

## 5. POTENTIAL FOR HUMAN EXPOSURE

### 5.1 OVERVIEW

Endrin was introduced in the United States in 1951 as an avicide, rodenticide and insecticide. Its principal use to control the cotton bollworm and tobacco budworm peaked in the early 1970s. In 1979, the EPA canceled some uses of endrin and indicated its intent to cancel all uses of endrin (EPA 1979f; USDA 1995). By 1986, all uses were voluntarily canceled (Bishop 1984, 1985, 1986; EPA 1993e; USDA 1995), except for its use as a toxicant on bird perches, which was canceled in 1991 (USDA 1995). Endrin also was a contaminant in dieldrin (Verschueren 1983); however, all uses of this pesticide have been canceled since the mid-1980s (EPA 1992b). Consequently, there are no longer any significant releases of endrin to the environment in the United States.

Endrin tends to persist in the environment mainly in forms sorbed to sediments and soil particles. A conservative estimate of its half-disappearance time in sandy loam soils is approximately 14 years (41% of endrin applied still remained in the soil after 14 years) (Nash and Woolson 1967). Therefore, the exposure risks from endrin to the general population of the United States are likely to steadily decrease over time.

Migration of endrin into groundwater would not generally be expected from normal agricultural application. However, endrin has been detected in some groundwater, suggesting that leaching may be possible in some soils under certain conditions (Cohen 1986; EPA 1989; HazDat 1996).

Biodegradation does not appear to be a significant fate process for endrin in soils (Nash and Woolson 1967). Hydrolysis in moist soils is also not expected to be significant (EPA 19798). In combination, losses from volatilization, photodegradation (Burton and Pollard 1974; EPA 1985e; Knoevenagel and Himmelreich 1976; Zabik et al. 1971), and heat transformation (primarily to endrin ketone, with minor amounts of endrin aldehyde) (EPA 19798; Phillips et al. 1962) account for the rapid decrease in endrin residues on soil surfaces exposed to bright sunlight.

In spite of its low vapor pressure, endrin has been found to volatilize significantly (20-30%) from soils within days after application (Nash 1983). In air, endrin will be primarily absorbed to particulates which may be re-entrained to soil or surface water via wet or dry deposition. Laboratory studies have indicated that a predominant mechanism for the transformation and degradation of endrin

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in air under field conditions is via photochemical reactions and rearrangements to yield primarily endrin ketone, with minor amounts of endrin aldehyde (Burton and Pollard 1974; EPA 1985e; Zabik et al. 1971). Endrin may also be transformed by heat in the atmosphere, yielding primarily the pentacyclic ketone and endrin aldehyde (EPA 1979g; Phillips et al. 1962). Endrin may also react with photochemically generated hydroxyl radicals in air, with a predicted half-life ranging from 1.45 hours (Howard 1991) to 1.8 days (SRC 1995a).

Endrin may be transported from soil to surface water via runoff from rain or irrigation. When released to water, endrin strongly adsorbs to sediment (Kenaga 1980) and bioconcentrates significantly in aquatic organisms (ASTER 1995; EPA 1980a; Metcalf et al. 1973). Endrin appears to be biomagnified only slightly through various levels of the food chain (Metcalf et al. 1973). It is likely that endrin released to surface water will undergo photoisomerization to endrin ketone, with minor amounts of endrin aldehyde also being formed (Burton and Pollard 1974; Zabik et al. 1971). Endrin may be biodegraded in water, but most laboratory studies indicate that this will not be a significant fate process (Eichelberger and Lichtenberg 1971; Sharom et al. 1980b; Tabak et al. 1981). In addition, neither hydrolysis nor volatilization is a significant fate process for endrin in water. The estimated half-life for endrin in water is more than 4 years (EPA 1979g; Howard 1991). Degradation of endrin in soils under field conditions is not a significant fate process with a half-disappearance time of the order of 14 years (Nash and Woolson 1967).

No studies on the environmental fate of endrin aldehyde or endrin ketone could be found in the available literature. Limited information on the physical and/or chemical properties of endrin aldehyde indicates that it is highly insoluble in water (EPA 1981a), highly immobile in soil, and will not volatilize significantly from water or soil. Any endrin aldehyde in air should exist predominantly in the adsorbed phase (Eisenreich et al. 1981). Atmospheric endrin aldehyde will be transported to soil and surface water via wet and dry deposition of associated particles. Endrin aldehyde may react with photochemically generated hydroxyl radicals in the atmosphere, with an estimated half-life of 3.6 hours (SRC 1995a). In water, adsorption to sediments and bioconcentration are likely to be significant transport processes. Neither hydrolysis nor oxidation (via peroxy radicals or singlet oxygen) of endrin aldehyde is expected to be significant in aquatic systems (EPA 1979g, 1981a). The estimated half-life for endrin aldehyde is more than four years (EPA 1979g). By analogy to aquatic systems, neither hydrolysis nor oxidation is expected to be a significant transformation process for

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endrin aldehyde in soil. No information could be found on the biodegradation of endrin aldehyde in aquatic systems, sediment, or soil.

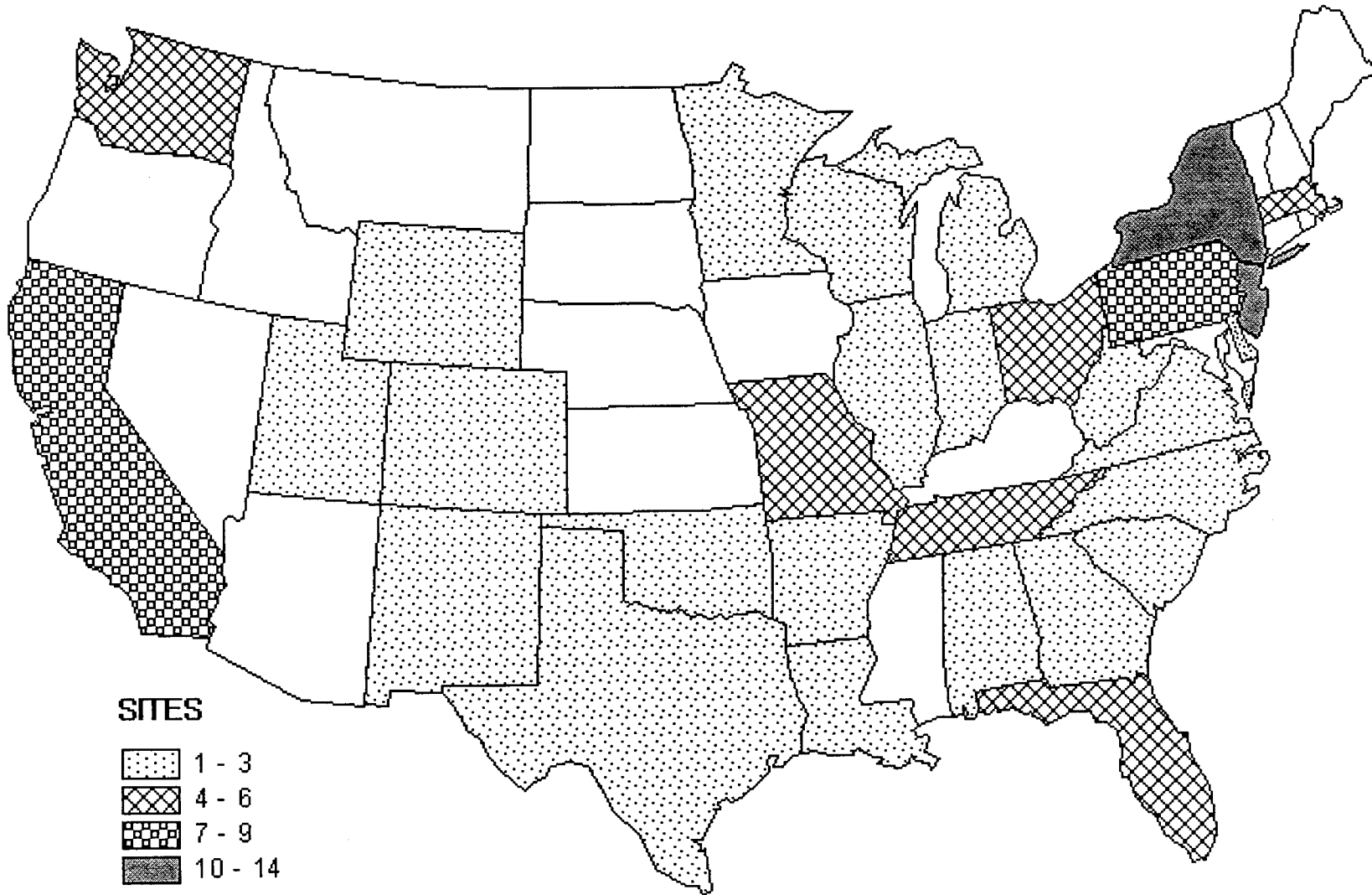
Endrin ketone may react with photochemically generated hydroxyl radicals in the atmosphere, with an estimated half-life of 1.5 days (SRC 1995a). Available estimated physical/chemical properties of endrin ketone indicate that this compound will not volatilize from water; however, significant bioconcentration in aquatic organisms may occur. In soils and sediments, endrin ketone is predicted to be virtually immobile; however, detection of endrin ketone in groundwater and leachate samples at some hazardous waste sites suggests limited mobility of endrin ketone in certain soils (HazDat 1996). No other information could be found in the available literature on the environmental fate of endrin ketone in water, sediment, or soil.

