P., 2015. Removal of pesticides from aqueous solutions by adsorption on zeolites as solid adsorbents. *Adsorpt. Sci. Technol*. 33, 457–485.

Dewan, A., Bhatnagar, V., Mathur, M., Chakma, T., Kashyap, R., Sadhu, H., Sinha, S., Saiyed, H., 2004. Repeated episodes of endosulfan poisoning. *J. Toxicol: Clinical Toxicol*. 42, 363–369.

Dinham, B., Malik, S., 2003. Pesticides and human rights. *Int. J. Occupat. Environ. Health* 9, 40–52.

EJF (Environmental Justice Foundation), 2009. *End of the road for endosulfan: Pushing for a global ban on a deadly pesticide*. EJF, London, UK. Second Version. ISBN No. 1-904523-18-8.

Eun, H., Choi, G., Choi, D.S., Hong, S.M., 2021. Performance evaluation for endosulfan removal by carbon-based adsorbents. *J. Pestic. Sci*. 25, 111–118.

EXTOXNET (Extension Toxicology Network), 1996. *Pesticide information profiles: Endosulfan*. http://extoxnet.orst.edu/pips/endosulf.htm (Accessed 7 July 2023)

Fan, S., 2008. *Endosulfan risk characterization document. Environmental fate*. Environmental Monitoring Branch, Department of Pesticide Regulation, Environmental Protection Agency, California, Sacramento.

Fang, Y., Nie, Z., Die, Q., Tian, Y., Liu, F., He, J., Huang, Q., 2016. Spatial distribution, transport dynamics, and health risks of endosulfan at a contaminated site. *Environ. Pollut*. 216, 538–547.

Forero, R.G., 2011. Degradation of organochlorine and organophosphorus pesticides by photocatalysis: Chlorpiryfos and endosulfan case study. In: Stoytcheva, M. (Ed.), *Pesticides-formulations, effects, fate*. InteChOpen, pp. 669–684.

Ghadiri, H., Rose, C.W., 2001. Degradation of endosulfan in a clay soil from cotton farms of Western Queensland. *J. Environ. Manage*. 62, 155–169.

Goel, P., Arora, M., 2022. Photocatalytic degradation efficiency of Cu/Cu_2O core-shell structured nanoparticles for endosulfan mineralization. *J. Nanopart. Res*. 24, 56. https://doi.org/10.1007/s11051-022-05436-0

Goswami, S., Vig, K., Singh, D.K., 2009. Biodegradation of α and β endosulfan by *Aspergillus sydoni*. *Chemosphere* 75, 883–888.

Guerin, T.F., 1999. The anaerobic degradation of endosulfan by indigenous microorganisms from low-oxygen soils and sediments. *Environ. Pollut*. 106, 13–21.

Gupta, T., 2021. The Endosulfan: Introduction, impacts, biotransformation and Kerela tragedy. *Int. J. Res. Appl. Sci. Engin. Technol*. 9, 2993–2998.

Gupta, V.K., Ali, I., 2008. Removal of endosulfan and methoxychlor from water on carbon slurry. *Environ. Sci. Technol*. 42, 766–770.

Hapeman, C.J., McConnell, L.L., Potter, T.L., Harman-Fetcho, J., Schmidt, W.F., Rice, C.P., Schaffer, B.A., Curry, R., 2013. Endosulfan in the atmosphere of South Florida: Transport to Everglades and Biscayne National Parks. *Atmos. Environ*. 66, 131–140.

Harikumar, P.S., Jesitha, K., Megha, T., Kokkal, K., 2014. Persistence of endosulfan in selected areas of Kasaragod district, Kerala. *Curr. Sci*. 1421–1429.

Harikumar, P.S.P., Jesitha, K., Sreechithra, M., 2013. Remediation of endosulfan by biotic and abiotic methods. *J. Environ. Protect*. 4, 418–425.

