

Endosulfan: Its Isomers and Metabolites in Commercially Aquatic Organisms from the Gulf of Mexico and the Caribbean

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Abstract

The organochlorine pesticide endosulfan is an insecticide and acaricide used on a variety of crops around the world. Its adverse effects on public health and aquatic biota have been widely documented in several studies, which are closely related to their primary route of exposure, by eating food contaminated with this compound. Therefore, it is necessary to concentrate the information in order to analyze and understand its impact on public health. The present objective is to review the characteristics of endosulfan, its isomers and their presence in aquatic organisms of commercial importance in the Gulf of Mexico and the Caribbean. The aquatic organisms involved were molluscs, crustaceans and fish. The highest concentrations of endosulfan have been detected in oysters, *Crassostrea virginica*, with a maximum value of 99.48 ± 16.21 ng g⁻¹. Although the use of this insecticide for pest control worldwide is prohibited, research conducted in the Gulf of México and Caribbean Sea indicate that it is still used, which will affect future public health and consumers.

Keywords: benthic organisms, bioaccumulation, biomarker, isomers, organochlorine

1. Introduction

The organochlorine pesticide endosulfan (3-oxide 6, 9-methano-2, 4, 3-benzodioxatiepina-6, 7, 8, 9, 10, 10-hexachloro-1, 5, 5a, 6, 9, 9-hexahydro) is considered a persistent organic pollutant (POP) due to its chemical characteristics and effects on public health and the environment (UNEP, 2009a). This pesticide is a high-risk pollutant to the environment, particularly in coastal aquatic environments due to its different transport routes including runoff and atmospheric deposition (Albert & Benítez, 1996; Albert, 2014).

In 1950, the German companies Hoechst AG and FMC Corporation first introduced this pesticide to be used on crops such as cereals, coffee, tea, fruits, vegetables, tobacco and cotton (Maier-Bode, 1968). In general, the trends for the total global endosulfan used and the total global emissions have increased continuously ever since the first year of application of it. Currently, total emissions are around 150 kilotons (Y. F. Li & D. C. Li, 2004; Li & Macdonald, 2005). Despite its widespread use in many countries, at least in 60 it is prohibited due to its high toxicity that affects public health and aquatic organisms, and due to its persistence in the environment (PANAP, 2009; Bauer et al., 2013; Negro et al., 2013; Aly & Khafagy, 2014; Schmidt et al., 2014).

The composition of the technical grade of endosulfan corresponds to a diastereomeric mixture of two biologically active isomers, alpha (α) and beta (β), with an approximate ratio of 2:1 to 7:3, in addition to impurities and degradation products (INIA, 1999; INE, 2011; UNEP, 2011). The appearance of this compound, as a solid, corresponds to cream or brown-colored crystals or flakes, whose existence does not occur naturally in the environment (ATSDR, 2000, 2001, 2013). As a technical grade product, it must contain at least 94% endosulfan according to the United Nations for Food and Agriculture (FAO Specification 89/TC/S), which stipulates that the alpha-isomer content is between 64 and 67% and the beta-isomer is between 29 to 32%. The alpha-isomer is asymmetric and is composed of two axial seat forms, while the beta-isomer has a symmetric shape. The beta-isomer is easily converted into endosulfan-alpha, while this is not possible for the alpha-isomer

(INIA, 1999; INE, 2011).

Due to the high negative impact of endosulfan and its isomers on public health and the environment, several investigations have been conducted with the objective of replacing this organochlorine in both Latin America and Europe (IPEN, 2005; Bejarano et al., 2008, 2009; Haffmans et al., 2008; UNEP, 2008). Thus, it is important to know the concentration levels of endosulfan and its isomers in commercially important aquatic organisms in the Gulf of Mexico and the Caribbean, and the possible risk to public health.

2. Primary Crops and Pests Controlled by Endosulfan

Endosulfan is an insecticide and acaricide used to control plant pests (Li & Macdonald, 2005; UNEP, 2009a). It is a broad spectrum compound applied in different countries to a variety of edible and non-edible crops (Table 1).

Table 1. Tropical crops and pests of economic importance controlled by the application of endosulfan

Family	Crop	Pest			
		Scientific name	Common name		
Rubiaceae	Coffee	<i>Hypothenemus hampei</i> Ferrari	Coffee berry borer		
Solanaceae	Tomato	<i>Trialeurodes vaporariorum</i> (Westwood)	Whitefly		
		<i>Aphis</i>	Aphids		
		<i>Manduca quinquemaculata</i> (Haworth)	Hornworm		
		<i>Helicoverpa zea</i> (Boddie), <i>Heliothis virescens</i> (Fabricius) <i>Trichoplusia ni</i> (Hübner)	Fruit and sprout worms Looper		
	Eggplant	<i>Myzus persicae</i> (Sulzer)	Aphids		
		<i>Phyllotreta</i> , <i>Epitrix</i> <i>Helicoverpa zea</i> , <i>H. virescens</i>	Flea hopper Fruit and sprout worms fruit and sprouts		
		Hot pepper	<i>Anthonomus eugenni</i> Cano <i>Epitrix</i> , <i>Chaetocnema</i> <i>Trialeurodes vaporariorum</i> <i>Acyrtosiphon pisum</i> (Harris)	Hot pepper borer Flea hopper Whitefly Green aphid	
	Tobacco	<i>Bemisia tabaci</i> (Gennadius) <i>Heliothis virescens</i> <i>Estigmene acrea</i> (Drury) <i>Alabama argillacea</i> (Hübner) <i>Myzus persicae</i>	Whitefly Tobacco sprout borer Hairy worm Looper Aphids		
		Fabaceae	Alfalfa	<i>Therioaphis maculata</i> (Buckton) <i>Acyrtosiphon pisum</i> <i>Melanopus</i> , <i>Sphenarium</i> , <i>Brachystola</i> <i>Hypera brunneipennis</i> (Boheman)	Spotted aphid Aphid Grasshoppers Egyptian weevil
				Green beans	<i>Acyrtosiphon pisum</i> <i>Trichoplusia ni</i> <i>Empoasca</i>
			Beans		<i>Apion godmani</i> Wagner <i>Trialeurodes vaporariorum</i> <i>Empoasca</i>
				Soy	<i>Anticarsia gemmatalis</i> Hübner <i>Bemisia tabaci</i> , <i>B. argentifolii</i> Bellows & Perring <i>Schistocerca piceifrons piceifrons</i> Walker <i>Nezara viridula</i> (L.) <i>Euschistus servus</i> (Say)
Malvaceae	Cotton	<i>Anthonomus grandis</i> <i>Heliothis virescens</i> <i>Trichoplusia ni</i>	Boll weevil Acorn worm Looper		