Information on current levels of endrin in the environment is limited; however, the available data indicate that concentrations in all environmental media are generally negligible or below levels of concern. The FDA has concluded that endrin is no longer present in the environment to the extent that it may be contaminating food or feed at levels of regulatory concern (USDA 1995). No information could be found in the available literature on levels of endrin aldehyde or endrin ketone in the environment.

The main sources for potential human exposure to endrin are residues on imported food items, unused stocks, unregistered use, inappropriate disposal, and hazardous waste sites; however, there is no current evidence of significant exposures from any of these sources. Furthermore, it should be noted that in environmental media, especially in contaminated soils and sediments, the amount of endrin chemically identified by analysis is not necessarily the amount that is toxicologically available.

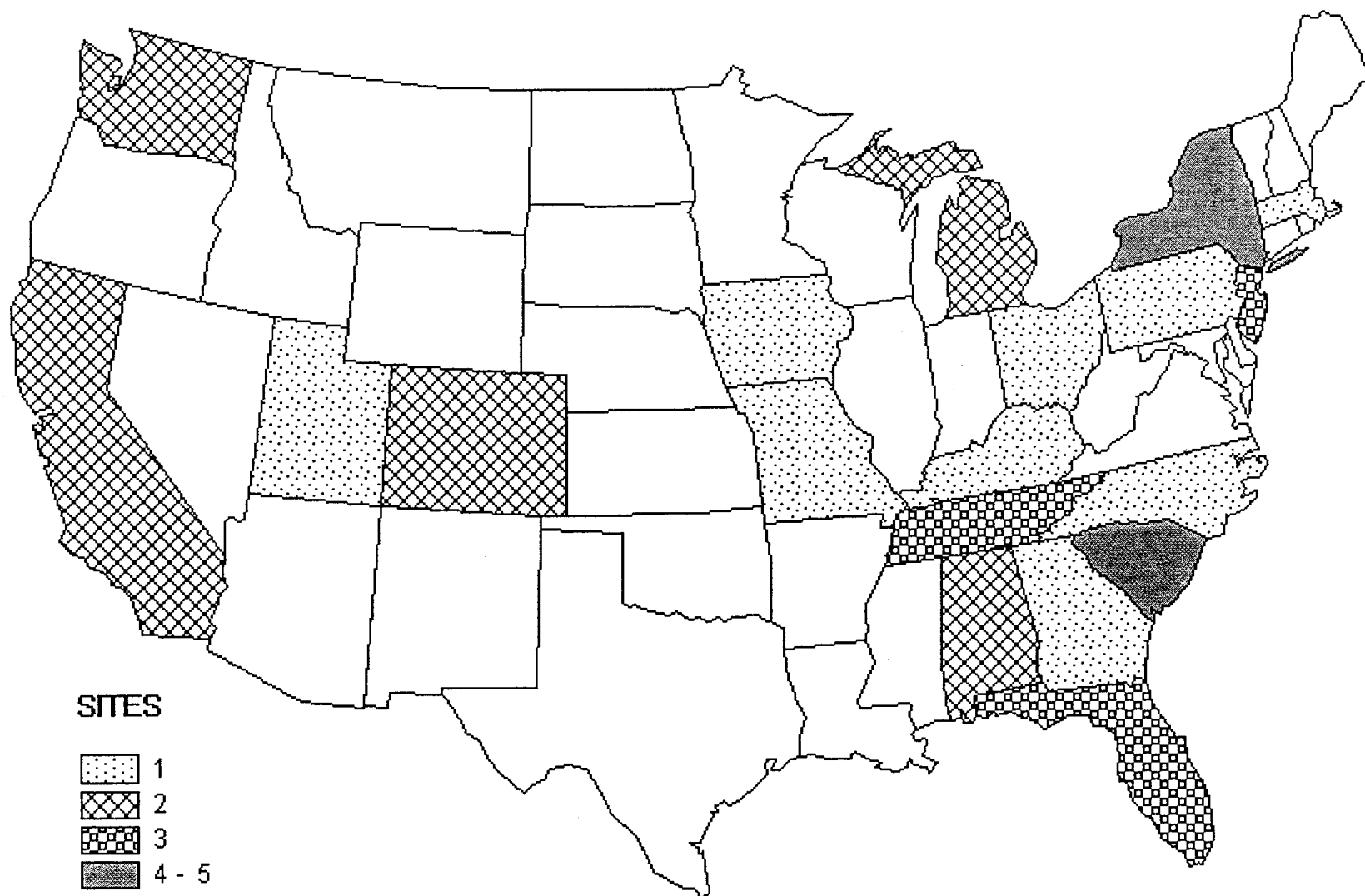
Endrin has been identified in at least 102 of the 1,430 current and former hazardous waste sites that have been proposed for inclusion in the NPL (HazDat 1996), although the total number of sites evaluated for endrin is not known. The frequency of these sites can be seen in Figure 5-1. Of these sites, 102 are located in the United States. Endrin ketone has been identified in at least 37 of the 1,430 current and former hazardous waste sites that have been proposed for inclusion in the NPL (HazDat 1996). However, the number of sites evaluated for endrin ketone is not known. The frequency of these sites can be seen in Figure 5-2. Of these sites, 37 are located in the United States.

Figure 5-1. Frequency of Sites with Endrin Contamination



Derived from HazDat 1996

Figure 5-2. Frequency of Sites with Endrin Ketone Contamination



Derived from HazDat 1996

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Endrin aldehyde has not been identified in any of the 1,430 current and former hazardous waste sites that have been proposed for inclusion in the EPA National Priorities List (NPL) (HazDat 1996); however, the number of sites evaluated for endrin aldehyde is not known.

### 5.2 RELEASES TO THE ENVIRONMENT

No information is available in the Toxic Release Inventory (TRI) database on the amounts of endrin, endrin aldehyde, or endrin ketone released to the environment from facilities, that manufacture or process these compound because these chemicals are not included under SARA, Title III and, therefore, are not required to be reported (EPA 1995a).

Because virtually all uses of endrin in the United States were voluntarily canceled by 1986 (Bishop 1984, 1985, 1986; EPA 1993e; USDA 1995) (see Section 4.3), releases to the environment of endrin, or of endrin aldehyde and endrin ketone which occur as impurities or degradation products of endrin, have decreased dramatically over the last decade.

#### 5.2.1 Air

In the past, emissions from endrin production and processing facilities and agricultural applications were primary sources of releases of endrin to the atmosphere. During the period when endrin was extensively used in agriculture, 33% of the applied endrin was found to volatilize within 11 days, after which time further evaporation ceased (Nash 1983).