Hossain, E., 2018. Hazardous pesticides in wide use in Bangladesh. *NEWAGE Bangladesh*. https://www.newagebd.net/article/50556/hazardous-pesticides-in-wide-use-in-bangladeshaccessed%20on%2025th%20July%202023 (Accessed on 25 July 2023)

Huong, P.T., Lee, B.K., Kim, J., Lee, C.H., 2016. Nitrophenols removal from aqueous medium using Fe-nano mesoporous zeolite. *Mater. Des*. 101, 210–217.

Hwang, J.I., Kim, J.E., 2021. Removal of organochlorine insecticide endosulfan in water and soil by Fenton reaction with ascorbic acid and various iron resources. *Environ. Sci. Pollut. Res*. 28, 28479–28489.

Hwang, J.I., Zimmerman, A.R., Kim, J.E., 2018. Bioconcentration factor-based management of soil pesticide residues: Endosulfan uptake by carrot and potato plants. *Sci. Total Environ*. 627, 514–522.

James, A., Emmanuel, D., 2021. An overview of endosulfan and the aftermath of its biohazardous administration in Southern India. *Eur. J. Mol. Clin. Med*. 8, 212–218.

Jeff, M., 2004. Four species of lamprey to be considered for protection under the endangered species act. *Cen. Biol. Div*. 510, 499–9185. https://www.biologicaldiversity.org/news/media-archive/Four%20Species%20of%20Lamprey%20Considered%20for%20Protection%20under%20ESA.pdf (Accessed on 11 November 2024)

Jesitha, K., Nimisha, K.M., Manjusha, C.M., Harikumar, P.S., 2015. Biodegradation of endosulfan by *Pseudomonas fluorescens*. *Environ. Process*. 2, 225–240.

Jhaveri, J.H., Murthy, Z.V.P., 2016. A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes. *Desalination* 379, 137–154.

Jia, H., Li, Y.F., Wang, D., Cai, D., Yang, M., Ma, J., Hu, J., 2009. Endosulfan in China 1 – gridded usage inventories. *Environ. Sci. Pollut. Res*. 16, 295–301.

Jimenez-Torres, C., Ortiz, I., San-Martin, P., Hernandez-Herrera, R.I., 2016. Biodegradation of malathion, α- and β-endosulfan by bacterial strains isolated from agricultural soil in Veracruz, Mexico. *J. Environ. Sci. Health* B51, 853–859.

Jonsson, C.M., Toledo, M.C.F., 1993. Acute toxicity of endosulfan to the fish *Hyphessobrycon bifasciatus* and *Brachydanio rerio*. *Arch. Environ. Contam. Toxicol*. 24, 151–155.

Jung, G.H., Lee, H.S., Choi, G.H., Park, S.W., Kim, J.H., Cho, J.Y., Choi, H., 2023. Developing a safety management method for endosulfan using biochar in ginseng fields. *Agronomy*, 13, 756. https://doi.org/10.3390/agronomy13030756

Kalsoom, Ali, A., Khan, S., Ali, N., Khan, M.A., 2023. Enhanced ultrasonic adsorption of pesticides onto the optimized surface area of activated carbon and biochar: Adsorption isotherm, kinetics, and thermodynamics. *Biomass Convers. Biorefin*. 14: 15519–15534.

Kong, L., Zhu, S., Zhu, L., Xie, H., Su, K., Yan, T., Wang, J., Wang, J., Wang, F., Sun, F., 2013. Biodegradation of organochlorine pesticide endosulfan by bacterial strain *Alcaligenes faecalis* JBW4. *J. Environ. Sci. (China)* 25, 2257–2264.

Kong, L., Zhu, S., Zhu, L., Xie, H., Wei, K., Yan, T., Wang, J., Wang, J., Wang, F., Sun, F., 2014. Colonization of *Alcaligenes faecalis* strain JBW4 in natural soils and its detoxification of endosulfan. *Appl. Microbiol. Biotechnol*. 98, 1407–1416.

Kullman, S.W., Matsumura, F., 1996. Metabolic pathways utilized by *Phanerochaete chrysosporium* for degradation of the cyclodiene pesticide endosulfan. *Appl. Environ. Microbiol*. 62, 593–600.

