

DDT and Metabolites

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Abstract Dichlorodiphenyltrichloroethane (DDT) is a well-known insecticide that was introduced and widely used during World War II. In total more than 4.5 million tonnes DDT have been produced. Although its use and production stopped worldwide during the 1970s, it was reintroduced in the 2000s as a malaria vector control by the World Health Organization (WHO). DDT is toxic to animals and humans. Its main characteristics are its persistence, lipophilicity, and bioaccumulative potential. DDT and its metabolites are normally determined in organisms, sediments, or soil by gas chromatography combined with either electron capture detection or, preferably, mass spectrometry. Many interlaboratory studies have been carried out on the analysis of DDT and its metabolites, and certified reference materials are now available. DDT and its metabolites have been found in air, water, sediment, and biota from all over the world. As a consequence of global fractionation and cold condensation, DDT and its metabolites accumulate in the Arctic. Since the reintroduction of DDT against malaria in Africa in 2005, monitoring of DDT compounds is again highly relevant to detect changes in environmental levels of DDT. Such monitoring is particularly needed in Africa. The first indications show an increase of DDT in humans and wildlife.

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1 Introduction

1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) was one of the first synthetic pesticides used. It was first synthesized by an Austrian chemist, Othmar Zeidler, in 1874 [1], but its insecticidal properties were not discovered until 1939, by Paul Muller, a Swiss entomologist, who won the Nobel Prize for this discovery [2]. Its first use as an insecticide was during World War II for the protection of the Allied forces from diseases such as typhus and malaria, which were spread by mosquitoes and lice to humans [2, 3]. This breakthrough, in addition to its effectiveness and low price, led to its commercialization and use for agricultural purposes [1, 2]. One of its great successes was the elimination of malaria from Europe and the USA [1].

According to the World Health Organization (WHO) specifications for public health pesticides, technical DDT is a white- or cream-colored powder consisting of DDT and manufacturing impurities. Its mixture consists of 80% *p,p'*-DDT and 20% *o,p'*-DDT [4].

Dicofol (Fig. 1) is a widely used pesticide, synthesized from DDT. It contains DDT as impurity which must not be above 0.1% according to European legislation [5].

The mass production of DDT started in 1944, and only that year, in the USA alone, 4,366 t were produced, reaching its peak in 1963 (81,154 t) because of the export market. According to the Organization for Economic Cooperation and

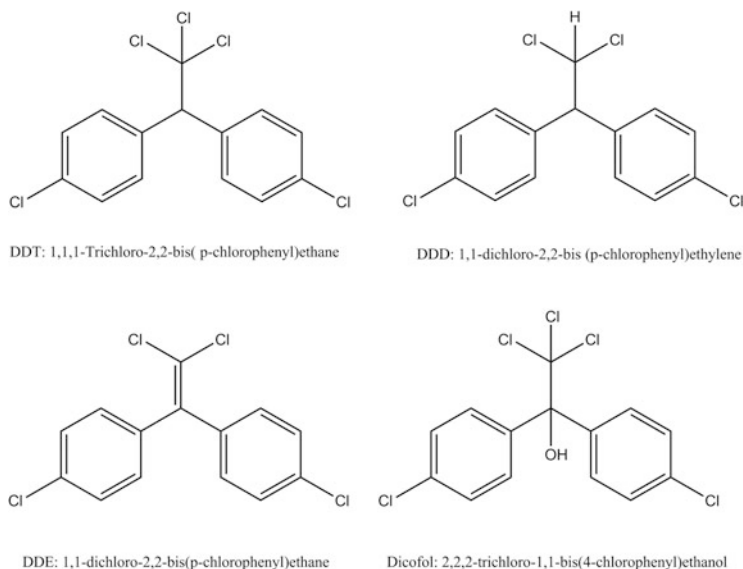


Fig. 1 DDT and its metabolites. *p,p'*- DDT, 1,1,1-trichloro-2,2-bis (*p*-chlorophenyl)ethane; *p,p'*-DDE, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; *p,p'*-DDD, 1,1-dichloro-2,2-bis (*p*-chlorophenyl)ethylene; dicofol, 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol

Development (OECD), the worldwide annual production of DDT in 1974 was 60,000 t [6]. In the former Soviet Union, the mass production of DDT began in 1946 in Moscow, and during the 1950s–1970s, 20,000 t per year were produced. Despite its ban, the production of DDT still continued in the former USSR, and in 1986 10,000 t per year were recorded [7]. According to Li and Macdonald [8], the total worldwide production of DDT from the 1940s until now is estimated to be 4.5 million tonnes, which is almost 3.5 times higher than the estimated total PCB production, according to Breivik et al. [9, 10].

Despite its advantages, DDT was banned in most developed countries during the 1970s. This was due to its harmful effects on the environment and wildlife [11]. Properties such as chemical stability, lipophilicity, and bioaccumulation in the food chain caused a rising concern on its negative effect on humans and wildlife. These properties were also characteristic for 1,1-dichloro-2,2-bis (*p*-chlorophenyl)ethylene (DDE), one of DDT's metabolites [1].

Rachel Carson's book *Silent Spring*, in which the author outlined the global character of the DDT problem, had a great impact on the environmental movement and initiated changes in laws that protected the environment [11]. By the mid-1950s, several studies showed that DDT and its metabolites had adverse effects on the reproduction of many animals. For example, thinning of eggshells due to hormonal effects and changes in calcium metabolism by DDT [1] resulted in the potential extinction of the bald eagle, as nesting females were accidentally crushing their eggs [12]. High mortality in fish was also observed, such as young salmon and trout,

species that feed on small insects [11]. Also, a mass decline in seal population was observed with their population dropping from 3,000 to 500 within two decades, due to consumption of polluted fish [13]. The wide use of DDT resulted not only in the eradication of malicious pests but also in the death of beneficial insects. As a result, populations of previously minor insects arose [2].