There is also a potential for atmospheric release of endrin, endrin aldehyde, and endrin ketone from hazardous waste sites. Endrin has been detected in air samples collected at 4 of the 102 NPL sites where endrin has been detected in some environmental medium (HazDat 1996). No information was found on detections of endrin aldehyde or endrin ketone in air at any NPL hazardous waste site (HazDat 1996)

#### 5.2.2 Water

In the past, endrin could have been released to surface water from manufacturing and processing facilities. No information on direct discharges or loadings of endrin into surface water was found. Based on amounts measured in rainfall at various stations in Canada, loading estimates for endrin and

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a number of other organochlorine pesticides have been attempted for portions of the Great Lakes basin (Strachan 1988). The sources for such loadings to receiving waters are not clear, but would likely involve in-place contaminants related to endrin's past uses as a pesticide agent. Current studies in Oklahoma indicate that in some areas of the United States endrin is still being released to surface water from farmland soils that have been treated with endrin in the past (Petty et al. 1995).

There is also a potential for release of endrin, endrin aldehyde, and endrin ketone to water from hazardous waste sites. Endrin has been detected in surface water samples collected at 10 of the 102 NPL sites, in groundwater samples collected at 37 of the 102 NPL sites, and in leachate samples collected at 2 of the 102 NPL sites where endrin has been detected in some environmental medium (HazDat 1996). Endrin ketone has been detected in surface water samples collected at 5 of the 37 NPL sites, in groundwater samples collected at 16 of the 37 NPL sites, and in leachate samples collected at 2 of the 37 NPL sites where endrin ketone has been detected in some environmental medium (HazDat 1996). No information was found on detections of endrin aldehyde in surface water, groundwater, or leachates at any NPL hazardous waste site (HazDat 1996)

### 5.2.3 Soil

Past use of endrin as an agricultural pesticide has been the principal source of its release to soils or aquatic sediments. There is also a potential for release of endrin, endrin aldehyde, and endrin ketone to soils and sediments from hazardous waste sites. Endrin has been detected in soil samples collected at 44 of the 102 NPL sites, and in sediment samples collected at 19 of the 102 NPL sites where endrin has been detected in some environmental medium (HazDat 1996). Endrin ketone has been detected in soil samples collected at 23 of the 37 NPL sites, and in sediment samples collected at 5 of the 37 NPL sites where endrin ketone has been detected in some environmental medium (HazDat 1996). No information was found on detections of endrin aldehyde in soils or sediments at any NPL hazardous waste site (HazDat 1996).

## 5.3 ENVIRONMENTAL FATE

### 5.3.1 Transport and Partitioning

Endrin is extremely persistent when released to the soil. It adsorbs strongly to soil particles and tends to be immobile, based on an estimated  $K_{oc}$  of 34,000 (Kenaga 1980; Swann et al. 1983). Endrin on

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soil may be transported to surface water via runoff from rain or irrigation. Since endrin in solid form is hydrophobic and sorbs strongly to soil particles, migration into groundwater would not generally be expected from normal agricultural application. In laboratory studies, endrin was found to be almost completely adsorbed to samples of sandy loam and organic soil (Sharom et al. 1980a). In sandy soil only 13.6% of the endrin was leached from the soil after 10 successive 200 mL water rinses. In organic soil, only 1.5% of the endrin was leached from the soil after 10 successive 200 mL water rinses. The mobility factors calculated for the sandy soil and organic soil were 0.52 and 0.040, respectively. Only dieldrin, leptophos, and p,p'-DDT were less mobile in the 2 soil types than endrin.

However, endrin has been detected in some leachates and groundwaters from NPL hazardous waste sites (see Section 5.2.2) and in various other groundwaters, suggesting that leaching may be possible in some soils under certain conditions (Cohen 1986; EPA 1989; HazDat 1996). Furthermore, because endrin formulations in solvent carriers such as xylene or hexane were also commonly used, endrin could move into groundwater from spills of such formulations. Similarly, migration to groundwater might also occur at waste sites where endrin residues become mixed with organic solvents (Jaquess et al. 1989).

Despite endrin's low vapor pressure of  $2.0 \times 10^{-7}$  mm Hg (EPA 1981a), initial volatilization of 20-30% after agricultural application to soil has been reported to be rapid (Nash 1983). Within 11 days, however, further volatilization was no longer detected (Nash 1983). Unlike some other chlorinated pesticides, endrin volatilization was not enhanced after a rainfall. Small amounts of endrin in soil may also be transported to the air by dust particles.

The presence of significant concentrations of endrin transformation products (including endrin ketone, endrin aldehyde, and endrin alcohol) in a variety of plants grown in soil treated with endrin for periods as long as 16 years prior to planting (Beall et al. 1972; Nash and Harris 1973) indicates that there may be significant uptake of endrin and/or its transformation products by plants from endrin-treated soil.

Because of its high  $\log K_{oc}$  and  $\log K_{ow}$  values (4.53 and 5.34-5.6, respectively; see Table 3-2), when released to water, endrin strongly adsorbs to sediment (Kenaga 1980; Swann et al. 1983) and bioconcentrates significantly in aquatic organisms (ASTER 1995; EPA 1980a; Metcalf et al. 1973). Typical bioconcentration factors (BCFs) for freshwater and marine organisms range from 80 to 49,000



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(Table 5-1). Biomagnification of endrin with increasing trophic level is not expected to be significant (Leblanc 1995). Metcalf et al. (1973) reported a ratio of biomagnification through the aquatic food chain to bioconcentration by direct uptake from water to be 2 for endrin compared to 2.50 for DDT. These authors used a model laboratory aquatic ecosystem containing algae (*Oedogonium cardiacum*), snails (*Physa sp.*), water fleas (*Daphnia magna*), mosquito larvae (*Culex pipens quinquefasciatus*), and mosquito fish (*Gambusia affinis*).

Based on its very small calculated Henry's law constant of  $4.0 \times 10^{-7}$ - $5.4 \times 10^{-7}$  atm-m<sup>3</sup>/mol (see Table 3-2) and its strong adsorption to sediment particles, endrin would be expected to partition very little from water into air (Thomas 1990). The half-life for volatilization of endrin from a model river 1 meter deep, flowing 1 meter per second, with a wind speed of 3 meters per second, was estimated to be 9.6 days; whereas, a half-life of greater than 4 years has been estimated for volatilization of endrin from a model pond (Howard 1991). Adsorption of endrin to sediment may reduce the rate of volatilization from water.

In air, endrin is expected to be associated primarily with particulate matter, based on its low vapor pressure and high  $K_{oc}$  (Kenaga 1980). However, small amounts of endrin in the atmosphere may exist in the vapor phase (Eisenreich et al. 1981). Because of its low solubility (200 µg/L, see Table 3-2) endrin would not be expected to be removed significantly from the atmosphere by wet deposition. Particle-adsorbed endrin will be removed from the atmosphere by both wet and dry deposition. In recent studies in the Great Lakes area, endrin was found in 5% of 450 wet deposition (rain/snow) samples collected between 1986-1991, at volume weighted mean concentrations ranging from 0.02 to 0.98 ng/L (ppt) (Chan et al. 1994).