Kumar, A.D.D., Jayakumar, C., 2019. From precautionary principle to nationwide ban on endosulfan in India. *Bus. Hum. Rights J*. 4, 343–349.

Kumar, M., Philip, L., 2017. Remediation of endosulfan contaminated system by microbes. In: Singh, S. (Ed.), *Microbe-induced degradation of pesticides. Environmental science and engineering*, Springer, Cham, pp. 59–81.

Kwon, J.S., Sohn, H.Y., Shin, K.S., Kim, E., Seo, B.I., 2005. Biodegradation of the organochlorine insecticide, endosulfan, and the toxic metabolite, endosulfan sulfate, by *Klebsiella oxytoca* KE−8. *Appl. Microbiol. Biotechnol*. 67, 845–850.

Landeros, C.R., Díaz, C.E.B., Bilyeu, B., 2018. Dissemination of endosulfan into the environment. In: Donuinah, S.K. (Ed.), *Persistent organic pollutants*. IntechOpen, pp. 5–16.

Lewis, K.A., Tzilivakis, J., Warner, D.J., Green, A., 2016. An international database for pesticide risk assessments and management. *Human Ecolog. Risk Assess. Int. J*. 22, 1050–1064.

Li, Y.F., Macdonald, R.W., 2005. Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: A review. *Sci. Tot. Environ*. 342, 87–106.

Li, Z., 2018. Health risk characterization of maximum legal exposures for persistent organic pollutant (POP) pesticides in residential soil: An analysis. *J. Environ. Manage*. 205, 163–173.

Lu, L.C., Wang, C.I., Sye, W.F., 2011. Applications of chitosan beads and porous crab shell powder for the removal of 17 organochlorine pesticides (OCPs) in water solution. *Carbohydr. Polym*. 83, 1984–1989.

Luttah, I., Onunga, D.O., Shikuku, V.O., Otieno, B., Kowenje, C.O., 2023. Removal of endosulfan from water by municipal waste incineration fly ash-based geopolymers: Adsorption kinetics, isotherms, and thermodynamics. *Front. Chem*. 4, 1164372. https://doi.org/10.3389/fenvc.2023.1164372

Mansour, M., 2018. *Fate and prediction of environmental chemicals in soils, plants, and aquatic systems*. CRC Press. ISBN 0-87371-616-7.

Maqbool, Z., Hussain, S., Imran, M., Mahmood, F., Shahzad, T., Ahmed, Z., Azeem, F., Muzammil, S., 2016. Perspectives of using fungi as bioresource for bioremediation of pesticides in the environment: A critical review. *Environ. Sci. Pollut. Res*. 23, 16904–16925.

Matamoros, V., Puigagut, J., Garcia, J., Bayona, J.M., 2007. Behavior of selected priority organic pollutants in horizontal subsurface flow constructed wetlands: A preliminary screening. *Chemosphere* 69, 1374–380.

Mathanakeerthi, S., Sadheesh, S., Gowtham, S., Kumar, V.M., 2021. Adsorption of endosulfan from aqueous solution using graphene clay matrix (GCM). *Mater. Today: Proc*. 45, 5665–5671.

May, P., 2011. Molecule of the month: Endosulfan: The controversial insecticide. https://doi.org/10.6084/m9.figshare.5255521

Melangadi, F., 2017. Environmental crime and victimization: A green criminological analysis of the endosulfan disaster, Kasargod, Kerala. *Int. Annals Criminol*. 55, 189–204.

Memon, S.A., Shaikh, H., Memon, S., Mahar, F.K., Khatri, Z., 2022. Diallylcalix[4]arene incorporated polystyrene nanofibers for the removal of endosulfan from an aqueous environment. *React. Funct. Polym*. 175, 105280. https://doi.org/10.1016/j.reactfunctpolym.2022.105280

Menezes, R.G., Qadir, T.F., Moin, A., Fatima, H., Hussain, S.A., Madadin, M., Pasha, S.B., Al Rubaish, F.A., Senthilkumaran, S., 2017. Endosulfan poisoning: An overview. *J. Forensic Leg. Med*. 51, 27–33.