		<i>Bemisia tabaci</i> , <i>T. vaporariorum</i>	Whitefly
		<i>Aphis gossypii</i> (Glover)	Cotton aphid
Apiaceae	Celery	<i>Lygus</i>	Lygus bug
Brassicaceae	Broccoli	<i>Trichoplusia ni</i>	Looper
	Cabbage	<i>Pieris rapae</i> (L.), <i>Pontia protodice</i> (Boisduval & Leconte), <i>Leptophobia aripa</i> (Boisduval)	White cabbage butterfly Diamondback moth
		<i>Plutella xylostella</i> (L.)	Cabbage aphid
		<i>Brevicoryne brassicae</i> (L.)	Harlequin Cabbage Bug
		<i>Murgantia histrionica</i> (Hahn)	Looper
		<i>Trichoplusia ni</i>	
	Cauliflower	<i>Epitrix</i> , <i>Phyllotreta</i>	Fleahopper
		<i>Spodoptera exigua</i> (Hübner)	Armyworm
		<i>Trichoplusia ni</i>	Looper
Poaceae	Sugarcane	<i>Aeneolamia postica</i> (Walker) Fennah, <i>Prosapia bicincta</i> (Say), <i>P. simulans</i> (Walker)	Spittlebug Stem worm borer
		<i>Eoreuma loftini</i> (Dyar), <i>Diatraea considerata</i> Heinrich, <i>D. grandiosella</i> Dyar	Yellow aphid Lace bug
		<i>Sipha flava</i> (Forbes)	
		<i>Leptodyctia tabida</i> (Herrich-Schaeffer)	
	Corn	<i>Spodoptera frugiperda</i> (J.E. Smith), <i>Rhopalosiphum maidis</i> (Fitch)	Bud aphid Foliage aphid
		<i>Schizaphis graminum</i> (Rondani)	Pink borer
		<i>Sesamia calamistis</i> Hampson, <i>S. inferens</i> (Walker)	Stem worm borer
		<i>Diatraea grandiosella</i> , <i>D. lineolata</i> (Walker)	Corn worm
		<i>Helicoverpa zea</i>	
	Wheat	<i>Diuraphis noxia</i> Kurdjumov	Russian wheat aphid
		<i>Rhopalosiphum maidis</i>	Aphid bud
		<i>Schizaphis graminum</i>	Foliage aphid
		<i>Sitobion avenae</i> Fabricius	Grain aphid
		<i>Sesamia calamistis</i>	Pink borer
	Rice	<i>Orseolia oryzae</i> Wood-Mason	Gill fly
		<i>Euethela bidentata</i> Burmeister	Hispid or rice louse
		<i>Rupela albinella</i> Becker & Solis	Stem worm
	Barley	<i>Rhopalosiphum maidis</i>	Aphid bud
		<i>Sitobion avenae</i>	Grain aphid
	Pasture	<i>Aeneolamia postica</i> , <i>Prosapia simulans</i>	Whitefly
		<i>Macrodactylus</i>	Puffin
		<i>Dalbulus elimatus</i> (Ball)	Leafhopper
		<i>Sphenorium</i> , <i>Melanoplus</i>	Grasshoppers
Asteraceae	Lettuce	<i>Trichoplusia ni</i>	Looper
		<i>Epicaerus cognatus</i> Sharp	Potato weevil
		<i>Aphididae</i>	Aphids
		<i>Epitrix</i>	Fleahopper
		<i>Leptinotarsa decemlineata</i> (Say)	Catarina potato
Cucurbitaceae	Zucchini	<i>Aphis gossypii</i>	Melon aphid
	Melon	<i>Trichoplusia ni</i>	Looper
		<i>Diaphania nitidalis</i> (Stoll), <i>D. hyalinata</i> (L.)	Fruit borer
		<i>Melittia satyriformis</i> Hübner	Guide borer
		<i>Bemisia tabaci</i> , <i>Trialeurodes</i>	Whitefly
	Cucumber	<i>Trichoplusia ni</i>	Looper
	Watermelon	<i>Aleyrodidae</i>	Whitefly
		<i>Aphis gossypii</i>	Cotton aphid
Bromeliaceae	Pineapple	<i>Thecla basilides</i> (Harris)	Pineapple borer

		<i>Dysmicoccus brevipes</i> (Cockerell)	Mealy louse
Anacardiaceae	Mango	<i>Anastrepha ludens</i> (Loew)	Fruit fly

Sources: Nieto (2001), EPA (2002), Bejarano et al. (2008, 2009), Weber et al. (2010), UNEP (2009b, 2011), ATSDR (2013), TecnoAgro (2013), Pro-Agro (2014a, 2014b).

The extensive use of pesticides in a wide variety of crops has contributed to their release into the environment (FAO, 2000). The irrigation systems are an example of the mechanisms of modern agriculture that have contributed to a more efficient spreading of fertilizer and pesticides like endosulfan, where the former have generated pollution of groundwater with nitrates and nitrites by overuse mode (Galaviz et al., 2010). Meanwhile, the pesticides applied using these systems can influence the transport of these compounds, which are in use or previously used as the organochlorine, helping to transport to remote areas like the lagoon systems.