No studies on the environmental transport and partitioning of endrin aldehyde could be found in the available literature. Values of the estimated log  $K_{ow}$  for endrin aldehyde vary widely, ranging from 3.1 to 5.6 (see Table 3-2). Based on the lowest estimated log  $K_{ow}$ , the  $K_{oc}$  value for endrin aldehyde can be estimated to be approximately 1,000 (Lyman 1990), indicating a low mobility in soil (Swann et al. 1983). Using the higher estimated values of log  $K_{ow}$  (4.7-5.6), the  $K_{oc}$  value for endrin aldehyde can be estimated to range from 8,500 to 380,000 (Lyman 1990), indicating that this compound will be virtually immobile in most soils (Swann et al. 1983). Because of its low vapor pressure of

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Table 5-1. Bioconcentration Data for Endrin

Species common name scientific name	Exposure type	Duration (days)	BCF <sup>a</sup>	Reference
<u>Freshwater</u>				
Algae				
<i>Microcystis aeruginosa</i>	–	7	200	Vance and Drummond 1969 (cited in EPA 1980a)
Algae				
<i>Anabaena cylindrica</i>	–	7	222	Vance and Drummond 1969 (cited in EPA 1980a)
Algae				
<i>Scenedesmus quadricauda</i>	–	7	156	Vance and Drummond 1969 (cited in EPA 1980a)
Algae				
<i>Oedogonium sp.</i>	–	7	140	Vance and Drummond 1969 (cited in EPA 1980a)
Water flea				
<i>Daphnia magna</i>	S	1	2,600	Metcalf et al. 1973
Mosquito				
<i>Culex pipiens quinquefasciata</i>	S	1	2,100	Metcalf et al. 1973
Stonefly				
<i>Pteronarcys dorsata</i>	F	28	1,000	Anderson and Defoe 1980
Pouch snail				
<i>Physa sp.</i>	S	33	49,000	Metcalf et al. 1973
Mussels				
<i>Mixed species</i>	–	21	3,000	Jarvinen and Tyo 1978
Channel catfish				
<i>Ictalurus punctatus</i>	–	41–55	2,000	Argyle et al. 1973 (cited in EPA 1980a)
Flagfish				
<i>Jordanella floridae</i>	–	65	15,000	Hermanutz 1978
Flagfish				
<i>J. floridae</i>	F	15	7,000	Hermanutz et al. 1985
Fathead minnow				
<i>Pimephales promelas</i>	F	47	10,000	Mount and Putnicki 1966 (cited in EPA 1980a)
Fathead minnow				
<i>P. promelas</i>	–	56–300	7,000	Jarvinen and Tyo 1978
Fathead minnow				
<i>P. promelas</i>	F	2–304	80 <sup>b</sup>	Veith and Kosian 1983
Black bullhead				
<i>Ictalurus melas</i>	F	4	3,700	Anderson and Defoe 1980
Black bullhead				
<i>I. melas</i>	F	7	6,200	Anderson and Defoe 1980

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Table 5-1. Bioconcentration Data for Endrin (continued)

Species common name scientific name	Exposure type	Duration (days)	BCF <sup>a</sup>	Reference
<u>Saltwater</u>				
Grass shrimp <i>Palaemonetes pugio</i>	F	145	1,600	Tyler-Schroeder 1979
American oyster <i>Crassostrea virginica</i>	F	2	1,670	Mason and Rowe 1976
American oyster <i>C. virginica</i>	F	7	2,780	Mason and Rowe 1976
Sheepshead minnow (embryo-juveniles) <i>Cyprinodon variegatus</i>	–	33	4,800	Schimmel et al. 1975 (cited in EPA 1980a)
Sheepshead minnow <i>C. variegatus</i>	–	141–161	6,400	Hansen et al. 1977
Spot <i>Leiostomos xanthurus</i>	–	5–8 mos	1,450	Lowe 1966 (cited in EPA 1980a)

<sup>a</sup>BCF listed is the highest bioconcentration factor (BCF) value reported in the cited reference

<sup>b</sup>Calculated quantitative structure-activity relationship (QSAR) value

F = flow-through exposure system; mos = months; S = static system

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$2.0 \times 10^{-7}$  mm Hg and Henry's Law constant ranging from  $2 \times 10^{-9}$ - $3.7 \times 10^{-8}$  atm-m<sup>3</sup>/mol (see Table 3-2), endrin aldehyde would not be expected to volatilize significantly from soil or water (Eisenreich et al. 1981; Thomas 1990). Any endrin aldehyde in air should exist predominantly in the adsorbed phase (Eisenreich et al. 1981). Atmospheric endrin aldehyde will be transported to soil and surface water via wet and dry deposition of associated particles. In water, adsorption to sediments and bioconcentration are likely to be significant partitioning processes. Based on the lowest estimated value of 3.1 for log  $K_{ow}$  (see Table 3-2), the BCF value for endrin aldehyde can be estimated to be only 86 (Veith et al. 1979), indicating little tendency to bioconcentrate in aquatic organisms. Using the higher estimates of 4.7-5.6 for log  $K_{ow}$  (see Table 3-2), BCF values for endrin aldehyde are estimated to range from 2,000 to 11,000 (Veith et al. 1979), indicating a much higher tendency for bioconcentration.

No studies on the environmental transport or partitioning of endrin ketone could be found in the available literature, and only limited information was found on estimated values of physical and chemical properties. The very low estimated value of  $2.02 \times 10^{-8}$  atm-m<sup>3</sup>/mole for Henry's Law constant for endrin ketone (see Table 3-2) indicates that this compound will not volatilize from water. Based on the estimated log  $K_{ow}$  of 4.99 (see Table 3-2), the BCF value for endrin ketone can be estimated to be 3,500 (Veith et al. 1979), indicating that endrin ketone may be removed from water via bioconcentration in aquatic organisms. Also based on an estimated log  $K_{ow}$  of 4.99, the  $K_{oc}$  value for endrin ketone can be estimated to range from 5,500 to 90,000 (Lyman 1990), indicating that this compound will be virtually immobile in soil and sediments (Swann et al. 1983). However, detection of endrin ketone in groundwater and leachate samples at some NPL sites suggests some limited mobility of endrin ketone in certain soils (HazDat 1996).

### 5.3.2 Transformation and Degradation

#### 5.3.2.1 Air

Field studies on the transformation of endrin in the atmosphere were not located in the available literature. Photochemical isomerization of endrin, primarily to the pentacyclic ketone commonly called delta ketoendrin or endrin ketone, was observed after exposure of thin layers of solid endrin on glass to sunlight (Burton and Pollard 1974). Minor amounts of endrin aldehyde were also formed in this reaction. Results of seasonal studies indicated that this isomerization would proceed with a half-life

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(first-order kinetics) of 5-9 days in intense summer sunlight, with complete conversion to the pentacyclic ketone in 15-19 days. Knoevenagel and Himmelreich (1976) reported that photodegradation of solid endrin in the laboratory proceeded with a half-life (first-order kinetics) of 20-40 hours. In laboratory studies conducted by Zabik et al. (1971) on endrin formulations in hexane and cyclohexane (similar to those commonly used for pesticide applications), endrin was found to undergo photolytic dechlorination when exposed to ultraviolet radiation, yielding a pentachlorinated half-cage ketone as the major product. This degradation product was also detected in environmental samples. Endrin may also be transformed by heat in the atmosphere, yielding primarily the pentacyclic ketone and endrin aldehyde (EPA 19798; Phillips et al. 1962). Endrin may also react with photochemically generated hydroxyl radicals in air, with a predicted half-life (first-order kinetics) ranging from 1.45 hours (Howard 1991) to 1.8 days (SRC 1995a). No information could be found on the products of this reaction. The reaction of endrin with ozone in air is not significant. The predicted first-order rate constant for this reaction is  $3.6 \times 10^{-20}$  cm<sup>3</sup>/molecule-sec, corresponding to a half-life of 320 days (SRC 1995a).

Endrin aldehyde may react with photochemically generated hydroxyl radicals in the atmosphere, with an estimated overall first-order rate constant of  $106 \times 10^{-12}$  cm<sup>3</sup>/molecule-see, which corresponds to a half-life of 3.6 hours, assuming a 24-hour concentration of hydroxyl radicals of  $0.5 \times 10^6$  molecules/cm<sup>3</sup> (SRC 1995a). Endrin ketone may react with photochemically generated hydroxyl radicals in the atmosphere, with an estimated overall first-order rate constant of  $10.8 \times 10^{-12}$  cm<sup>3</sup>/molecule-set, which corresponds to a half-life of 1.5 days, assuming a 24-hour concentration of hydroxyl radicals of  $0.5 \times 10^6$  molecules/cm<sup>3</sup> (SRC 1995a). No other information could be found in the available literature on the transformation and degradation of endrin aldehyde or endrin ketone in air.

**5.3.2.2 Water**

Laboratory studies of the fate of endrin in water samples suggest a significant degree of stability, although there is evidence of varying degrees of biodegradation in some systems. Endrin was among the more stable of 12 insecticides incubated in water collected from the drainage canal of a vegetable-growing site near Toronto, with about 80% of endrin remaining in the natural water after incubation for 16 weeks (Sharom et al. 1980b). There was little indication of chemical degradation of endrin in these studies. Studies in which sealed water samples from the Little Miami River were exposed to

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sunlight and artificial fluorescent light showed no measurable degradation of endrin over an 8-week period (Eichelberger and Lichtenberg 1971). However, microorganisms in fish pond water and algae from a fish pond were able to metabolize endrin (Patil 1972). In the case of the algae, the metabolite was 12-ketoendrin. The rate of metabolism was 35% for the water sample and 24% for the algal culture in one month. Using the static culture procedure, Tabak et al. (1981) found no biodegradation of endrin in domestic waste water samples.