In January 1970, Sweden was the first country to ban the use of DDT due to its effect on the environment, and in the same year, the former USSR prohibited DDT for agricultural purposes. Despite its ban, DDT production and use continued illegally at many places until 1986. In the early 1970s, the USA banned the use of DDT apart from emergency public health use, and later in 1970, DDT was also banned in Norway as a general pesticide.

Now, many years after its ban, DDT is recommended again by the WHO (World Health Organization) as a malaria vector control in many African countries. As a result, the use and production of DDT is continued in countries such as Mexico, India, and several countries in Africa (e.g., Ethiopia, Mozambique, Zambia, Zimbabwe, South Africa), with India being the largest producer of DDT (4,100–4,500 t for the period 2003–2007) [14, 15]. However, until now and in spite of substantial investments in research, no other alternatives to DDT have been found with the same efficiency.

2 Toxicology

2.1 Human Toxicity

Not many cases of direct human poisoning have been reported, but there is a high concern about the chronic effects of DDT and its metabolites [2]. As a result, many studies have been conducted on the association of DDT with illnesses such as leukemia, brain cancer, prostate cancer, liver cancer, diabetes, and breast cancer [1]. The negative impact on humans of DDT and its metabolites is a rather controversial subject.

Everett et al. [16] reported an association between diabetes and DDT, not only with diagnosed diabetes but also with total diabetes [16].

In vitro studies have shown that DDT shows estrogenic activity in humans, while DDE acts as an androgen antagonist. Some of these studies suggest that DDT is also responsible for the decrease of semen quality [17–19]. Due to their lipophilic nature, DDT and its metabolites are found in relatively high concentrations in breast milk, leading to exposure of children when breast-feeding. This can turn out to be an important contamination factor for infants, especially because earlier studies showed that in Africa, mothers breast-feed their children for up to 2 years [14, 20]. In utero exposure to DDT, even in low concentrations, is shown to alternate thyroid hormones, decrease cognitive skills, and increase asthma in infants [21]. Many researchers also suggest that, due to its bioaccumulative properties,

DDT is also responsible for premature death of humans, infant mortality, and effects on the neurological development of infants [2, 21].

After the early 1990s, many studies have focused on the correlation between DDT and breast cancer. Many of them suggested that DDT and its metabolites act as tumor promoters. On the other hand, many reviews pointed out that no correlation between breast cancer and DDT exists [22–25]. Due to these inconsistent data, more research is still needed on this topic [1, 2].

The acceptable daily intake (ADI) of Σ DDT (which consists of *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD) is 20 $\mu\text{g}/\text{kg}/\text{day}$ as established by the FAO/WHO in 1984 [20]. According to the European Union pesticides database, the maximum residue level (MRL) for Σ DDT is 0.05 mg/kg, as set by the Commission Regulation (EU) No. 212/2013. The Codex Alimentarius recently set the MRL for Σ DDT in milk at 20 $\mu\text{g}/\text{kg}$ [20].

The International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency (EPA) have categorized DDT as a 2B classification (possibly carcinogenic to humans with sufficient evidence from animal bioassay data, with little or no human data), according to the IARC monograph volumes and EPA's carcinogen risk assessment guidelines.

2.2 Ecotoxicity

Toxic effects of DDT and its metabolites in animals include a disruption of the endocrine function causing, e.g., feminization of male embryos of many bird species and transformation of male fish embryos to females, among other non-desirable effects [2].

Recently, a correlation between DDT and the size of certain brain regions in birds, which are responsible for mating behavior and song, was reported. Especially in male songbirds, DDT and DDT metabolites reduced brain nuclei that are responsible for the reproductive success, reproductive behavior, and parental care with increasing levels of DDT. A significant reduction of brain and forebrain size was found after exposure to DDT during early development [26].

DDT has also an effect on many animals' main nervous system. Animals such as rats, guinea pigs, rabbits, and cats, treated with DDT, start to show tremor, ataxia, and finally epileptiform convulsions. Death is noticed due to respiratory failure. In many species DDT may cause arrhythmia and ultimately death due to ventricular fibrillation. The liver is also affected by DDT. Tests that were conducted in mice and rats showed that if fed for long periods with DDT (>2 mg/kg for mice and >5 mg/kg for rats), hypertrophy of the liver has been reported, the first changes being observed after 4 days of administration (exposure times not mentioned) [6].

2.3 Acute Toxicity

Acute toxicity of DDT to mammals is considered moderate. Oral LD50 of DDT in rats ranges from 113 to 118 and 150 to 300 mg/kg in mice, for oral administration in oil. It is less toxic for these animals when exposed via the skin, with an LD50 of 3,000 mg/kg in rats and 1,000–1,500 mg/kg in mice [6, 27]. It mainly affects the central nervous system and the liver. Low levels of DDT in humans may cause nausea, diarrhea, increased liver enzyme activity, and irritation of the eyes, nose, and/or throat [6].

The LD50 in rats of *p,p'*-DDD is 2,400 and 575 mg/kg of dicofol [6].

3 Analysis

DDT and its main metabolites can be analyzed by gas chromatography (GC) after extraction and cleanup, which should be optimized for each matrix.

3.1 Sampling, Extraction, and Cleanup

3.1.1 Air

Air samples are usually collected with denuder sampling devices, which concentrate the vapor insecticide in a single step. Materials such as polyurethane foam (PUF), Texan, or PUF/Texan are the most common absorbents for the collection and concentration of DDT [28, 29]. Solvent extraction is required before the sample is ready for GC analysis. Thermal desorption is an alternative method with which solvent extraction steps can be avoided [29]. Martin et al. [28] have developed this desorption method for the quantification of DDT in air. One important limitation of this method is the DDT degradation to DDE and DDD due to high temperatures during thermal desorption, which makes it difficult to measure the DDT degradation that may occur in the environment [28].