Mersie, W., Seybold, C.A., McNamee, C., Lawson, M.A., 2003. Abating endosulfan from runoff using vegetative filter strips: The importance of plant species and flow rate. *Agric. Ecosyst. Environ*. 97, 215–223.

Milesi, M.M., Varayoud, J., Ramos, J.G., Luque, E.H., 2017. Uterine ERα epigenetic modifications are induced by the endocrine disruptor endosulfan in female rats with impaired fertility. *Mol. Cell. Endocrinol*. 454, 1–11. https://doi.org/10.1016/j.mce.2017.05.028.

Mir, Z.A., Ali, S., Tyagi, A., Ali, A., Bhat, J.A., Jaiswal, P., Qari, H.A., Oves, M., 2017. Degradation and conversion of endosulfan by newly isolated *Pseudomonas mendocina* ZAM1 strain. *3 Biotech* 7, 211. https://doi.org/10.1007/s13205-017-0823-5

Misra, S.S., 2010. India still in endosulfan denial. *Down to Earth*. https://www.downtoearth.org.in/news/india-still-in-endosulfan-denial-2177 (Accessed on 19 July 2023)

Mitra, D., Varshney, L., 2013. Remediation of pesticide endosulfan in solution by ionizing radiation, advanced oxidation process and copper nano particle interaction a comparative study using GC–MS analysis. *IOSR J. Environ. Sci. Toxicol. Food. Technol*. 7, 8–11.

Mitton, F.M., Gonzalez, M., Monserrat, J.M., Miglioranza, K.S.B., 2016. Potential use of edible crops in the phytoremediation of endosulfan residues in soil. *Chemosphere* 148, 300–306.

Mourabit, F., Boulaid, M., 2019. Pesticide removal in drinking water treatment using biodegradable polymers. *Mate. Today: Proc*. 13, 1033–1038.

Mudhoo, A., Bhatnagar, A., Rantalankila, M., Srivastava, V., Sillanpää, M., 2019. Endosulfan removal through bioremediation, photocatalytic degradation, adsorption and membrane separation processes: A review. *J. Chem. Eng*. 360, 912–928.

Mukherjee, A., Mehta, R., Saha, S., Bhattacharya, A., Biswas, P.K., Kole, R.K., 2020. Removal of multiple pesticide residues from water by low-pressure thin-film composite membrane. *Appl. Water Sci*. 10, 1–8.

Mukherjee, I., Gopal, M., 1994. Degradation of beta-endosulfan by *Aspergillus niger*. *Toxicol. Environ. Chem*. 46, 217–221.

Nawaz, A., Razpotnik, A., Rouimi, P., De Sousa, G., Cravedi, J.P., Rahmani, R., 2014. Cellular impact of combinations of endosulfan, atrazine, and chlorpyrifos on human primary hepatocytes and HepaRG cells after short and chronic exposures. *Cell Biol. Toxicol*. 30, 17–29.

Nekooie, R., Ghasemi, J.B., Badiei, A., Shamspur, T., Mostafavi, A., Moradian, S., 2022. Design and synthesis of g-C_3N_4/(Cu/TiO_2) nanocomposite for the visible light photocatalytic degradation of endosulfan in aqueous solutions. *J. Mol. Struct*. 1258, 132650. https://doi.org/10.1016/j.molstruc.2022.132650

Odukkathil, G., Vasudevan, N., 2015. Biodegradation of endosulfan isomers and its metabolite endosulfate by two biosurfactant producing bacterial strains of *Bordetella petrii*. *J. Environ. Sci. Health B* 50, 81–89.

Oktay, C., Goksu, E., Bozdemir, N., Soyuncu, S., 2003. Unintentional toxicity due to endosulfan: A case report of two patients and characteristics of endosulfan toxicity. *Vet. Hum. Toxicol*. 45, 318–320.