Based on laboratory experiments on solid endrin (Burton and Pollard 1974) and on endrin in organic solvents (Zabik et al. 1971), it is likely that endrin released to surface water will undergo photoisomerization to endrin ketone, with minor amounts of endrin aldehyde also being formed. Under real world conditions, endrin released to surface waters would not be expected to biodegrade or hydrolyze to any significant extent (Eichelberger and Lichtenberg 1971; EPA 19798). Endrin is very resistant to hydrolysis, with an estimated half-life (first-order kinetics) of more than 4 years (EPA 19798). The predominant removal of endrin from water by photodegradation and sorption to suspended particulates or sediments (see Section 5.3.1) is consistent with the observed low incidence of detected endrin in ambient surface waters based on analyses of EPA National Urban Runoff Program (Cole et al. 1984) and STORET (Staples et al. 1985) data as described in Section 5.4.2.

Little information could be found in the available literature on the transformation and degradation of endrin aldehyde in water. Neither hydrolysis nor oxidation (via peroxy radicals or singlet oxygen) are expected to be significant in aquatic systems (EPA 1981a). By analogy to endrin, the hydrolysis half-life (first-order kinetics) of endrin aldehyde in water is probably greater than four years (EPA 1979g). No information could be found on the biodegradation of endrin aldehyde in aquatic systems.

No information could be found in the available literature on the transformation and degradation of endrin ketone in water.

### **5.3.2.3 Sediment and Soil**

Biodegradation does not appear to be a significant degradation process for endrin in soils. The actual measurement of biodegradation of endrin under field conditions on well drained agricultural soil indicate a biodegradation half-disappearance time of approximately 14 years (Nash and Woolson

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1967), suggesting that endrin is resistant to biodegradation in soils under natural conditions. In this study, 41% of the initial endrin applied to an agricultural field was present in the soil after 14 years,

Laboratory studies indicate that endrin can be biodegraded in various soils under various conditions; however, caution should be exercised in extrapolating laboratory results to field conditions. Twenty different isolates of soil organisms belonging to several different species (5 identified, 4 unidentified) were found to biodegrade endrin in the laboratory under aerobic conditions (Patil et al. 1970). The study revealed endrin as one of the more easily biodegradable insecticides, while lindane, for example, was not degraded by any of the 20 isolates. In contrast, Bartha et al. (1967) found no biodegradation of endrin, but they used rather insensitive analytical techniques compensated for by high endrin concentrations (0.25 ppm) that would not occur in normal agricultural practice. Nitrification was enhanced by endrin in this experiment. Endrin was also biodegraded to four unidentified metabolites in laboratory microcosms using flooded rice soils (Gowda and Sethunathan 1976). The most rapid degradation was seen in the saline acid sulfate soil, pokkali, followed by alluvial and laterite soils, where endrin concentrations dropped 10-20-fold in 55 days. Sandy soils were least active and reduced endrin concentration only by about 40% in 55 days. The addition of organic matter, such as rice straw, approximately doubled the rate of biodegradation. Half-disappearance times of endrin in soils ranged from less than 20 days under optimal conditions to about 80 days under less favorable conditions. A degradation half-life (first-order kinetics) of 26-32 weeks was reported for endrin (initial concentration approximately 1.6-2.0 ppm) in a clay soil under controlled, aerobic environmental conditions (30 °C; soil water content 10-33%), with slower degradation observed in soils with the lowest moisture content (Ghadiri et al. 1995). First-order rate equations best described the degradation. Virtually complete anaerobic biodegradation of endrin in laboratory microcosms within 4 days has been reported; however, the researchers caution that under natural conditions redox environments in many soils will not be suitable for anaerobic degradation, and that endrin residues sorbed to soil particles would often be rendered unavailable to bacteria (Maule et al. 1987).

In combination, losses from volatilization, photodegradation (Burton and Pollard 1974; EPA 1985e; Knoevenagel and Himmelreich 1976; Zabik et al. 1971), and heat transformation (primarily to endrin ketone, with minor amounts of endrin aldehyde) (EPA 1979g; Phillips et al. 1962) are likely to account for a rapid decrease in endrin residues on soil or plant surfaces exposed to bright sunlight. Studies have also been conducted indicating significant concentrations of endrin transformation

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products (including endrin ketone, endrin aldehyde, and endrin alcohol) in plants grown in endrintreated soil (Beall et al. 1972; Nash and Harris 1973).

Little information could be found in the available literature on the transformation and degradation of endrin aldehyde in sediment and soil. By analogy to aquatic systems, neither hydrolysis nor oxidation (via peroxy radicals or singlet oxygen) would be expected to be significant transformation processes. No information could be found on the biodegradation of endrin aldehyde in sediment or soil.

No information could be found in the available literature on the transformation and degradation of endrin ketone in sediment and soil.

### 5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to endrin depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Endrin's sensitivity to thermal degradation, however, may sometimes make it difficult to interpret analytical work conducted in the 1960s and 1970s because temperatures used in many types of gas chromatography analytical procedures for organochlorine pesticides at that time have been shown to isomerize endrin into a variety of ketones, aldehydes, alcohols, and other unidentified products (Phillips et al. 1962). In reviewing data on levels monitored or estimated in the environment, it should also be noted that the amount of the chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

#### 5.4.1 Air

Endrin is relatively nonvolatile with a vapor pressure of  $2.0 \times 10^{-7}$  mm Hg (EPA 1981a; Worthing and Walker 1983). Despite its low volatility, initial loss of agriculturally applied endrin through volatilization was found to be comparable to more volatile pesticides (Nash 1983). No recent data on atmospheric concentrations of endrin could be found in the available literature. Endrin was detected in air samples collected at 4 of the 102 NPL sites where endrin has been detected in some environmental medium; however, concentrations were not available (HazDat 1996).



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Limited information was found on atmospheric concentrations of endrin between 1970 and the mid-1980s, prior to cancellation of virtually all uses (Bishop 1984, 1985, 1986; EPA 1993e; USDA 1995) (see Section 4.3). The data were insufficient to identify any trends. The mean and maximum airborne concentrations of endrin in the United States in 1970-71 were reported to be 0.2 ng/m<sup>3</sup> and 19.2 ng/m<sup>3</sup>, respectively (Lee 1977). For that same time period, mean airborne concentrations at suburban sites near Jackson, Mississippi, and Columbia, South Carolina, were reported to be 0.1 ng/m<sup>3</sup> and 0.2 ng/m<sup>3</sup>, respectively (Bidleman 1981; Kutz et al. 1976). Endrin was not detected at Boston, Massachusetts, suburban sites (Bidleman 1981). A survey of airborne contaminants in the Great Lakes area in 1981 did not detect endrin (Eisenreich et al. 1981).

Atmospheric concentrations of endrin in the vicinity of manufacturing facilities were higher than those found in non-source areas of the United States. Eight hundred meters from 2 formulation plants in Arkansas and 275 meters from one formulation plant in Tennessee, mean airborne concentrations of endrin were reported to be 3.3 ng/m<sup>3</sup> and 3.5 ng/m<sup>3</sup>, respectively, during 1970-72 (Lewis and Lee 1976). Endrin was also detected in air in industrial or source-dominated regions of the Mississippi Delta in 1972-74, and in Tennessee in 1971 (EPA 1985e).

Endrin may also be found in atmospheric precipitation. In an analysis of pesticides in rainfall from four stations in Canada in 1984, detectable concentrations of endrin were found at each site (Strachan 1988). There was a noticeable pattern of decline in detections within the summer season (May-August). In more recent studies in the Great Lakes area, endrin was found in 5% of 450 wet deposition (rain/snow) samples collected between 1986 and 1991, at volume weighted mean concentrations ranging from 0.02 to 0.98 ng/L (ppt) (Chan et al. 1994).