Knowledge about the status of irrigation systems at global and national level is of importance for present and future transport of pesticides like endosulfan. Among the most recent works on this subject are those by Valipour (2012, 2014a, 2014b, 2014c, 2015). In addition, this author indicated that irrigation systems in any crop should be implemented to achieve sustainable agriculture in the future.

3. Route of Exposure to Endosulfan

Due to the non-systemic nature of endosulfan, the major route of action occurs through direct skin contact and ingestion (Kidd & James, 1991). It is a very toxic chemical for nearly every type of organism (UNEP, 2007). Endosulfan and its degradation by products are also highly toxic to aquatic organisms (UNEP, 2011). Exposure occurs by absorption through contact, inhalation and ingestion (Nieto, 2001).

Diet is the primary route of exposure to endosulfan for most organisms resulting from food contaminated by this compound (ATSDR, 2013; Singh et al., 2014; Wang et al., 2014). In rats, rapid absorption of it occurs in the gastrointestinal tract at levels from 60% to 87%; where 60% of this compound is absorbed within 24 hours (UNEP, 2011).

4. Effect of Endosulfan on Public Health

Major impact to public health by endosulfan is the nervous system damage due to its affinity to gamma-aminobutyric acid receptors (GABA) in the brain, where it acts as a noncompetitive antagonist of GABA, blocking or inhibiting neurotransmitter reception. Therefore, the blocking activity means partial repolarization of the neuron and a state of uncontrolled excitation (UNEP, 2011). Exposure to high concentrations of this compound produces hyperactivity and seizures, regardless of the route of exposure. Symptoms of acute poisoning include vomiting, agitation, convulsions, cyanosis, dyspnoea, foaming at the mouth and noisy breathing. Severe poisoning can cause death. Furthermore, animal research has shown that prolonged ingestion of endosulfan in food mainly affects kidneys (Bejarano et al., 2009; Scremin et al., 2011; UNEP, 2011; ATSDR, 2013).

However, there are conflicting reports; endosulfan has no genotoxic or mutagenic effects *in vitro* or *in vivo* for somatic cells. Neither has it been classified as an endocrine disruptor, or an immunotoxicant, although carcinogenic effects have been observed in studies on mice and rats (Nandar et al., 2011). However, the results obtained in studies of germ cells *in vivo* suggest that mutations could be induced specifically in spermatogonia (UNEP, 2011).

Recent studies also indicate that endosulfan can cause cell death in exposed Sertoli germ cells due to oxidative damage, causing further damage to the quality of gametes produced (Rastogi et al., 2014). Such contradictions regarding the adverse effects on public health could be related to the limited amount of research performed on humans, as a high percentage of such studies are focused on laboratory animals such as mice, rats, dogs, and other mammals.

Besides, the effect of endosulfan as an endocrine disruptor not only in terrestrial and aquatic species, but also in public health, because this chemical has an estrogenic effect and causes the proliferation of breast cancer cells MCF-7 sensitive to human estrogen, and interferes with male sex hormones such as testosterone (Bejarano et al., 2009). Endosulfan isomers and its primary metabolite have been on the TEDX list of potential endocrine disruptors since 2011, in which is included the evidence that supports the consideration of this chemical as an endocrine disruptor (TEDX, 2015). Study results suggest that exposure to endosulfan in young men can delay sexual maturity and interfere with the synthesis of sex hormones (Saiyed et al., 2003).

In the Kerala state of India, helicopters sprayed endosulfan on nut crops for 25 years, leading to adverse effects

on human health and calves with congenital deformities since 1979. During the 1990s, an unusual increase in health problems was reported in Kasaragod, one district of Kerala. In 2001, more cases of children with hydrocephalus, cerebral palsy, blindness, deformed hands, and chronic skin problems were reported (Bejarano et al., 2008).

Study results on the genotoxicity and mutagenicity caused by this chemical have been equivocal and the genotoxicity of its metabolites is largely unknown. Studies on the damage to human lymphocyte DNA caused by endosulfan isomers has shown that exposure to endosulfan and its metabolites in sublethal doses induces damage to DNA and promotes mutation (Bajpayee et al., 2006). The induction of teratogenic effects by endosulfan in pregnant rats also was tested, showing the number of fetuses with visceral and skeletal malformations to be significantly higher than controls. The malformations obtained were mainly skeletal (ribs), vertebral, and in the liver and kidneys (Singh et al., 2007); it was also observed an effect of the developing chick embryos (Mobarak & Al-Asmari, 2011).

No observable effects levels (NOEL) were established for endosulfan risk assessment during reproductive development and its neurotoxicity. For acute oral exposure in rabbits, $0.7 \text{ mg}^{-1} \text{ kg}^{-1} \text{ d}^{-1}$, and for breeding rats, values for subchronic and chronic oral exposure were $1.2 \text{ mg}^{-1} \text{ kg}^{-1} \text{ day}^{-1}$ and $0.6 \text{ mg}^{-1} \text{ kg}^{-1} \text{ d}^{-1}$, respectively. Silva and Gammon (2009) concluded that endosulfan toxicity during development or reproduction results in endocrine disruption only at doses that cause neurotoxicity ($0.5 \text{ mg}^{-1} \text{ kg}^{-1} \text{ d}^{-1}$ for rat pups). Risks to human health from endosulfan exposure were assessed using NOELs to compare acute, subchronic and chronic exposure; resulting in 0.7, 1.18 and $0.57 \text{ mg}^{-1} \text{ kg}^{-1} \text{ day}^{-1}$, respectively. The acute oral NOEL reported by the EPA was found to be twice as high as reported values ($1.5 \text{ mg}^{-1} \text{ kg}^{-1} \text{ day}^{-1}$) (Silva & Beauvais, 2010). Silva and Carr (2010) found that children from 1-6 years old have a higher risk of exposure to endosulfan in the diet (Silva & Carr, 2010).