3.1.2 Water

The usual method for DDT extraction from water samples is solid-phase extraction (SPE). It is used as either an extraction technique or a cleanup technique [30, 31]. Zhou et al. [32] optimized this technique, using silica as an adsorbent. In another study, a one-step extraction of DDT and its metabolites using microwave-assisted headspace controlled-temperature liquid-phase micro-extraction was developed. Results from tests on various water samples showed that this is a rapid, sensitive, cost-effective, and eco-friendly preparation method for the determination of DDT

and its metabolites in environmental water samples [32]. Solid-phase micro-extraction (SPME) is also used for the extraction and cleanup of DDT and its metabolites in water samples. Its main advantages are the reduction of sample handling and the use of small amounts of solvents [31]. An interlaboratory study was carried out on the suitability of SPME as a sample preparation method for water samples in pesticide analysis. Eleven laboratories participated. The results showed coefficients of variation (RSD) from 24.7% to 73.3%, with 4 out of 12 results being outliers and two stragglers [33, 34]. Probably due to its limited reproducibility, SPME is not broadly used [31].

3.1.3 Soil, Sediment, and Biota

Soil and sediment are more complex matrices as these can contain sulfur and many other interfering compounds. Soxhlet extraction is the most common method of choice for the extraction of organochlorine pesticides (OCPs) in general [35, 36]. The use of a mixture of polar/nonpolar solvents is essential for the extraction of DDT that is adsorbed to organic carbon in the samples. Other techniques that are being used for DDT extraction from soil samples are supercritical fluid extraction (SFE); accelerated soil extraction (ASE), also known as pressurized liquid extraction (PLE); and microwave-assisted solvent extraction (MASE). Methods such as saponification and sulfuric acid treatment should not be used as degradation may readily occur. Several studies showed that *p,p'*-DDE degrades immediately after sulfuric acid treatment, and DDT and DDD convert to DDE after saponification [35]. Taylor et al. [37] used PLE for the determination of 13 OCPs, DDT and its metabolites included. Hexane–acetone (1:1 v/v) was considered to be the optimum solvent mixture for the extraction. The removal of sulfur from soil and sediment samples is important as sulfur appears as a broad peak in the chromatograms, thus disturbing the determination of DDT. Several methods can be used to remove sulfur from the extracts, such as copper rods, copper powder, mercury (although not environmentally friendly!), gel permeation chromatography (GPC), and AgNO₃-modified silica columns, with the last one being the most effective one, as it removes both elemental sulfur and organosulfur compounds [37, 38].

Extraction and cleanup techniques for most biota are comparable to those used for sediments. Instead of sulfur, fat is the most confounding factor. The solvent mixture is an essential factor to quantitatively extract the OCPs with the lipids from the sample [35]. In most cleanup methods, Florisil, alumina, and silica gel column chromatography are used, as they are suitable for the separation of fat and plant waxes from the samples [35, 39].

3.2 Gas Chromatography

The method of choice for the final chromatographic separation of DDT and its metabolites is capillary GC [32]. The most common detectors are the electron capture detector (ECD) and a number of mass spectrometers (MS) [28, 35, 36]. Most of the environmental sample extracts are complex mixtures. As a result co-elution of compounds may easily occur. Heart-cut multidimensional gas chromatography (MDGC) and comprehensive two-dimensional gas chromatography (GCxGC) are more effective in separation [40]. In GCxGC two ovens can be used, and specific software provides two-dimensional chromatograms [41, 42]. The splitless mode is used most frequently for injection in order to improve sensitivity [30, 32, 35]. Attention must be paid to the temperatures used with this technique, as high temperatures in the splitless mode may result in conversion of DDT into DDD. Due to dirty glass inserts and due to the use of glass wool in the liner conversion of DDT into DDE during GC injection may also occur. Open liners are, therefore, strongly recommended. Degradation over 10% was mentioned as a consequence of a dirty glass liner [44].

Nowadays, fused silica capillary columns are almost exclusively used for the determination of OCPs in general and DDT in particular. The length is usually 25–50 m with an internal diameter of 0.15–0.25 mm. The film thickness should be >0.15 μm to prevent on-column degradation. Fifty meter columns provide a better separation of the analytes but result in longer retention times, thus increasing on-column degradation [35]. Using 50 m columns, PCBs may be separated from DDT, but this needs to be validated. Alternatively, PCBs can be separated from DDT and other OCPs using silica gel column chromatography prior to the GC analysis [45]. The most common capillary column used for the detection of DDT and its metabolites is the HP5-MS column [30, 32, 46].

During GC analysis, interferences may be present. For example, toxaphene may be present in some samples. Toxaphene is a pesticide consisting of a complex mixture of chlorinated camphenes, bornanes, and bornenes, and the peaks may interfere with DDT and its metabolites, hindering their quantification. Numerous studies showed that it is very difficult to separate these compounds in a mixture, even when using different columns in GC. Toxaphene is an aliphatic mixture, which means that the response factors with ECD are much lower than those of the aromatic DDT compounds. That means that in samples from most areas, toxaphene is not a very serious interference. Attention should however be paid to samples from areas that are highly polluted with toxaphene, such as samples from the Arctic. GCxGC may also help for such samples.

The combination of GC and ECD is a valuable and relatively inexpensive method for the determination of DDT and its metabolites, as ECD has a high sensitivity for halogenated aromatic compounds such as DDT [35, 47, 48]. The so-called micro-ECDs are even more sensitive. It is a very common detector, especially for routine environmental analysis, and it is much more affordable than a mass spectrometric (MS) detector [41]. Its only drawback is its poor linearity

especially in the low pg range. This problem can be solved with multilevel calibration [35].

GC coupled to MS is another useful technique for the identification of DDT and its metabolites. The MS linearity is much better than that of ECD [35]. It is suitable for qualitative and quantitative analysis of DDT, as it has the ability to detect ultra-trace concentration levels of these compounds [32]. The only disadvantage of GC-MS is its relatively high running cost for a laboratory that carries out routine analysis in environmental samples. However, there has been a major development in MS during the last decades. Sensitivity has increased a lot, whereas prices have dropped considerably. High-resolution sector MS systems are not needed any longer to obtain enough sensitivity for many compounds including DDT. Benchtop quadrupole MS systems, time-of-flight (ToF) MS, orbitraps, and many other systems are nowadays available. These are still more expensive than ECD, but they do offer a wealth of possibilities, including a very high resolution and great sensitivity, which are all very useful for the analysis of DDT, in particular in combination with many other compounds. Another possibility is tandem mass spectrometry, which monitors specific collision-induced dissociation reactions, thus lowering the chemical background and increasing the signal to noise ratio. Also in GC-MS, DDT degradation can occur.