No information was found in the available literature on concentrations of endrin aldehyde or endrin ketone in ambient outdoor air or in indoor air. In addition, no information was available on occupational exposures to these chemicals.

### 5.4.2 Water

Very little recent information on concentrations of endrin in water could be found in the available literature. Unlike DDT, chlordane, aldrin, dieldrin, and a variety of other chlorinated pesticides, endrin was never used extensively in urban areas. This is reflected in the results from EPA's Nationwide

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Urban Runoff Program, which showed no detections in 86 high-flow water samples from 51 urbanized watersheds from 19 cities (Cole et al. 1984). Analysis of EPA STORET monitoring information from ambient surface water showed a significant percentage of detections for endrin (32% of 8,789 samples), but most were near the detection limits, with a national median concentration of 0.001 ppb (Staples et al. 1985). A similar analysis of STORET data for endrin aldehyde showed that this compound was not found in 770 samples of ambient surface water. More recently, endrin was not detected (detection limit 49 ng/L [0.045 ppb]) in surface water from the Yakima River Basin, Washington (Foster et al. 1993). However, in 1991-92, endrin was detected in first flush (first 20 minutes) stormwater runoff samples at 4 of 6 sites in Louisville, Kentucky, at levels that exceeded U.S. Federal criteria (0.003 ( $\mu\text{g}/\text{L}$ , [ppb]) (Marsh 1993). Maximum, minimum, and mean concentrations at the 4 sites ranged from 0.03 to 0.05, 0.02 to 0.04, and 0.03 to 0.04 (ppb), respectively. Endrin was not detected (detection limit not specified) in 3-hour composite samples of stormwater runoff from any of the 6 sites. Endrin has been detected in surface water samples collected at 10 of the 102 NPL sites where it was detected in some environmental media (HazDat 1996).

Recent studies using semipermeable membrane devices to determine bioavailable (dissolved) organochlorine pesticide residues in streams receiving irrigation rainwater from agricultural activity in the Luger Altus Watershed in southwestern Oklahoma indicate that endrin may still be present in this aquatic ecosystem several years after discontinuation of its use (Petty et al. 1995). Calculated concentrations of bioavailable endrin at 6 sampling sites ranged from not detected (detection limit not specified) to 110 ( $\mu\text{g}/\text{L}$  (ppb). Concentrations were higher in spring than in summer. There is an uncertainty in these estimates because they were derived from the dialysate data using models and preliminary data on uptake kinetics.

Endrin is rarely detected in drinking water and any trace amounts of endrin that might be encountered in raw drinking water supplies will likely be removed in the treatment systems used by most communities. In 1966 and 1967, when the use of endrin was not restricted, endrin was detected in 5 of 67 raw water samples from the Mississippi and Missouri Rivers (Schafer et al. 1969). At a later time when endrin use was substantially restricted, an Iowa study of 33 community water supplies using surface water found no detectable concentrations of endrin in the distribution systems (Wnuk et al. 1987). In an extensive water quality monitoring program conducted by the California Department of Health Services, endrin was detected (detection limit not specified) in only 2 of 5,109 public drinking water sources sampled from 1984 to 1992, at mean and maximum concentrations of 0.06 and

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0.10 ppb, respectively (Storm 1994). Concentrations did not exceed the Maximum Concentration Level (MCL) of 0.2 ppb. In another recent study, endrin was not detected (detection limit not specified) in 32 samples each of raw water and highly treated reclaimed waste water undergoing evaluation as a possible supplement to raw water sources in San Diego, California (De Peyster et al. 1993).

Detections of endrin in groundwater are also rare except from wells near hazardous waste sites. The EPA Pesticides in Groundwater Data Base (EPA 1989) contains groundwater data collected with good quality assurance/quality control (QA/QC) provisions from areas with significant agricultural land uses as well as from urban areas. Analysis of these data indicated there were only two wells with detectable levels of endrin within the entire United States. A detection occurred in a well in California (concentration not reported) where point source problems or spills were deemed the likely sources. Endrin contamination found in an Illinois well at an average concentration of 0.02 ppb was considered likely to have resulted from ordinary agricultural uses. In a groundwater contamination study of California's 58 counties, in which over 50 pesticides were evaluated from both point and nonpoint sources, endrin was detected in only one sample (Cohen 1986). In a more recent study, endrin was detected at 0.9% of 178 CERCLA sites and 1.3% of 156 RCRA sites sampled; however, endrin concentrations were not reported (Plumb 1987). Endrin was also found in groundwater samples collected at 37 of the 102 NPL and in leachate samples collected at 2 of the 102 NPL sites where endrin has been detected in some environmental media; however, concentrations were not reported (HazDat 1996).

No information was found in the available literature on levels of endrin aldehyde or endrin ketone in surface or groundwater. Endrin ketone has been detected in surface water samples collected at 5 of the 37 NPL sites, in groundwater samples collected at 16 of the 37 NPL sites, and in leachate samples collected at 2 of the 37 NPL sites where endrin ketone has been detected in some environmental medium; however, concentrations were not reported (HazDat 1996).

### 5.4.3 Sediment and Soil

Very little recent information on levels of endrin in soils was found in the available literature. From the available data it appears that, in general, endrin was found infrequently and at relatively low levels in both urban and cropland soils in the United States. Endrin was detected in only 10 of

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1,483 cropland soil samples in 1972 at concentrations up to 2.13 ppm (detection limit of 0.01 ppm) (Carey et al. 1979). These studies were part of the National Soils Monitoring Program carried out by EPA and the USDA under the National Pesticide Monitoring Program, which covered a total of 1,533 sampling sites in 37 states. Endrin detections were documented in the following states: Alabama, Arkansas, Georgia, Illinois, Louisiana, Nebraska, New York, North Carolina, and South Dakota, as well as at sites from one or more of the mid-Atlantic states of Delaware, Maryland, and New Jersey. Endrin was also detected at a level of 0.017 ppm at a single site in California in a study that targeted rice-growing cropland soils in Arkansas, California, Louisiana, Mississippi, and Texas (Carey et al. 1980). Endrin was not detected in urban soils from 13 of 14 U.S. cities included in a 1970 study of pesticide residues in urban soils (25-30 soil sampling sites were used for each of the urban areas) (Carey et al. 1976). The only detection was at a single site near Memphis, Tennessee, where the Velsicol Chemical Company (which produced endrin at that time) is located. The reported concentration for this site was 0.07 ppm; the mean concentration for all 28 Memphis sites was <0.01 ppm.

Relatively little literature was identified concerning the analysis of endrin in aquatic sediments. The available data indicate that, historically, sediment concentrations of endrin have been very low. In a recent study of sediment contaminants in Casco Bay, Maine, endrin was found at concentrations near or below the method detection limit (<0.25 ppb) (Kennicutt et al. 1994). In the National Surface Water Monitoring Program conducted from 1976 to 1980, endrin was detected in 1.3% of the sediment samples analyzed (detection limit not reported) with a maximum concentration of 2.9 ppb (Carey and Kutz 1985). An analysis of EPA STORET data indicated endrin was detected in 24% of the 1,802 sediment records listing endrin as a parameter code. The median endrin concentration for all records was 0.001 ppb (Staples et al. 1985). A similar analysis of STORET data indicated that endrin aldehyde was not found in any of 251 samples of sediment (Staples et al. 1985). In a study by Ford and Hill (1991) to evaluate organochlorine pesticide residues in sediments and aquatic animals in the vicinity of the Yazoo National Wildlife Refuge in the Mississippi Delta, a region that has experienced very high usage of pesticide agents, detectable levels of endrin were not found in sediments (detection limit 0.01 ppm [10 ppb]). Similarly, endrin was not detected in sediment or pore water samples (detection limits 0.49 and 0.01 ppm [490 and 10 ppb], respectively) from 18 mosquito control impoundments in St. Lucie County, Florida, where organochlorine pesticides had been heavily used through the early 1960s (Parkinson et al. 1993).