5. Transformation and Transport in the Environment

The primary metabolite obtained from the degradation of endosulfan is endosulfan sulfate, which has the same toxicity of the parent compound (UNEP, 2008). However, the metabolite is even more persistent because it degrades slowly compared to more polar metabolites such as endosulfan diol, endosulfan lactone, and endosulfan ether (Bejarano et al., 2009; UNEP, 2011, 2013). Endosulfan transforms primarily through two channels: the diol route in water and as endosulfan sulfate in soils and sediments (Hose et al., 2003).

The presence of endosulfan residues has been reported in several countries, in all environmental systems studied, including air, rain, snow, fog, lakes, rivers, river sediments, groundwater, well-water, spring-water, city water supplies, seawater and marine sediment, shrimp ponds, lagoons, estuary sediment, soil, and tree bark. In addition, it is reported in biota like aquatic plants, fish, crocodile eggs and several organisms in such remote areas as the Arctic (CE, 2005; Bejarano et al., 2008; Rendon & Bejarano, 2010). Due to its presence in a variety of environments, its degree of persistence varies depending on the environmental system and conditions present. The persistent characteristics for the major environmental systems (air, soil and water) are described below.

In air, endosulfan is stable regarding photolysis, but photooxidation occurs to produce endosulfan sulfate (UNEP, 2011). Therefore, the atmosphere is a major transport route of semi-mobile pesticides such as endosulfan. The deposition of this compound is associated with its physicochemical properties, patterns of use and climatic conditions, on local, regional and global scales. Therefore, endosulfan and its metabolites can affect human health and have adverse ecological effects (Potter et al., 2014). This coincides with what is known about endosulfan as a global pesticide, particularly the persistence of α -endosulfan and its ability to travel great distances through atmospheric transport (UNEP, 2009a). The persistence and volatility of endosulfan contribute to its dissemination in the environment after being applied and its ability to travel great distances, making it the organochlorine with the highest concentration in the atmosphere worldwide (Bejarano et al., 2009; UNEP, 2011; UNEP, 2011); providing a dispersal distance of 10-20 kilometers for low to moderate use (Gioia et al., 2005), and up to 150 kilometers for regional transportation (Hageman et al., 2006).

Evaluations of endosulfan wet deposition via precipitation in an area of high agricultural use in South Florida and near to the Biscayne and Everglades National Parks, recorded a detection rate of 55-98%, average concentrations between $5\text{-}87 \text{ ng L}^{-1}$ and a total daily deposition of $200 \text{ ng m}^{-2} \text{ day}^{-1}$. The compound showed a strong seasonal trend in its concentration, with significantly higher values associated with peak use periods when vegetable crops were grown (Potter et al., 2014). Within an area, the simple intensive aerial application of a pesticide such as endosulfan results in volatile releases to the atmosphere. In addition to regional characteristics, such as calcareous soils, the presence of frequent rainfall, high humidity and temperature help to accelerate the process of regional volatilization (Hapeman et al., 2013).

The levels of total endosulfan (Σ) were analyzed in ambient air in southern Mexico; the highest levels of

α -endosulfan occurred at two sites in Tabasco and one in Veracruz, with an average concentration of 367 and 78 pg m^{-3} , and 83 pg m^{-3} , respectively (Alegria et al., 2005). Mobilization and atmospheric deposition are partly responsible for the presence of organochlorine pesticides in coastal areas and its atmospheric transport at a regional scale (Alegria et al., 2005). A persistence of 27 ± 11 days in the atmosphere (and 75°C for photolysis) was noted, with a $\text{DT}_{50} > 2.7$ days for the alpha isomer and >15 days for the beta isomer (UNEP, 2008, 2009a). However, neither endosulfan sulfate nor total endosulfan were reported. A persistence of the total composite for a scenario in the United States yielded 1.3 days, while 2 days for Europe was recently indicated; although no explanation for these variations has been provided (INE, 2011).

The persistence of endosulfan in soil is high because it is strongly adsorbed and relatively immobile (Nieto, 2001; Singh et al., 2014). Table 2 shows the persistence of endosulfan and its isomers in soil. Its semidegradation period (DT_{50}) varies depending on whether it occurs under aerobic conditions, the region, (temperate or tropical) and the conditions of the land where it was applied. Under aerobic conditions it is estimated that soil and sediment are acidic to neutral. The DT_{50} for total endosulfan (alpha and beta isomers and endosulfan sulfate) ranges from 9 months to 6 years (UNEP, 2009). Persistence also is associated with laboratory or field conditions under studies are conducted. In the laboratory, DT_{50} values < 30 days have been reported, indicating that the persistence of alpha and beta endosulfan in soil is low. Yet, field investigations have indicated DT_{50} values for endosulfan sulfate and the technical grade compound as being 3-8 months (UNEP, 2011).

Table 2. Persistence (DT_{50}) of endosulfan and its isomers in soil

Environmental System	Isomers				Reference
	Alfa (α)	Beta (β)	Sulfate	Total (Σ)	
Soil	12-39 days	108-264 days	N.D.	7.4 days	CE (2005)
	21 to 22 $^\circ\text{C}$	21 to 22 $^\circ\text{C}$		DT_{90} : 24.6 days	
	Acidic to neutral soils, 1-2 months	Acidic to neutral soils, 3 to 9 months	N.D.	288 to 2,241 days	UNEP (2007)
	Average: 27.5 days	Average: 157 days		Tropical soils from Brazil, 161 to 385 days	
	Average: 27.5 days	Average: 157 days	117 to 137 days	9 months to 6 years	Bejarano et al. (2008)
	$\alpha + \beta$, laboratory aerobic degradation, 25-128 days		Aerobic degradation	28 to 391 days	UNEP (2009)
	$\alpha + \beta$ in temperate regions, 7, 4 and 92 days		123-391 days		
	Neutral pH, 35 days	Neutral pH, 150 days	N.D.	Acid pH, 50 days	INECC (2014)
	12 to 39 days	108 to 264 days	123 to 391 days	9 months to 6 years	UNEP (2011)
		Field studies: 900 days	Field studies: 3 to 8 months		

Note. N.D. = Not defined.