When using a mass spectrometry analysis, much interference from the matrix of the sample can occur. The internal standard method is the ideal one, in order to overcome such interferences. ^{13}C -labeled standards in an isotope dilution can be used for best results, as they have the same physicochemical properties and chromatographical behavior as the target compound, but different m/z ratio [49].

3.3 *Interlaboratory Studies and Certified Reference Materials (CRMs)*

Since the late 1970s, the analysis of DDT compounds has been evaluated in many interlaboratory tests. There are numerous organizations that conduct such tests, among which the United Nations Environment Programme (UNEP, Geneva, Switzerland); SETOC/WEPAL, Wageningen, Netherlands; and QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe), also in Wageningen, Netherlands. A recent interlaboratory study with a participation of 103 laboratories from all over the world was conducted by UNEP for the evaluation of the level of performance on persistent organic pollutant (POP) analysis. The laboratories were requested to analyze two test solutions and fish, sediment, fly ash, and human milk. The extraction and cleanup protocol, spiking schemes, standards, and internal QA/QC were left to the choice of the participating laboratories, but validation of their methods was very much emphasized. The only mandatory parameter was the use of capillary gas chromatography columns, to

Table 1 Assigned values, relative standard deviations (RSDs), and number of submitted results (*n*) in the first UNEP interlaboratory study on POPs [43]

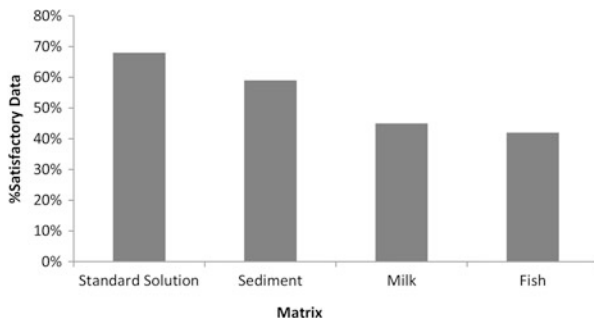
	Standard solution				Sediment			
	<i>n/n</i> ^a	Assigned value (ng/mL)	Model RSD (%)	Inclusion rate ^b (%)	<i>n/n</i> ^a	Assigned value (µg/kg)	Model RSD (%)	Inclusion rate ^b (%)
<i>p,p'</i> -DDT	46/0	36	18	66	32/1	18.1	48	66
<i>p,p'</i> -DDE	52/0	35	15	69	37/1	15.4	44	74
	Fish				Milk			
	<i>n/n</i> ^a	Assigned value (µg/kg)	Model RSD (%)	Inclusion rate ^b (%)	<i>n/n</i> ^a	Assigned value (ng/kg)	Model RSD (%)	Inclusion rate ^b (%)
<i>p,p'</i> -DDT	28/0	NA	107	79	13/2	0.003	40	56
<i>p,p'</i> -DDE	34/0	8.88	80	73	20/0	NA	64	72

NA due to the limited quality of the data, no assigned value could be designed

^aNumber of submitted results not including values below limit of detection (LOD) or limit of quantification (LOQ) (first number) and (second number) the number values below LOD or LOQ

^bpercentage of laboratories on which assigned value is based

Fig. 2 Percentage of laboratories with satisfactory z-scores (i.e., $z \pm 2$) in the test solution, sediment, milk, and fish for Σ DDT [43]



achieve the right separation for the determination of the analytes. Table 1 shows the results of this study.

The percentage of satisfactory results is given in Fig. 2. The best z-scores were obtained for the standard solution. From this study it became clear that not all laboratories perform well in the analysis of all compounds, but many were specialized in specific categories [43]. It should be noted that many of the participants were from developing countries who participated in such a test for the first time, sometimes after having received only a basic training. The QUASIMEME proficiency tests show a better comparability, caused by the participation of more experienced laboratories. In general GC-MS results are better than those from ECD, due to the higher resolution of GC-MS and lower specificity of ECD [43].

The concern on the presence of DDT and OCPs in general and their effect on the environment has led to an increasing demand for certified reference materials

(CRMs) or standard reference materials (SRMs). However, there are not many CRMs/SRMs available for these compounds, as their production and certification is a relatively expensive and slow process. The European Institute for Reference Materials and Measurements (IRMM, Geel, Belgium), the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), and the Canadian National Research Council (NRC, Ottawa, Canada) are the three main producers in the world of CRMs. For OCPs, eight CRMs are available in biota: two cod liver oils, four mussel tissues, whale blubber, and a sea plant homogenate, which are shown in Table 2 [50].

4 Environmental Occurrence

4.1 Air

The most common DDT disposal into the atmosphere is by agricultural spray drift, post-application volatilization, and wind erosion [51]. A study conducted in China showed that DDT and DDT metabolite concentrations were higher in urban areas than in nonurban areas [47]. The concentrations were measured in the gaseous and particulate phase and showed that the DDT compounds mainly occur in the gaseous phase (Fig. 3) [47].

Seasonal influences play a role in the DDT monitoring in air, as DDT levels are usually higher in summer than winter (Fig. 4) [47, 51].

The Global Monitoring Plan (GMP) for persistent organic pollutants (POPs) was built with the support of the United Nations Environment Programme (UNEP)/Global Environmental Facility (GEF) involving countries from West and East Africa, the Caribbean, Latin America, and the South Pacific. Air was sampled by the use of PUF disks for passive sampling, and DDT and its metabolites were often the compounds occurring in the highest concentrations (Table 3) [46].