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There is a potential for endrin to be present in soils and sediments at hazardous waste sites. Endrin has been detected in soil samples collected at 44 of the 102 NPL sites and in sediment samples collected at 19 of the 102 NPL sites where endrin has been detected in some environmental medium; however, concentrations were not reported (HazDat 1996). Endrin was not detected (detection limit 0.01 ppm [10 ppb] wet weight), however, in soils derived from dredged materials at 9 confined disposal facilities bordering the Great Lakes (Beyer and Stafford 1993).

No information was found in the available literature on levels of endrin aldehyde in soil or endrin ketone in sediment or soil. Endrin ketone has been detected in soil samples collected at 23 of the 37 NPL sites and in sediment samples collected at 5 of the 37 NPL sites where endrin ketone has been detected in some environmental medium; however, concentrations were not reported (HazDat 1996).

### 5.4.4 Other Environmental Media

Endrin has been found in many foods, but current levels appear to be very low and not of concern for human health. The FDA has concluded that endrin is no longer present in the environment to the extent that it may be contaminating food or feed at levels of regulatory concern (USDA 1995). An FDA survey of pesticide residues in samples of domestic and imported food and feed commodities from Fiscal Year (FY) 1982 to 1986 lists endrin levels for specific food items up to 0.50 ppm (500 ppb) (Hundley et al. 1988). This study was conducted by surveillance sampling with follow-up compliance sampling for sources of foodstuffs where the concentrations in surveillance samples violated EPA tolerance levels. In surveillance sampling, endrin was detected in 0.05% (3 of 6,391 samples) and 1.5% (183 of 12,044 samples) of domestic and imported foods, respectively. The incidence of violative surveillance samples (endrin residues  $\geq 0.05$  ppm [50 ppb]) was higher for imported foods (0.1%; 12 violations) than for food items from domestic sources (0.02%; 1 violation). In follow-up compliance monitoring of 1,239 samples of imported foods, endrin was found in 11 samples (0.9%); 2 of these samples (0.2%) were violative. In imported foods, endrin was detected in mung beans, cucumbers, pickling cucumbers, cantaloupe, acorn squash, cabocha squash, Italian squash, summer squash, and yellow squash (Hundley et al. 1988). No follow-up compliance monitoring of domestic samples for endrin residues was performed.

In a more recent study of pesticide residues in food conducted in 10 states between 1988 and 1989, endrin was not detected in any of the 13,980 samples analyzed in 1988. In 1989, the detection

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frequencies for endrin and endrin ketone were 0.084% and 0.007%, respectively, for the 13,085 samples analyzed (Minyard and Roberts 1991). In a Canadian study, reported concentrations of endrin in composite samples of fresh root vegetables, fruit, leafy and other above-ground vegetables, and cows' milk ranged from 0.27 to 0.37 ppb; endrin was not detected in composite samples of fresh meat and eggs (detection limit 0.01 ppb) (Davies 1988). Endrin was detected each year in regulatory monitoring of domestic and imported foods conducted by the FDA from 1989 to 1994 as part of its Pesticide Residue Monitoring Program (FDA 1990, 1991, 1992, 1993, 1994, 1995). Concentrations were not reported; however, <1% of the surveillance samples had any pesticide residue levels that were above established tolerances. Endrin was also detected in the FDA Total Diet Studies in 1987, 1988, 1989, and 1991, but not in 1990 (FDA 1988, 1989, 1990, 1991, 1992). Reports of 1992-94 FDA Total Diet Studies did not indicate whether endrin was detected in those years (FDA 1993, 1994, 1995). In the years in which endrin was detected in the FDA Total Diet Studies, it was not among the most frequently detected pesticides. Concentrations of endrin found in the FDA Total Diet studies were not reported. However, in an overall summary for the 5-year period 1986-91, average dietary intakes of endrin for 8 age/sex groups (6-11-month-old infants, 2-year-old children, 14-16-year-old males and females, 25-30-year-old males and females, and 60-65-year-old males and females) were all estimated to be <0.0001 ( $\mu\text{g}/\text{kg}$  body weight per day, less than 0.03% of the EPA RfD of 0.3 ( $\mu\text{g}/\text{kg}$  body weight per day (FDA 1993). A food basket survey patterned after the FDA approach that was conducted in San Antonio, Texas did not find detectable concentrations of endrin (detection limit 0.050 ppm [50 ppb]) in 6,970 produce items (Schattenberg and Hsu 1992).

Overall, in 234 ready-to-eat foods tested 37 times each as part of the FDA Total Diet Studies from 1982 to 1991, endrin was found only 26 times at an average concentration of 0.0027 ( $\mu\text{g}/\text{g}$  (2.7 ppb) in 9 different foods: broccoli, cantaloupe, collards, cucumbers, onion rings, dill pickles, pumpkin pie, summer squash, and winter squash (KAN-DO Office and Pesticides Team 1995). Concentrations ranged from 0.0011 ( $\mu\text{g}/\text{g}$  (1.1 ppb) (broccoli) to 0.0041  $\mu\text{g}/\text{g}$  (4.1 ppb) (summer squash). In a summary of 1985-91 FDA pesticide residue findings, endrin was not reported in more than 10,000 surveillance samples of domestic and imported foods that may be eaten by infants or children, or in more than 4,000 analyses of Total Diet Study foods eaten by infants and children (Yess et al. 1993).

Other studies further indicate that the occurrence of endrin in the US. food supply is very low. In a 1990-91 FDA survey of pesticide residues in milk representing most of the U.S. supply consumed in

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metropolitan areas, endrin was detected at trace levels (0.0005-0.001 ppm [0.5-1.0 ppb]) in only 2 of 806 composite samples (one sample each from Atlanta, Georgia and Dover, Delaware) (Trotter and Dickerson 1993). In another statistically based FDA study in 1992-93, endrin was not found as a violative residue in any of 710 domestic or 949 imported pear samples (Roy et al. 1995). Endrin was not reported among the pesticides detected in a 1994 FDA survey of pesticide levels in 160 samples of catfish, crayfish, shrimp, trout, salmon, oysters, and various other species from important aquaculture areas of the United States (FDA 1995). Comparable results were found in similar studies conducted by the FDA in 1990-93 (FDA 1995).

Because of the persistence of endrin in the environment and its potential to bioconcentrate significantly in aquatic organisms, there has been continued concern over the levels of endrin in fish and shellfish. This concern, however, appears to be limited primarily to specific sites where endrin was used heavily in agriculture or was discharged by industrial plants. In 1963, at the height of agricultural endrin use, endrin levels in catfish poisoned by endrin exceeded 4 ppm (4,000 ppb) during a fish kill (Mount and Putnicki 1966). Endrin was detected in 2 species of commercial *Penaeus* shrimp collected at 21 of 31 stations in the Calcasieu River Estuary in Louisiana, a Gulf Coast estuary receiving both industrial discharges, and urban and agricultural runoff (Murray and Beck 1990). The maximum, mean, and median concentrations of endrin reported were 9.47, 1.07, and 0.25 ppm (9,470, 1,070, and 250 ppb), respectively. Several more recent national studies, however, indicate that contaminated fish or shellfish currently are not a likely source of potentially high human exposure to endrin. In the National Contaminant Biomonitoring Program, maximum endrin concentrations in whole fish from around the United States for the periods 1976-77, 1978-79, 1980-81, and 1984 were 0.40, 0.11, 0.30, and 0.22 ppm (400, 110, 300, and 220 ppb), respectively. Corresponding geometric mean concentrations were  $\leq 0.01$  ppm (10 ppb) (Schmitt et al. 1985, 1990). The percentage of stations where detectable endrin residues were present also showed a relatively steady decline from 47.2% in 1976-77 to 28% in 1984. The maximum concentration of 0.22 ppm (220 ppb) in 1984 was recorded near Memphis in the vicinity of the Velsicol Chemical Company. In portions of the Mississippi Delta within or bordering the Yazoo National Wildlife Refuge, endrin was found at the 0.01 ppm (10 ppb) detection limit in whole-body tissue samples from such rough fish as carp, smallmouth buffalo, bowfin, and spotted gar collected in 1988 (Ford and Hill 1991). In the 1986 National Study of Chemical Residues in Fish conducted by the EPA, endrin was detected in fish tissue samples at 11% of the 362 sites surveyed. The maximum, mean, and median concentrations of endrin reported were

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0.162 ppm, 0.002 ppm, and not detected (<0.0025 ppm) (162, 2, and <2.5 ppb), respectively (EPA 1992b).