While, alpha endosulfan has an average DT_{50} of 27.5 days, the beta-isomer an average of 157 days, and endosulfan sulfate 117 to 137 days, anaerobic conditions may considerably extend the semidegradación rate in soils (UNEP, 2007; Ciglasch et al., 2008). However, there is variability among these degradation rates, such that degradation for the α isomers ranges from 12-128 days and for the endosulfan sulfate from 123-391 days (UNEP, 2011). The latter range is similar to reports indicating that the combined DT_{50} for the two isomers (α and β) and endosulfan sulfate in soil varied in the range of 28-391 days (UNEP, 2008).

For aquatic environments, only the persistence for total endosulfan has been determined, and that there is a strong association with pH (hydrolytic degradation). Low pH conditions (pH 5 and lower, acidic) and temperatures near 25°C promote longer periods of degradation, yielding a $\text{DT}_{50} > 200$ days. Under neutral pH conditions, a DT_{50} of 10 to 20 days exists, but less than a day to 0.2 days at pH 9 (alkali or basic). Among the metabolites obtained during this transformation are endosulfan sulfate, endosulfan diol, endosulfan lactone and endosulfan hydroxy acid (Bejarano et al., 2008; UNEP, 2007, 2011). The relationship between pH and the persistence of total endosulfan indicates that under anaerobic conditions, with an acid pH, persistence was four

days (INECC, 2014). In contrast, a DT_{50} of more than 120 days has been reported, but the authors do not describe the conditions under which this process occurs (UNEP, 2009). As for water-sediment conditions, retention of the compound was 3.3 - 273 days with pH 7; the persistence varied from 10 - 20 days with pH 9 and 25 °C, endosulfan remained for 0.2 days (Jones, 2002, 2003; UNEP, 2007). In summary, the route transport of endosulfan isomers and metabolites from agricultural areas to aquatic systems are described on Figure 1. Endosulfan isomers and metabolite can be found in the atmosphere; however, the α -isomer is more common due to its application results in volatile releases to the atmosphere and the β -isomer is easily converted into α -endosulfan. In soil, β -endosulfan and endosulfan sulfate are more common because they tend to strongly join to sediments. In aquatic environments, endosulfan can be found as α and β isomers, and sulfate and diol metabolites. These two metabolites predominate in this environment. Endosulfan sulfate is more persistent because it degrades slowly.

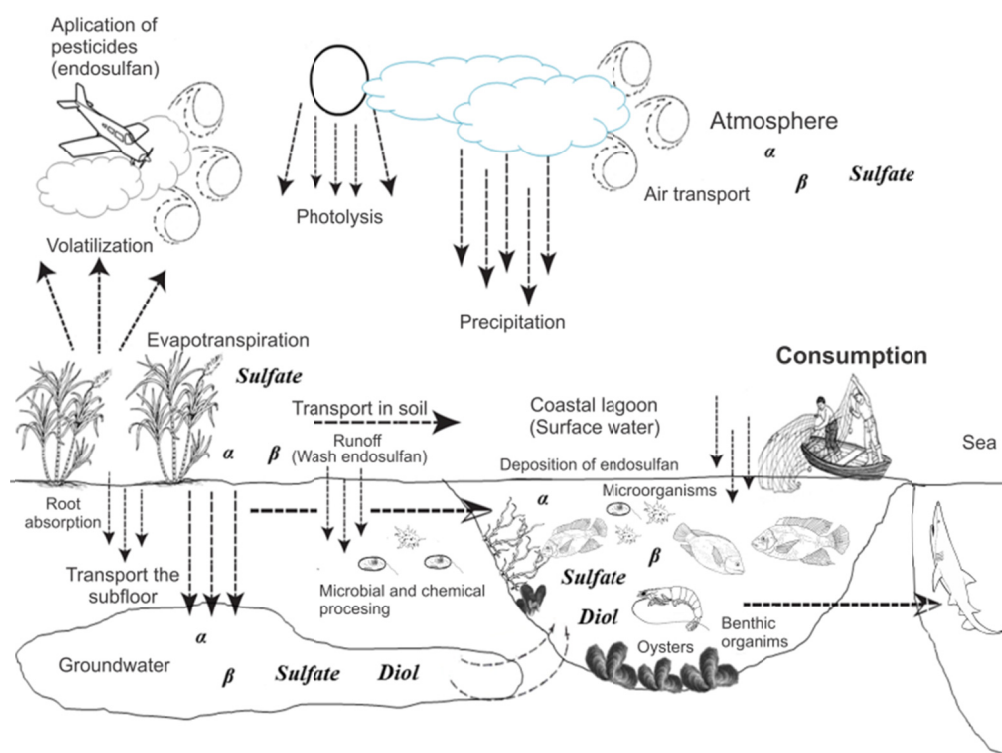


Figure 1. Transport of endosulfan isomers and metabolites from agricultural areas to lagoon systems

6. Permissible Limits of Endosulfan

Because of the toxicological effects related to the presence and use of endosulfan, permissible limits have been established to protect public health and aquatic life. Some of these guidelines are described below. The acceptable daily intake of endosulfan (ADI) is $6 \text{ ng g}^{-1} \text{ day}^{-1}$, and a reference dose for acute oral exposure (ARfD) is $15 \text{ ng g}^{-1} \text{ day}^{-1}$ (CE, 2005). Levels of endosulfan sulfate in lakes, rivers, streams and bodies must not exceed 62 ng g^{-1} to protect public health against adverse effects from the consumption of water and aquatic organisms (fish and shellfish) from contaminated waters. A limit of $89,000 \text{ ng L}^{-1}$ of endosulfan was established (EPA, 2009) for human consumption. Also, EPA (2002b) have established endosulfan doses for acute dietary exposure as $15 \text{ ng g}^{-1} \text{ day}^{-1}$ and $1.5 \text{ ng g}^{-1} \text{ day}^{-1}$ for adults and children, respectively. In case of chronic dietary exposure, reference doses are $6.0 \text{ ng g}^{-1} \text{ d}^{-1}$ for adults and $0.06 \text{ ng g}^{-1} \text{ day}^{-1}$ in children. However, other international organizations such as the *Canadian Council of Ministers of the Environment* have no guidelines on the quantity of endosulfan residues in tissues of aquatic biota that is safe for consumers (CCME, 2014). The same situation occurs in Mexico, where there is no legislation providing permissible concentrations of pesticides such as endosulfan and its isomers; the official standard NOM-242-SSA1-2009 (Diario Oficial, 2011), which specifically deals with commercially important aquatic organisms and is also responsible for regulating the conditions for fishery products (fresh, chilled, frozen or processed), does not consider such contaminants in its content.