4.2 Water

DDT concentrations in water are very low, as these compounds are highly hydrophobic. Much higher levels are found in particulate matter than in the dissolved phase [48, 49]. The most common sources of DDT in water are from former use in agriculture, atmospheric deposition, and diffuse pollution from erosion processes [49]. *o,p'*-DDT is more persistent than *p,p'*-DDT and found in higher concentrations in water samples [48, 49]. Iwata et al. [52] performed an impressive cruise during which they sampled air and analyzed ocean water for several organochlorine contaminants. They found total DDT concentrations to be much lower levels than HCH levels, obviously also related to the higher water solubility of HCHs.

Table 2 RMs in biota [50]

	SRM 1974a	SRM 1588a	SRM 1945	SRM 2974	SRM 2977	SRM 2978	140/OC	BCR 598
Organization	SRM NIST	SRM NIST	SRM NIST	SRM NIST	SRM NIST	SRM NIST	IAEA	BCR
Country of origin	USA	USA	USA	USA	USA	USA	Monaco	EC
Matrix	Mussel tissue	Cod liver oil	Whale blubber	Mussel tissue	Mussel tissue	Mussel tissue	Focus (sea plant homogenate)	Cod liver oil
Units	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
As	Dry weight	Wet weight	Wet weight	Dry weight	Dry weight	Dry weight	Dry weight	Wet weight
[±] expressed as	±95% CI	±95% CI	±95% CI	±95% CI	±95% CI	±95% CI	±95% CI	±95% CI
Units of issue	3 × 15 g	5 × 1.2 ml/ampoule	Set 2.15 g/ampoule	8 g	10 g	10 g	30 g	5 g
Form	Frozen	Oil	Frozen	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Oil
2,4'-DDE	5.26 ± 0.27*	22.0 ± 1.0	12.28 ± 0.87	5.26 ± 2.8*		4.41 ± 0.56		
4,4'-DDE	51.2 ± 505	651 ± 11	445 ± 37	51.2 ± 5.7	12.5 ± 1.63	37.5 ± 1.5	1.2 (0.86–1.6)	610 ± 40
2,4'-DDD	13.7 ± 2.8*	36.3 ± 1.4	18.1 ± 2.8	13.7 ± 2.8*	3.32 ± 0.29	10.5 ± 1.0		30 ± 4
4,4'-DDD	43.0 ± 6.3	254 ± 11	133 ± 10	43 ± 6.4	4.30 ± 0.38	38.8 ± 2.3	0.7 (0.61–0.90)	400 ± 30
2,4'-DDT	8.5 ± 4.9*	156.0 ± 4.4	106 ± 14	8.5 ± 1.9*		9.2 ± 1.6		
4,4'-DDT	3.91 ± 0.59	524 ± 12	245 ± 15	3.91 ± 0.60	1.28 ± 0.18	2.84 ± 0.28	2.2 (1.4–3.6)	179 ± 18

For non-IAEA materials, values indicated by an asterisk (*) are noncertified. For IAEA materials, values indicated by an asterisk are classified as information values; all other values are classified as recommended

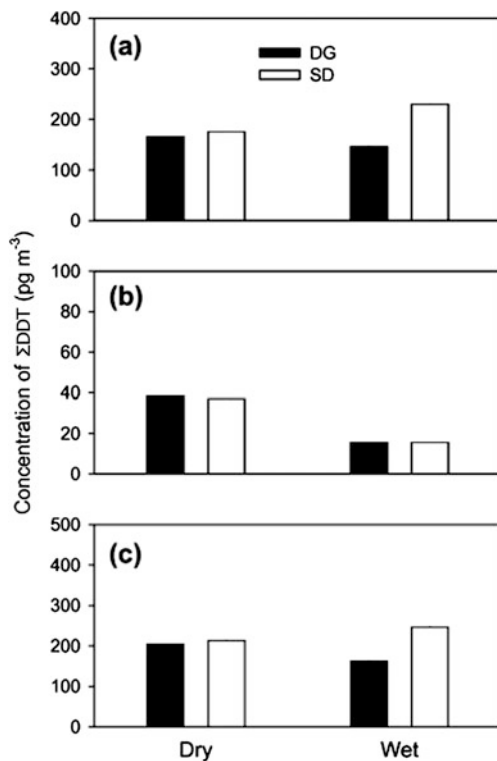


Fig. 3 Average concentrations of DDTs (sum of *o,p'*- and *p,p'*-DDT, DDE, and DDD) in (a) vapor phase, (b) particulate phase, and (c) air samples (gaseous + particulate phases) from Dongguan (DG) and Shunde (SD) obtained in dry and wet weather seasons [47]

Furthermore, they found DDT concentrations much higher in tropical waters and air from southern latitudes compared to northern areas.

4.3 Sediments and Suspended Particulate Matter

Suspended particulate matter and bottom sediments are the main reservoir of DDT in marine, lake, and river ecosystems [48, 49, 51]. The main inputs of DDT in sediments are agricultural runoff, sewage discharge, atmosphere disposition, and wastewater. Pham et al. [49] conducted a study on suspended sediment in the St. Lawrence River in Canada. Σ DDT concentration in 93 samples was found from non-detectable to 0.34 $\mu\text{g/g}$, with the most contaminated sediment coming from the Great Lakes and the Ottawa River. Higher concentrations were found during spring probably due to surface runoff and erosion [49]. Another study conducted in Greenland showed that concentrations of DDT in sediment from the

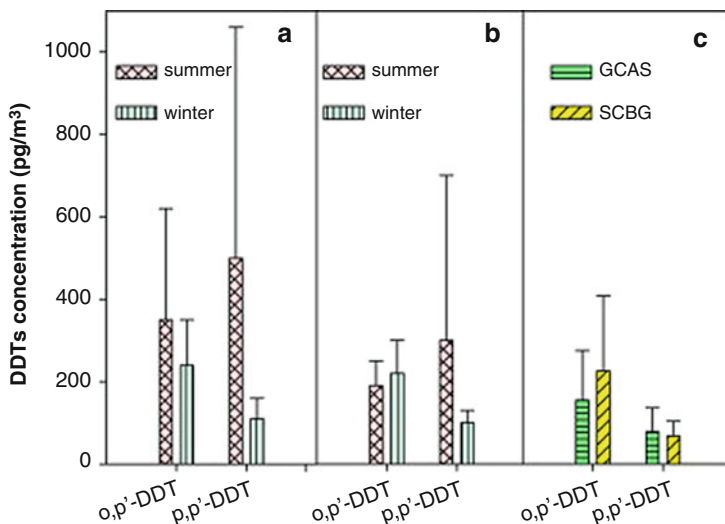


Fig. 4 Levels of DDTs (mean \pm standard deviation) in air of (a) the Pearl River Delta (b) Hong Kong and (c) Guangzhou at an urban site, Guangzhou Branch, Chinese Academy of Science (GCAS), and a suburban site, South China Botanical Garden (SCBG) [51]