Ozdal, M., Ozdal, O.G., Algur, O.F., Kurbanoglu, E.B., 2017. Biodegradation of α-endosulfan via hydrolysis pathway by *Stenotrophomonas maltophilia* OG2. *3 Biotech* 7, 113. https://doi.org/10.1007/s13205-017-0765-y

Parveen, S., Bhatti, I.A., Ashar, A., Javed, T., Mohsin, M., Hussain, M.T., Khan, M.I., Naz, S., Iqbal, M., 2020. Synthesis, characterization and photocatalytic performance of iron molybdate (Fe_2 (MoO4)3) for the degradation of endosulfan pesticide. *Mater. Res. Express* 7(3), 035016. https://doi.org/10.1088/2053-1591/ab73fa.

Patočka, J., Wu, Q., França, T.C., Ramalho, T.C., Pita, R., Kuča, K., 2016. Clinical aspects of the poisoning by the pesticide endosulfan. *Quím. Nova*. *39*, 987–994.

Paul, V., Balasubramaniam, E., 1997. Effects of single and repeated administration of endosulfan on behaviour and its interaction with centrally acting drugs in experimental animals: A mini review. *Environ. Toxicol. Pharmacol*. 3, 151–157.

Pillai, H.P., Kottekottil, J., 2016. Nano-phytotechnological remediation of endosulfan using zero valent iron nanoparticles. *J. Environ. Prot*. 7, 734. https://doi.org/10.4236/jep.2016.75066.

Pradeep, V., Subbaiah, U.M., 2012. Isolation, screening and identification of bacteria capable of degrading chlorpyrifos and endosulfan. *Int. J. Res. Pharm. Sci*. 2, 68–77.

Pradeep, V., Subbaiah, U.M., 2016. Use of Ca-alginate immobilized *Pseudomonas aeruginosa* for repeated batch and continuous degradation of endosulfan. *3 Biotech*. 6, 124. https://doi.org/10.1007/s13205-016-0438-2

Pradyumna, A., 2009. *India's endosulfan disaster: A review of the health impacts and status of remediation*. http://www.indiaenvironmentportal.org.in/files/IndiaEndosulfan.pdf (Accessed on 6 November 2024)

Prasad, S.M., Zeeshan, M., Kumar, D., 2011. Toxicity of endosulfan on growth, photosynthesis, and nitrogenase activity in two species of Nostoc (*Nostoc muscorum* and *Nostoc calcicola*). *Toxicol. Environ. Chem*. 93, 513–525.

Quijano, R.F., 2000. Risk assessment in a third-world reality: An endosulfan case history. *Int. J. Occ. Environ. Health* 6, 312–317.

Ramirez-Sandoval, M., Melchor-Partida, G.N., Muniz-Hernandez, S., Giron-Perez, M.I., Rojas-Garcia, A.E., Medina-Diaz, I.M., Robledo-Marenco, M.L., Velazquez-Fernandez, J.B., 2011. Phytoremediatory effect and growth of two species of *Ocimum* in endosulfan polluted soil. *J. Hazard. Mater*. 192, 388–392.

Rani, M., Shanker, U., 2023. Highly efficient removal of endocrine disrupting pesticides by metal ferrites loaded Guar gum based green nanomaterials. *J. Mol. Liq*. 122611. https://doi.org/10.1016/j.molliq.2023.122611

Rani, R., Kumar, V., 2017. Endosulfan degradation by selected strains of plant growth promoting rhizobacteria. *Bull. Environ. Contam. Toxicol*. 99, 138–145.

Richins, R., Mulchandani, A., Chen, W., 2000. Expression, immobilisation, and enzymatic characterisation of cellulose-binding domain-organophosphorus hydrolase fusion enzymes. *Biotechnol. Bioeng*. 69, 591–596.

Roberts, D.M., Karunarathna, A., Buckley, N.A., Manuweera, G., Sheriff, M.R., Eddleston, M., 2003. Influence of pesticide regulation on acute poisoning deaths in Sri Lanka. *Bull. World Health Organ*. 81, 789–798.