For occupational exposure, the National Institute for Occupational Safety and Health recommended a limit of 100 ng g^{-1} for endosulfan in air as an average over a period of 10 hours (NIOSH, 2011). An acceptable level of exposure of operators to endosulfan (AOEL) is a concentration of $0.0042 \text{ mg kg}^{-1} \text{ day}^{-1}$ (CE, 2005). However, the Administration of Occupational Safety and Health (OSHA) has not set a legal limit for endosulfan in the air for a period of 8 hours (ATSDR, 2013).

The reference values for α and β endosulfan for the protection of freshwater aquatic life indicate that the acute and chronic effects are reported at concentrations between 220,000,000 and 56,000,000 ng L^{-1} , respectively. As for marine organisms, acute effects exist at 34,000,000 ng L^{-1} and chronic effects begin at concentrations of 8,700,000 ng L^{-1} (EPA, 2014). A criterion for total endosulfan was established for protection of aquatic life in freshwater and seawater, where levels of 60 ng L^{-1} for acute exposure and 3.0 ng L^{-1} for chronic exposure were established for freshwater. For seawater, the values fluctuated between 90 and 2.0 ng L^{-1} for the acute and chronic exposure, respectively (CCME, 2014). As a result of comparing the various permissible limits stipulated by different international agencies, some discrepancies were found in the reference values established and the considerations that governed them. Therefore, the permissible limits for endosulfan application represent an important way to protect public health and the environment, particularly for food intake by aquatic organisms, which have been shown to contain contaminants such as endosulfan (Table 3).

Table 3. Regulation of endosulfan exposure dose based on exposure route

Exposure route	Specifying criteria	Permissible limits	Reference
Food	Assessment of exposure risk	Acceptable Daily Intake (ADI) of $6 \text{ ng g}^{-1} \text{ day}^{-1}$ Reference dose for acute oral exposure (RfD): $15 \text{ ng g}^{-1} \text{ day}^{-1}$	CE (2005)
	Total diet studies	Acceptable Daily Intake (ADI) of $6 \text{ ng g}^{-1} \text{ day}^{-1}$	WHO (2005)
	Acute dietary exposure to endosulfan	Adults, $15 \text{ ng g}^{-1} \text{ day}^{-1}$ Children, $1.5 \text{ ng g}^{-1} \text{ day}^{-1}$	EPA (2002b)
	Chronic dietary exposure to endosulfan	Adults, $6.0 \text{ ng g}^{-1} \text{ day}^{-1}$ Children, $0.06 \text{ ng g}^{-1} \text{ day}^{-1}$	
	Public health for endosulfan (α , β) and endosulfan sulfate	Endosulfan sulfate in lakes, rivers, streams plus organisms, $62,000 \text{ ng L}^{-1}$	EPA (2009)
	Public health for endosulfan (α , β) and endosulfan sulfate	A limit of $89,000 \text{ ng L}^{-1}$ was established in body organism only.	
	Fishery products (fresh, chilled, frozen and processed)	Not legislated	Diario Oficial (2011)
Occupational	National Institute of Health and Occupational Safety (NIOSH)	$1 \times 10^5 \text{ ng m}^3$ in the air, as an average 10 hours day^{-1}	NIOSH (2011)
	Acceptable level of exposure for operators (AOEL)	$4.2 \text{ ng g}^{-1} \text{ day}^{-1}$	CE (2005)
Aquatic life	Protection of aquatic life in fresh and marine waters	Freshwater: acute effects, 60 ng L^{-1} Chronic effects, 3.0 ng L^{-1} Freshwater: acute effects, 90 ng L^{-1} Chronic effects, 2.0 ng L^{-1}	CCME (2014)
	Protection of aquatic life in fresh and marine water against endosulfan α and β	Freshwater acute effects, $220,000,000 \text{ ng L}^{-1}$ Chronic effects, $56,000,000 \text{ ng L}^{-1}$ Marine water acute effects, $34,000,000 \text{ ng L}^{-1}$ Chronic effects, $8,700,000 \text{ ng L}^{-1}$	EPA (2014)
	Protection of freshwater aquatic life	Chronic exposure, 56 ng L^{-1}	EPA (2002)

7. Use of Endosulfan in Mexico

When identifying patterns of pesticide use along the Gulf of Mexico coast, a total application volume of endosulfan was reported as an active ingredient with 41,755 kg for the geographic units analyzed. Areas with the highest application volume were those for the Pánuco River with 33,826 kg, followed by Tuxpan, Czones and

Tecolutla rivers with 2,363 kg. Moreover, this pesticide represented 40% of the 41 compounds used in the area and ranked second in having a high relative value of environmental risk due to the large volumes used, toxicity and persistence (Benítez & Barcenas, 1996).

In Mexico, there is a lack of public information on the volume of pesticides applied, including endosulfan, which is authorized for 41 crops (Bejarano et al., 2008, 2009). An increase in the importation of this compound has been reported, from 119 t in 2002 to 731 t in 2006. There also is a total lack of public access to information on this chemical, such as where and how much was used, the extent of authorized permissions, their intrinsic characteristics as POPs, as well as the environmental dispersion to aquatic ecosystems (Rendón & Bejarano, 2010).