Greenland coast are comparable with those from other Arctic regions. On the other hand, data from European estuaries for DDTs were much higher than those found in Greenland [53]. Kelderman et al. [54] studied the pollution of Delft canal sediments and found that DDT and its metabolites were the dominant contaminants. Although DDT was banned in the Netherlands since 1973, these high concentrations of DDT are presumed to be due to their strong persistence in the environment [54].

4.4 Soil

In a study that took place in Guangzhou, China, surface and subsurface vegetable soil samples showed a large variation in DDT levels (3.6–831 ng/g) [51].

Depending on the conditions of the soil, two pathways of degradation may occur: aerobic (p,p' -DDE as a degradation product) and anaerobic (p,p' -DDD as a degradation product) [4]. A study conducted by Wang [55] showed that DDT concentrations in soil are dependent of its agricultural use. After growing specific plant species in DDT-contaminated soil, the total amount of DDT and DDE in soil had decreased, and this decrease was equal to the total amount of DDT and DDE measured in the plants [55]. In this way, phytoremediation of DDT-contaminated soil can take place. Another important factor for DDT degradation in soil is the pH value. There seems to be a strong correlation between pH and concentrations of DDT and its metabolites in soil. A study showed that at $\text{pH} < 8.0$, DDT metabolites were present in higher concentrations than at $\text{pH} > 8.0$. This may be caused by the

Table 3 DDT and its metabolite concentrations in selected first exposure PUF samples in ng/PUF measured by UNEP expert laboratory (IVM)

Country code	MLI	SEN	GHA	NIG	TGO	COD	ETH	KEN	ZMB	MUS	UGA	FJI	KIR	WSM	TUV	SLB	BRB
<i>o,p'</i> -DDE	56	9.5	<0.6	<1.3	<1.3	1.9 ^a	4.5 ^a	1.8 ^a	14	<1.6	1.3 ^a	6.4	0.32 ^a	52 ^a	<0.29	1.4	<0.06
<i>p,p'</i> -DDE	400	60	11	2.0 ^a	5.7	46	26	12	140	5.7	18	59	7.7	230	1.2	81	0.13 ^a
<i>o,p'</i> -DDD	26	2.8 ^a	1.3 ^a	1.3 ^a	<1.3	<1.5	<1.6	<1.6	2.8 ^a	<1.6	1.4 ^a	<1.4	1.5 ^a	5	4.4 ^a	2.2 ^a	<0.08
<i>p,p'</i> -DDD	27	3.2 ^a	3	<1.3	<1.3	<1.5	2.5 ^a	<1.6	6.6	<1.6	1.1	26	6.2	4.2	<1.5	9.6	<0.14
<i>o,p'</i> -DDT	34	9.7	3.7	<1.3	<1.3	10	29	3.1	180	6.9	<1.1	63	6.7 ^a	53	19	36	<0.14
<i>p,p'</i> -DDT	70	27	8.5	1.5	6.4	27	60	8.2	310	4.8	8.8	180	15	47	5.8 ^a	580	0.31

Country codes: MLI Mali, SEN Senegal, GHA Ghana, NIG Nigeria, TGO Togo, COD Congo, ETH Ethiopia, KEN Kenya, ZMB Zambia, MUS Mauritius, UGA Uganda, FJI Fiji, KIR Kiribati, WSM Samoa, TUV Tuvalu, SLB Solomon Islands, BRB Barbados [46]

^aIndicates value between limit of detection and limit of quantification

change of the humic acid structure from fibrous to smaller sheetlike structure, at $\text{pH} > 7.0$ [4].

4.5 Aquatic Organisms

Fishes are generally used for environmental monitoring, as the contaminant loading in fish can reflect the state of their ecosystem [51]. A study conducted in Baltic herring and pike showed large variations in DDT levels (ND–10 mg/kg), depending on the differences in the fat content of the fish. Also, DDT levels vary between tissues of muscle and some organs. For example, in the same study, kidney of pike appeared to be a possible storage site [56]. The fat content of the various tissues is determining the final concentrations of DDT. For example, in cod muscle tissue with a fat content of ca. 1%, the DDT concentrations are much lower than in cod liver, which has an average fat content of 50% [57]. On the contrary, in eel, the DDT concentrations are much higher in the muscle tissue, which has a fat content of 5–40%, compared to those in the liver of the eel with a fat content of <5% [58]. DDT levels in farmed fish (freshwater and seawater) vary with the contamination of the DDT level in their feed [51].

Marine shellfish, especially mussels, are often used as local indicators of DDT contamination, as these species are highly bioaccumulative and do not migrate. In a study on OCPs in mussels and oysters collected from the east coast of Thailand, DDT was the contaminant with the highest concentrations in both organisms. This study also concluded that there is a decreasing trend of DDT compounds in mussels since 1979 [59].