Rodriguez-Peña, M., Barrios, J.A., Becerril-Bravo, E., Rodrigo, M.A., Barrera-Díaz, C.E., 2020. Degradation of endosulfan by a coupled treatments in a batch reactor with three electrodes. *Fuel*. 281, 118741. https://doi.org/10.1016/j.fuel.2020.118741

Romero-Aguilar, M., Tovar-Sánchez, E., Sánchez-Salinas, E., Mussali-Galante, P., Sánchez-Meza, J.C., Castrejón-Godínez, M.L., Dantán-González, E., Trujillo-Vera, M.Á., Ortiz-Hernández, M.L., 2014. *Penicillium* sp. as an organism that degrades endosulfan and reduces its genotoxic effects. *Springerplus*, 3, 1–11.

Rose, M.T., Sanchez-Bayo, F., Crossan, A.N., Kennedy, I.R., 2006. Pesticide removal from cotton farm tailwater by a pilot-scale ponded wetland. *Chemosphere* 63, 1849–1858.

Rossi, L.A., 2002. *Reregistration eligibility decision for endosulfan*. EPA 738-R-02-013. Reregistration Report. US Environmental Protection Agency, Washington, DC.

Sadiq, S., Mahmood-ul-Hassan, M., Rafiq, N., Ahad, K., 2019. Spent mushroom compost of *Pleurotus ostreatus*: A tool to treat soil contaminated with endosulfan. *Compost Sci. Utiliz*. 27, 193–204.

Saiyed, H., Dewan, A., Bhatnagar, V., Shenoy, U., Shenoy, R., Rajmohan, H., Patel, K., Kashyap, R., Kulkarni, P., Rajan, B., Lakkad, B., 2003. Effect of endosulfan on male reproductive development. *Environ. Health Perspect*. 111, 1958–1962.

Sang, S., Petrovic, S., Cuddeford, V., 1999. Lindane – a review of toxicity and environmental fate. *World Wildl. Fund Can*. 1724. https://www.researchgate.net/publication/242513937_LINDANE_-_A_REVIEW_OF_TOXICITY?enrichId=rgreq-0d559f172cc75ee55f42bd70d6b40436-XXX&enrichSource

=Y292ZXJQYWdlOzI0MjUxMzkzNztBUzozMTQ5MzUwODk3OTUwNzJAMTQ1MjA5Nzc4NDM4NQ%3D%3D&el=1_x_2&_esc=publicationCoverPdf

Satheesh, S., 2017. Development as recolonization: The political ecology of the Endosulphan disaster in Kasargod, India. *Crit. Asian Stud*. 49, 587–596.

Sathishkumar, P., Mohan, K., Ganesan, A.R., Govarthanan, M., Yusoff, A.R.M., Gu, F.L., 2021. Persistence, toxicological effect and ecological issues of endosulfan – a review. *J Hazard. Mater*. 416, 125779. https://doi.org/10.1016/j.jhazmat.2021.125779

Schmidt, W.F., Hapeman, C.J., Fettinger, J.C., Rice, C.P., Bilboulian, S., 1997. Structure and asymmetry in the isomeric conversion of β-to α-endosulfan. *J. Agric. Food Chem*. 45, 1023–1026.

Seralathan, M.V., Sivanesan, S., Nargunanathan, S., Bafana, A., Kannan, K., Chakrabarti, T., 2015. Chemotaxis-based endosulfan biotransformation: Enrichment and isolation of endosulfan-degrading bacteria. *Environ. Technol*. 36, 60–67.

Sethunathan, N., Megharaj, M., Chen, Z.L., Williams, B.D., Lewis, G., Naidu, R., 2004. Algal degradation of a known endocrine disrupting insecticide, alpha-endosulfan and its metabolites, endosulfan sulfate, in liquid medium and soil. *J. Agric. Food Chem*. 52, 3030–3035.