Endosulfan, as reported by the Federal Commission for the Protection against Sanitary Risk (COFEPRIS-abbreviation by initials of a Mexican institution) in December 2008, had 85 authorized permissions for its agricultural use as an active ingredient, while as a formulated product it included 20 crops, such as vegetables, gramineous, legumes and fruits (Rendón & Bejarano, 2010). This agrees with reports indicating that in Mexico, the use of endosulfan as an insecticide is authorized for more than 20 crops (RAPAM, 2014). Due to the extensive use of the compound, nearly 4,000 t were imported for its formulation during the period from 2002 to 2010, with the primary sources being Germany, India and Israel (Rendón & Bejarano, 2010; RAPAM, 2014).

COFREPIS, through consultation on the commercial registering of authorized pesticides, indicates that endosulfan, as an active ingredient, has 35 records, which correspond to various trade companies, but whose validity is undetermined (COFREPIS, 2014). Therefore, it is important to know the historical trends of pesticides such as endosulfan in order to estimate dietary intake of various foods and to identify their origins to help ensure food safety for consumers (Desalegn et al., 2011).

The imports of endosulfan into Mexico in 2006 exceeded 640 t, representing the highest volume ever traded. Fluctuations in the imported volume of this pesticide over the past 10 years exist, with 303 and 504 t in 2009 and 2010, respectively (INE, 2011). According to the Tariff Information System via Internet (SIAVI), the same trend was evident where 435.55 t were imported in 2012, and by 2013 it had decreased to only 60 t (SIAVI, 2014). However, despite the decline in imported endosulfan, according to SIAVI the presence of this compound in food products such as aquatic organisms remained alarmingly high. Thus, despite the commitment to eradicating its use, endosulfan is still used in Mexico. Also, through the consultation of various sources of information (Bejarano et al., 2008, 2009; INE, 2011; RAPAM, 2014; COFEPRIS, 2014), some discrepancy was found in the number of authorized records reported for this pesticide, which highlights the need for accurate information on how much endosulfan is used and how it is applied.

8. Presence in Aquatic Organisms

8.1 Bivalve Molluscs

The oyster *Crassostrea virginica* (Gmelin) is one of the molluscs most commonly used as a bioindicator in the Gulf of México. The species has been used as an important indicator of various persistent organic compounds, among them endosulfan, not only for its ecological significance, but also for its economical importance. However, investigations on levels of organochlorine pesticides such as endosulfan are widely scattered and scarce in some regions of Mexico.

The ecological risk of Σ endosulfan in *C. virginica* and filtered water samples in Términos Lagoon was at a concentration of 0.45 pg L⁻¹, causing toxic effects such as immobility in embryos of this oyster, and a value range of 0-37 pg L⁻¹ for the water (Carvalho et al., 2009b). Given the economic, ecological and social importance of oysters, *C. virginica* is a vulnerable benthic organism in the lagoon systems in the Gulf of México due to the presence of chemical contaminants such as organochlorine pesticides (Lango et al., 2013b).

In the Gulf of México, *C. virginica* is the characteristic bivalve mollusc in lagoon systems. It has been extensively studied for the presence of pesticides including endosulfan and its isomers. Given that this species filter-feeds and is benthic, it is an organism with a potential for bioaccumulation of chemical contaminants from lakes that are directly influenced by agricultural activities in the areas surrounding these lakes. Table 4 shows the concentrations of endosulfan and its isomers chronologically (by report) and by organismal group.

Table 4. Concentration of endosulfan and its isomers (ng g⁻¹) in aquatic organisms of commercial importance in the Gulf of Mexico

Coastal lagoon	Groups and species	Isomers				Reference
		α	β	Sulfate	Σ	
<i>Bivalves</i>						
P. Viejo	<i>Crassostrea virginica</i> (Gmelin)	--	0.06	--	--	Rosales (1979)
Tampama			N.D.			
Alvarado			N.D.			
Machona			N.D.			
Carmen			0.06			
E. Tamulte			0.06			
P. Rico			N.D.			
Términos (BA)			0.4			
Términos (PV)			N.D.			
Alvarado	<i>C. virginica</i>	1.22±0.76	17.65±7.76	N.D.	--	Botello et al. (1994)
Carmen		N.D.	14.93±6.26	N.D.		
Machona		0.83±0.38	8.78±4.52	N.D.		
Palizada River and Términos	<i>C. virginica</i>	--	--	--	9.84 (BT) 111	Gold et al. (1995)
	<i>Brachidontes recurvus</i>				8.23	
Alvarado	<i>C. virginica</i>	1.22	17.65	N.D.	--	Díaz and Rueda (1996)
Carmen		0.83	14.93	N.D.		
Machona		N.D.	8.78	N.D.		
Términos, Campeche	<i>C. virginica</i>	0.010-0.080	0.084-0.013	0.560-0.670	0.604-0.670	Carvalho et al. (2009a)
	<i>C. rhizophorae</i> Guilding					
Madre	<i>C. virginica</i>	13.97±0.30	N.D.	--	--	Lango-Reynoso et al. (2013a)
Mandinga		37.27±0.00	99.48±16.21			
Mecoacán		14.89 ±1.16	N.D.			
Alvarado	<i>C. virginica</i>	1.27, d	N.D.	0.22, r	--	Palmerín et al. (2014)
	<i>Rangia cuneata</i> (G.B. Sowerby I)	9.10 (max), d	4.92 (max), r	22.4 (max), r		
	<i>Rangia flexuosa</i> (Conrad)	0.64, r	0.66, r	4.83, r		
	<i>Polymesoda caroliniana</i> (Bosc)	N.D., r	N.D, r	1.35, r		
<i>Crustaceans</i>						
Palizada River and Términos	<i>Litopenaeus setiferus</i> (L.)	--	--	--	0.94	Gold et al. (1995)
<i>Fish</i>						
Chetumal Bay	<i>Ariopsis assimilis</i> (Günther)	--	R: 5±8 B: 4±5 N: 3±6 PVe: 1±3 PCa: 0.3±1	--	--	Vidal et al. (2003)
Chetumal Bay	<i>A. assimilis</i>	--	26.57 (max)	--	--	Noreña et al. (2004)
Candelaria-Panlau	<i>Arius melanopus</i> Günther	10.83±16.45	2.86±7.56	31.24±74.44	--	Díaz et al. (2005)
East Candelaria, Términos	<i>Cichlasoma</i> spp.	99	35.8	49.7		
	<i>A. melanopus</i>	22.38	N.D	N.D		
	Both species	21.68±35.77	5.11±13.53	7.10±18.78		
Chetumal Bay	<i>A. assimilis</i>	--	--	--	21.5 (m)	Álvarez (2009)