5 Time Trends

Several publications have appeared on temporal trends of DDT and its metabolites. A study on DDT and its metabolites in cod liver oil from the Baltic Sea during the period 1971–1989 showed that DDT concentrations were rapidly declining from 1974 onwards. Σ DDT ranged from 0.4 to 25 $\mu\text{g/g}$ (on a lipid weight (lw) basis). *p*, *p'*-DDE was the dominant compound followed by *p*,*p'*-DDD and *p*,*p'*-DDT [60]. The NOAA mussel watch program shows a decline of total DDT concentrations (mainly DDE) from 1,600 to 300 ng/g dw over the period 1986–2002 in Palos Verdes, CA, USA [61]. Macgregor et al. [62] reported a declining trend in eel in most, but not all, locations in Scotland. On the other hand, Suns et al. [63], after studying Σ DDT temporal trends in spottail shiners from the Great Lakes over the period 1975–1990, concluded that although there has been a decline in DDT concentrations during these years, they tend to stabilize after the 1980s, especially DDE [63]. Zhang et al. [64] reported increasing DDT levels in sediment cores from the Pearl River Delta, China. They assumed that excessive soil runoff enhanced by the large-scale land transform and regional flooding in the Pearl River Delta might

have contributed to the transport of organochlorine pesticides from soil to the sedimentary system in the early 1990s. They also found increasing DDE/DDT ratios, pointing to former rather than recent use of DDT. An atmospheric monitoring program (1993–2006) in the Arctic showed, in general, low levels of DDT-related compounds during the entire period. Although there was a reduction in concentration of these compounds in the Arctic during the 1990s, this reduction was lower during later years, and concentrations of DDT and its metabolites are almost stable now. The only exception was during the summer of 2004 when a summer forest fire occurred in Yukon, Canada. During that period, high concentrations of *p,p'*-DDE and *o,p'*-DDE were observed at two stations, probably due to biomass burning. No seasonal profiles were observed, apart for *p,p'*-DDE, in which concentrations were higher during the winter period [65]. Guglielmo et al. [66] studied the global environmental cycling of DDT in the 1980s for one decade. Figure 5 shows that multiple cycles are responsible for the DDT burden in soil, vegetation, ocean water, and sea ice [66]. The study concludes that after 10 years, approximately 12% of DDT would have accumulated in the Arctic. Assuming continuing low DDT emissions, Schenker et al. [67] showed in a model that concentrations will decrease by a factor of 30 in temperate regions and by a factor of 100 in the Arctic, as compared to the concentrations in the 1960s and 1970s. In the tropics, levels decrease by a factor of 5 to 10, only.

In 2002, a POP assessment in the Arctic occurred by the Arctic Monitoring and Assessment Programme (AMAP). In this assessment, temporal trends of POPs in air, water, sediment, and Arctic biota were examined. Many interesting conclusions came out of this assessment. Data of temporal trends of POPs in Arctic air were available from five air monitoring stations in the Arctic. Data was collected from 1993 to 2000. The main DDT metabolites that were found were *o,p'*-DDE and *p,p'*-DDE. Seasonal variation was present at all sites. According to Hung et al. [68], *p,p'*-DDE is decreasing slightly at the Alert station, while a slight increase of *o,p'*-DDT during the period 1993–1998 was also reported. This could be due to an unknown source causing technical DDT entering the Arctic [68].

There are a number of temporal trend data of DDT in freshwater and sediments in the Arctic. Zhulidov et al. [69] reported Σ DDT changes in water and sediments from eight Russian Arctic rivers during the period 1988–1994. Concentrations of Σ DDT declined over the years, reaching detection limits of ng/L magnitude by 1992 (Fig. 6) [69].

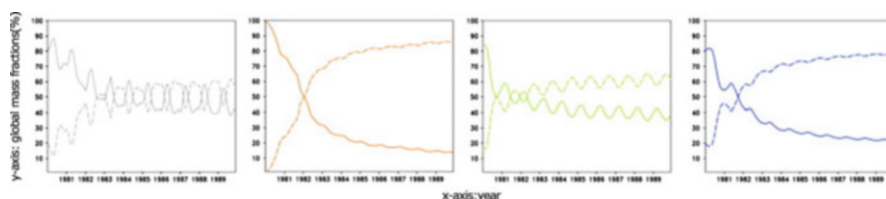


Fig. 5 DDT global mass fractions (%) in atmosphere (gray), soil (orange), vegetation (green), and ocean and sea ice (blue) in first cycle (single hop, full line) and during subsequent cycles (multi-hop, dashed line) [67]

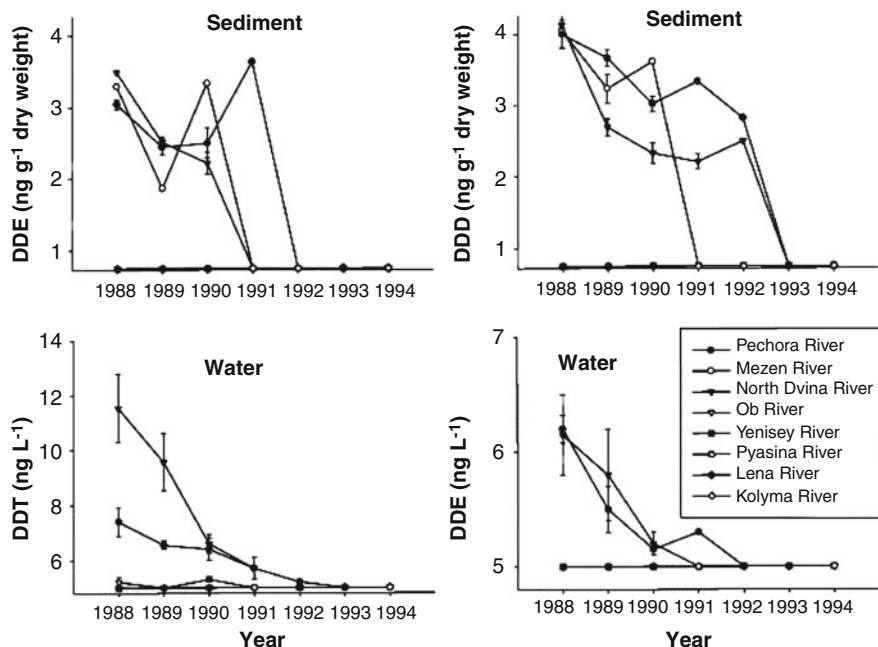


Fig. 6 Temporal changes in DDT, DDD, and DDE concentrations (mean \pm S.E.) in the water and sediments of eight Russian rivers [69]

All temporal trend studies carried out in the Arctic indicate that, although there has been a substantial decrease of DDT and its metabolites in biota since the 1970s, concentrations of Σ DDT stabilized from the 1990s to the 2000s [70].