Sharma, A., Kaninathan, A., Dahal, S., Kumari, S., Choudhary, B., Raghavan, S.C., 2022. Exposure to endosulfan can cause long term effects on general biology, including the reproductive system of mice. *Front. Genet*. 13, 1047746. https://doi.org/10.3389/fgene.2022.1047746

Sharma, S., Malhotra, L., Mukherjee, P., Kaur, N., Krishanlata, T., Srikanth, C.V., Mishra, V., Banerjee, B.D., Ethayathulla, A.S., Sharma, R.S., 2023. Putative interactions between transthyretin and endosulfan II and its relevance in breast cancer. *Int. J. Biol. Macromol*. 235, 123670. https://doi.org/10.1016/j.ijbiomac.2023.123670

Shunthirasingham, C., Gouin, T., Lei, Y.D., Ruepert, C., Castillo, L.E., Wania, F., 2011. Current use pesticide transport to Costa Rica's high-altitude tropical cloud forest. *Environ. Toxicol. Chem*. 30, 2709–2717.

Silambarasan, S., Abraham, J., 2013. Mycoremediation of endosulfan and its metabolites in aqueous medium and soil by *Botryosphaeria laricina* JAS6 and *Aspergillus tamarii* JAS9. *PLoS ONE* 8(10), e77170. https://doi.org/10.1371/journal.pone.0077170

Silambarasan, S., Abraham, J., 2014. Halophilic bacterium JAS4 in biomineralisation of endosulfan and its metabolites isolated from *Gossypium herbaceum* rhizosphere soil. *J. Taiwan Inst. Chem. Eng*. 45, 1748–1756.

Singh, M., Singh, D.K., 2014a. Biodegradation of endosulfan in broth medium and in soil microcosm by *Klebsiella* sp. M3. *Bull. Environ. Contam. Toxicol*. 92, 237–242.

Singh, N.K., Chhillar, N., Banerjee, B.D., Bala, K., Basu, M., Mustafa, M., 2013. Organochlorine pesticide levels and risk of Alzheimer's disease in North Indian population. *Human Exp. Toxicol*. 32, 24–30.

Singh, N.S., Singh, D.K., 2011. Biodegradation of endosulfan and endosulfan sulfate by *Achromobacter xylosoxidans* strain C8B in broth medium. *Biodegradation* 22, 845–857.

Singh, V., Lehri, A., Singh, N., 2018. Assessment and comparison of phytoremediation potential of selected plant species against endosulfan. *Int. J. Environ. Sci. Technol*. 16, 3231–3248.

Singh, V., Singh, N., 2014b. Uptake and accumulation of endosulfan isomers and its metabolite endosulfan sulfate in naturally growing plants of contaminated area. *Ecotoxicol. Environ. Saf*. 104, 189–193.

Sood, S., Umar, A., Mehta, S.K., Kansal, S.K., 2015. Highly effective Fe-doped TiO_2 nanoparticles photocatalysts for visible-light driven photocatalytic degradation of toxic organic compounds. *J. Colloid Interface Sci*. 450, 213–223.

Stover, R.H., Simmonds, N.W., 1987. *Bananas*. 3rd Edition. Longman, London, pp. 468.

Sudhakar, Y., Dikshit, A., 1999. Adsorbent selection for endosulfan removal from water environment. *J. Environ. Sci. Health* B34, 97–118.

Suresh, S., Thangadurai, P., 2019. Coupling of zero-valent magnesium or magnesium–palladium-mediated reductive transformation to bacterial oxidation for elimination of endosulfan. *Int. J. Env. Sci. Technol*. 16, 1421–1432.

Sutherland, T., Horne, I., Lacey, M., Harcourt, R., Russell, R., Oakeshott, J., 2000. Enrichment of an endosulfan-degrading mixed bacterial culture. *Appl. Environ. Microbiol*. 66, 2822–2828.

Sutherland, T.D., Horne, I., Harcourt, R.L., Russel, R.J., Oakeshott, J.G., 2002. Gene cloning and molecular characterization of a two enzyme system catalyzing the oxidative detoxification of β-endosulfan. *Appl. Environ. Microbiol*. 68, 6237–6245.