					40.0 (max)	
					13.0 (min)	
Términos, Campeche	<i>Lepisosteus tropicus</i> Gill	<0.002	<0.003	0.026	0.026	Carvalho et al. (2009a)

Note. N.D.: Not detected; --: Not analyzed; P. Viejo: Pueblo Viejo; Tampama: Tampamachoco; P. Rico: Puerto Rico; BA: Boca Atasta; PV: Palizada Vieja; Max: Maximum; Min: Minimum; r: rain; d: dry; AE: both species; m: Mediana; BT: Boca de Laguna Términos; R: Ramonal; B: Bellavista; N: Nictechan; PVe: PuntaVerde; PCa: Punta Calera.

8.2 Crustaceans

Studies on the presence of endosulfan in crustaceans in the Gulf of Mexico are scarce and mainly limited to the genus *Penaeus*. The few studies that exist are mainly focused on determining the presence of endosulfan, identifying dispersion of DDT residues and their metabolites in environmental matrices. Therefore, about 90% of research along the Mexican coast lacks information about endosulfan residues in environmental systems and aquatic biota (Rendón & Bejarano, 2010).

The ecological risks of Σ endosulfan in pink shrimp, *Farfantepenaeus duorarum* (Burkenroad) and samples of filtered water from Términos Lagoon were assessed, yielding toxic effects on shrimp at 0.04 $\mu\text{g L}^{-1}$ and LC_{50} concentrations in water at 8 to 22 $\mu\text{g L}^{-1}$ (Carvalho et al., 2009b). These results contrast with other studies where endosulfan sulfate was found in higher concentrations, followed by alpha and beta isomers, suggesting the predominance of degraded forms produced mainly during oxidation of the alfa isomer (Montes et al., 2012).

Aquatic organisms of commercial importance such as bivalves, crustaceans and fish in the Gulf of México and the Caribbean Sea had higher concentrations of beta endosulfan, followed by the alpha isomer and endosulfan sulfate, indicating recent use of the pesticide. In previous studies, a lower concentration of the Σ endosulfan was reported on crustaceans compared to that from analyzed bivalves; a difference explained by the physiological and ecological characteristics of each species. This trend can be explained on the genus *Farfantepenaeus*, mainly because of its position on the water column and capacity for movement, although it has detritophagos habits (Table 4).

8.3 Fish

Studies on the concentration of endosulfan in fish from the Gulf of Mexico and Caribbean Sea are scarce. The potential interaction between the presence of β -endosulfan and parasitization in Mayan catfish *Ariopsis assimilis* (Günther) in the Bay of Chetumal were assessed, and revealed a lack of a positive correlation between the presence of the β -isomer and the intensity of parasitic infestation (Vidal et al., 2003). The detected concentrations were lower than those reported for the same species (Noreña-Barroso et al., 2004; Álvarez, 2009).

Higher concentrations of this compound in fish can be explained as a process of biomagnification, given that these organisms feed on shrimp, crabs and small fish. The concentrations are also associated with the amount of lipids present within consumer tissues, which promotes the accumulation of organochlorine compounds such as endosulfan due to their lipophilic affinity. Thus, within fish species of commercial importance in the Gulf and Caribbean, only four were found in studies that address this pollutant. Reports indicated that through management programs such as Fisheries Management Plans (FMP), which provide insight into the impacts of production and development activities in each lagoon system, FMP strategic targets can be met for sustainable fisheries (Castañeda et al., 2014).

Analysis of endosulfan concentrations in the different organism groups show different sources of influence on the bioaccumulation of organochlorine pesticides such as endosulfan in aquatic organisms: feeding habits, position in the water column (ecological habits) and the incorporation of these pollutants, either through water or sediment, which can promote progressive bioaccumulation.

8.4 Strategies for Endosulfan Reduction Use

Certainly, endosulfan is an organochloride pesticide that affects the aquatic life in the Gulf of México and collaterally has an impact on public health, which is a concern that should be seriously taken in account by many actors in the society, especially with the aid of government-funded programs. In this case, the short and long-term strategy proposed by Galavis-Villa et al. (2010) to reduce water contamination by nitrate and nitrite could be applied to reduce endosulfan contamination in different environments. In the short-term workshops can be implemented to teach people not only about the danger of using endosulfan and the implicated risks but

inform them of the different/reduction options available, and to train them when using it. As a long-term strategy it is important to reduce the use of the pesticide by optimizing timing and rates based on a protective program. These strategies to reduce the negative impacts on the environment and public health can be implemented at municipality level in developing countries. In other cases or situations, such strategies can be accomplished at smaller scales depending on the educational and economical levels of the society under consideration.

9. Conclusions

The presence of endosulfan and its isomers indicates the need to increase the number of studies of its effect on water quality and pollution of shellfish and fish for human consumption due to the various adverse effects reported on public health. Moreover, there are large gaps in information because of the lack of continuity in monitoring programs. Therefore, it is necessary to identify the exact sources of emission of these compounds, to know how they are mobilized toward coastal lagoons, and to understand their effects on wildlife (plant and animal, aquatic and terrestrial) in these ecosystems. Efficient screening mechanisms should also be employed to reduce exposure to endosulfan in consumer products such as aquatic organisms. Finally, it is necessary to have more strict national laws to ensure that the consumption of aquatic organisms is free of toxic compounds such as endosulfan.

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