Research on POPs was not only conducted in the Arctic ecosystem but also in Antarctica. Most of the studies concluded that *p,p'*-DDE in particular is the most persistent organic contaminant in Antarctic biota [71–73]. Trends of DDT and its metabolites in Antarctic biota showed a decreasing pattern during the period 1980–1995, but increased again in 2000–2002 [74]. The main reasons that these compounds are found in the Arctic and the Antarctic are the global fractionation and cold condensation processes [75]. Comparing data from research in the Arctic and the Antarctic shows that concentrations of DDT found in the Arctic are much higher than those found in the Antarctic. This is mainly due to geographical features. The Antarctic region is surrounded by the Southern Ocean, which can act as a boundary for POPs. Therefore, they can reach the Antarctic only through air mass transport [74, 75]. The Southern Hemisphere contains less land mass, which is also relatively far away from the South Pole. In addition, the population density at the Southern Hemisphere is relatively low, while, on the contrary, the dense population of the Northern Hemisphere causes a higher DDT level in the Arctic [74]. The increase of DDT in Antarctica is, therefore, very interesting, as the question is if this is related to the renewed application of DDT in southern Africa. Although based on a limited data set, Alava et al. [15] reported a significant increase in DDT concentrations in

Galapagos sea lion pups between 2005 and 2008 (280–530 $\mu\text{g}/\text{kg}$ lipid weight). These levels are able to affect the immune system and population dynamics during periods of nutritional stress such as El Niño events. The authors concluded that DDT and associated health risks in wildlife are generally believed to be declining, but this may no longer be the case in tropical countries where DDT is increasingly used. Lopez-Carillo et al. [76] expressed their concern in 1996 about relatively high DDT levels in Mexico, higher than in other Latin-American countries. Women living in Mexico City showed up to 0.6 mg/kg lipid weight in their breast milk. Increasing DDT trends were also suggested by Manaca et al. [77]. Examination of the distributions of DDT and its metabolites in the walls of 43 dwellings from Manhica (Mozambique) showed median levels of 19, 130, and 23 ng/g for *o*, *p'*-DDT, *p,p'*-DDT, and *p,p'*-DDE, respectively, directly after indoor residual spraying (IRS). The concentrations of these compounds at the onset of the IRS campaign ($n=48$) were 5.5, 47, and 2.2 ng/g , respectively. In another study, Manaca et al. [78] reported concentrations of DDT compounds in the cord blood of 214 children born between 2003 and 2006, so before IRS, in Manhica (Mozambique) of 0.8 and 0.4 ng/ml for *p,p'*-DDE and *p,p'*-DDT, respectively, were similar to those found in western countries. However, the *p,p'*-DDT/*p,p'*-DDE ratio was high indicating an association with recent use of DDT. A significant increase in *p*, *p'*-DDT and its main metabolite, *p,p'*-DDE, in mother's milk samples from Manhica was observed between 2002 (median values 2.4 and 0.9 ng/ml , respectively) and 2006 (7.3 and 2.6 ng/ml , respectively). Grimalt [79] reports a further significant increase of DDT and its metabolites in the same mother and newborn cohort in 2010. Channa et al. [17] found elevated *p,p'*-DDT/*p,p'*-DDE ratios in coastal KwaZulu-Natal, also outside the endemic malaria areas, which indicates recent ongoing and possibly illegal use, since DDT use is only allowed in designated areas. The DDT concentrations reported by Manaca et al. [77] and Grimalt [79] are above the thresholds for deleterious effects in cognitive skill observed in children at 4 years of age. This was also confirmed by Bouwman et al. [80] who reported DDT levels in 163 breast milk samples from South Africa. Mean ΣDDT levels in breast milk were 18, 11, and 9.5 mg/kg lipid weight from three DDT-sprayed villages, respectively, including the highest ΣDDT level ever reported for breast milk from South Africa (140 mg/kg lipid weight). A provisional tolerable daily intake for DDT by infants was significantly exceeded. Van Dyk et al. [81] reported elevated DDT levels in the Limpopo province in South Africa and raise concern on the potential health effects in residents living in the immediate environment following DDT IRS.

6 Conclusions

At present, DDT's use is mainly as an insecticide in African countries for the fight against malaria. However, its effect on future generations is concerning many researchers [82]. Its persistence, estrogenic activity, lipophilic nature, and ability

to bioaccumulate in higher organisms of the food chain are the main factors of concern as DDT, and its metabolites seem to be responsible for illnesses such as diabetes, asthma, and cancer. More than 75 years after its introduction, DDT and its metabolites are still present in many organisms and abiotic environmental compartments all over the world which shows the extreme persistence of this compound. As its main use is for malaria vector control, there is a need to search for alternatives of DDT, which would be less toxic to living organisms and more environmentally friendly. The two main alternatives are indoor residual spraying and insecticide-treated bed nets with pyrethroids instead of DDT [14]. The main drawback of pyrethroids is that some mosquito breeding, particularly in Africa, seems to be resistant to this particular insecticide [14]. Another alternative that has the prospect to eliminate completely malaria is malaria vaccination. Much research has been done on this matter for more than 30 years [83–85], but only recently tests and clinical trials have been conducted [84]. DDT is still present in the environment and it is unknown for how long it will exist. Most trend studies show that there has been a decreasing trend of DDT concentrations in the environment, but these concentrations seem to stabilize over the last decade. This may be caused by its reintroduction as a malaria vector control in many African countries, but this needs further evidence. There is no concrete evidence that DDT and its metabolites can be eliminated completely from the environment. Ongoing environmental monitoring is important, especially in Africa, to detect a possible increase in DDT levels in the environment, as is suggested by a study in sea lion pups from the Galapagos Archipelago [15] and several studies recently carried out in Africa [21, 77, 78, 80, 86]. The Global Monitoring Plan of the Stockholm Convention may enable such monitoring in the near future [46].

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