Syed, J.H., Alamdar, A., Mohammad, A., Ahad, K., Shabir, Z., Ahmed, H., Ali, S.M., Sani, S.G.A.S., Bokhari, H., Gallagher, K.D., Ahmad, I., Eqani, S.A.M.A.S., 2014. Pesticide residues in fruits and vegetables

from Pakistan: A review of the occurrence and associated human health risks. *Environ. Sci. Pollut. Res*. 21, 13367–13393.

Thangadurai, P., Suresh, S., 2013. Reductive transformation of endosulfan in aqueous phase using magnesium–palladium bimetallic systems: A comparative study. *J. Hazard. Mater*. 246, 245–256.

Ton, P., Tovignan, S., Vodouhe, S.D., 2000. Endosulfan deaths and poisonings in Benin. *Pestic. News* 47, 20.

Turkyilmaz, M., Kucukcongar, S., 2023. A comparison of endosulfan removal by photocatalysis process under UV-A and visible light irradiation: Optimization, degradation byproducts and reuse. *J. Environ. Health Sci. Eng*. 21, 355–371.

USEPA, 2002. *Reregistration eligibility decision for endosulfan*. https://archive.epa.gov/pesticides/reregistration/web/pdf/endosulfan_red.pdf

USEPA, 2007. *Note to reader. Endosulfan readers guide*. November 16. EPA-HQ-OPP-2002-0262-0057.

Verma, A., Ali, D., Farooq, M., Pant, A.B., Ray, R.S., Hans, R.K., 2011. Expression and inducibility of endosulfan metabolizing gene in *Rhodococcus* strain isolated from earthworm gut microflora for its application in bioremediation. *Bioresour. Technol*. 102, 2979–2984.

Verma, K., Agrawal, N., Farooq, M., Misra, R.B., Hans, R.K., 2006. Endosulfan degradation by a *Rhodococcus* strain isolated from earthworm gut. *Ecotoxicol. Environ. Saf*. 64, 377–381.

Wang, Y., Zhang, B.W., Chen, N.J., Wang, C., Feng, S., Xu, H., 2018. Combined bioremediation of soil co-contaminated with cadmium and endosulfan by *Pleurotus eryngii* and *Coprinus comatus*. *J. Soils Sediments* 18, 2136–2147.

Wen, J., Yi, Y., Zeng, G., 2016. Effects of modified zeolite on the removal and stabilization of heavy metals in contaminated lake sediment using BCR sequential extraction. *J. Environ. Manag*. 178, 63–69.

Wilson, V.S., LeBlanc, G.A., 1998. Endosulfan elevates testosterone biotransformation and clearance in CD-1 mice. *Toxicol. Appl. Pharmacol*. 148, 158–168.

Yazgan, M.S., Kinaci, C., 2004. β-endosulfan removal from water by ozone oxidation. *Water Sci. Technol*. 48, 511–517.

Yu, H., Wang, X., Sun, H., Huo, M., 2010. Photocatalytic degradation of malathion in aqueous solution using an Au–Pd–TiO_2 nanotube film. *J. Hazard. Mater*. 184, 753–758.

Zaffar, H., Sabir, S.R., Pervez, A., Naqvi, T.A., 2018. Kinetics of endosulfan biodegradation by *Stenotrophomonas maltophilia* EN-1 isolated from pesticide-contaminated soil. *Soil Sediment Contam*. 27, 267–279.

Zhao, C., Xie, H.J., Mu, Y., Xu, X., Zhang, J., Liu, C., Liang, S., Ngo, H.H., Guo, W., Xu, J., Wang, Q., 2014. Bioremediation of endosulfan in laboratory-scale constructed wetlands: Effect of bioaugmentation and biostimulation. *Environ. Sci. Pollut. Res*. 21, 12827–12835.

Zieliński, B., Miądlicki, P. Przepiórski, J., 2022. Development of activated carbon for removal of pesticides from water: Case study. *Sci. Rep*. 12, 20869. https://doi.org/10.1038/s41598-022-25247-6