Endrin concentrations also have been monitored in several studies in the Great Lakes region. Endrin was detected in 8 fish species from 3 Great Lakes-influenced rivers in Michigan at average concentrations ranging from not detected (detection limit not specified) to 8.03 ppb wet weight (Giesy et al. 1994). Average concentrations exceeded 1.5 ppb for samples from only 2 of 23 species/site combinations and were less than 0.5 ppb for samples from 17 of 23 species/site combinations. Endrin was detected (detection limit 0.02 ppm [20 ppb] wet weight) in 5 of 10 samples of lake trout (mean concentration  $0.03 \pm 0.01$  ppm [ $30 \pm 10$  ppb]) collected in Lake Michigan in 1982 (Miller 1993). It was not detected in 10 samples of lake trout collected in Lake Superior or in 18 samples of chinook salmon collected in Lake Michigan. Endrin was not detected (detection limit 2 ng/g [ppb] wet weight) in 16 skinless fillets of both rainbow trout (*Oncorhynchus mykiss*) and black bullheads (*Ameiurus melas*) cultivated for 6 and 3.5 months, respectively, in Lake Ontario waters (Buttner et al. 1995). Endrin also was not detected (detection limit not specified) in samples of whole Zebra mussels (*Dreissena polymorpha*) from populations infesting two power generating stations in Lake Erie (Doherty et al. 1993).

Endrin has been detected in several marine fish species in regional or state monitoring studies. From 1990 to 1993, endrin was found in 40 of 47 whole or fillet samples of red drum (*Sciaenops ocellatus*) at 2 of 4 sites along the South Carolina coast, at mean concentrations of  $5.61 \pm 8.94$  and  $0.65 \pm 3.67$  ppb wet weight (Mathews 1994). In this same study, endrin was found in 33 of 74 flounder (*Pamlichthys lethostigma*) samples, and in 19 of 58 seatrout (*Cynoscion nebulosus*) samples at only one coastal site, at mean concentrations of  $0.14 \pm 0.81$  and  $2.68 \pm 11.13$  ppb, respectively. Endrin was detected in all of 10 liver tissue samples from cod (*Gadus morhua*) in the Northwest Atlantic at a mean concentration of 9 ppb (range, 5-19 ppb), but not in muscle or ovary samples (Hellou et al. 1993).

There may be a potential for contamination of fish and wildlife in the vicinity of hazardous waste sites. Endrin was detected in fish samples collected at 4 of the 102 NPL sites and in game animal samples collected at one of the 102 NPL sites where endrin has been detected in some environmental medium; however, levels of contamination were not reported (HazDat 1996).



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Endrin was not detected (detection limit 0.005 ppm, wet weight) in liver samples of 118 mink from declining populations in coastal plain regions of Georgia, North Carolina, and South Carolina (Osowski et al. 1995). These results were not significantly different from levels found in nondeclining control populations (n= 46, median concentration 0.012 ppm, maximum concentration 0.49 ppm) from the Piedmont areas of these states. Endrin also was not detected (detection limit 0.01 ppm wet weight) in earthworms from 9 confined disposal facilities bordering the Great Lakes (Beyer and Stafford 1993).

No information was found on concentrations of endrin aldehyde or endrin ketone in other environmental media.

### 5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Endrin is no longer registered for use in the United States. Consequently, the current potential for exposure of the general population to endrin appears to be very limited and will likely continue to diminish even more over time. Members of the general population may be exposed to very low levels of endrin through ingestion of contaminated foodstuffs, particularly those that are imported from areas where endrin is still being used. However, the FDA has concluded that endrin is no longer present in the environment to the extent that it may be contaminating food or feed at levels of regulatory concern (USDA 1995). Several studies indicate that human exposures are far below the levels of concern for human health. Based on results of FDA Total Diet Studies conducted from 1978 to 1982, estimated average dietary intakes were <0.001 ( $\mu\text{g}/\text{kg}$  (ppb) body weight/day for infants and toddlers for all 5 years (Gartrell et al. 1986). However, actual intakes must have been lower than these estimates because the reported average dietary intakes were based on the mean concentration of the positive samples only. A report summarizing the FDA Total Diet Studies from April 1982 to April 1984, indicated an estimated daily intake for 6-11-month-old infants of 0.0003 ( $\mu\text{g}/\text{kg}$  (ppb) body weight/day for that period, with estimated daily intakes for 14-16-year-old males and 60-65-year-old females essentially zero (Gunderson 1988). Endrin intakes, in ( $\mu\text{g}/\text{kg}$  (ppb) body weight/day, estimated from the Total Diet Study analyses, were <0.0001, <0.0001, and 0.0001 in FY 1989 for 6-11-month-old infants, 14-16-year-old males, and 60-65-year-old females, respectively (FDA 1990), and <0.0001 in FY 1991 for all age categories (FDA 1992). Estimated endrin intakes were not reported for FY 1990 (FDA 1991). In an overall summary of FDA Total Diet Studies for the 5-year period 1986-91, average dietary intakes of endrin for 8 age/sex groups (6-11-month-old infants, 2-year-old children,

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14-16-year-old males and females, 25-30-year-old males and females, and 60-65-year-old males and females) were all estimated to be  $<0.0001 \mu\text{g}/\text{kg}$  (ppb) body weight per day, less than 0.03% of the EPA oral RfD of  $0.3 \mu\text{g}/\text{kg}$  (ppb) body weight per day (FDA 1993). In Canada, where endrin was registered for use from 1954 to 1990, a dietary intake study estimated the adult annual intake of endrin at approximately  $32 \text{ g}$  ( $0.001 \mu\text{g}/\text{kg}$  [ppb] body weight/day) (Davies 1988).

Although endrin bioaccumulates significantly in aquatic organisms (ASTER 1995; EPA 1980a; Metcalf et al. 1973), recent studies indicate that in the United States endrin levels in fish and shellfish are not of concern for human health (EPA 1992a; Ford and Hill 1991; Murray and Beck 1990; Schmitt et al. 1985, 1990). Dietary exposures to endrin from domestic fish were estimated from 1984 to 1988 FDA surveillance data to be  $1.7 \times 10^{-5} \mu\text{g}/\text{kg}$  (ppb) body weight/day (Ahmed et al. 1993). At present, there are no fish consumption advisories for endrin in effect in the United States (EPA 1995b).

The most recent National Human Adipose Tissue Survey did not detect endrin in adipose tissues from the general U.S. population (Stanley 1986). Endrin also was not detected in adipose breast tissue from breast cancer patients ( $n=5$ ) or controls ( $n=5$ ) in the United States (Djordjevic et al. 1994). A 1984 study based on autopsied adipose tissue from 141 cadavers from six Canadian Great Lakes municipalities showed no detectable concentrations of endrin (detection limit  $2.4 \text{ ppb}$ ) (Williams et al. 1988). In a 1990-91 survey, only very low levels of endrin (average concentration  $3.27 \text{ ng/g}$  (ppb); range  $0.23\text{-}8.56 \text{ ng/g}$  [ppb] lipid) were found in adipose tissue samples from 3 of 41 residents of British Columbia, Canada, where endrin was registered for use from 1954 to 1990 (Teshke et al. 1993).

Endrin has been detected in the milk of lactating women living outside the United States; however, no data from the United States could be located. Data from other countries indicate that there is some correlation between the levels of endrin used in or transported to an area and concentrations found in breast milk. Endrin was not detected in breast milk samples from a remote area of Papua, New Guinea (Spicer and Kereu 1993). In a recent investigation of Inuit exposure to organochlorine pesticides through the aquatic food chain in arctic Quebec, endrin was detected in only 1 of 107 breast milk samples from Inuit women, at a concentration of  $<8 \text{ ng/g}$  (ppb) in milk fat, and in none of 50 samples from southern Quebec Caucasian women (Dewailly et al. 1993). In France, where endrin has not been used for over 20 years, endrin was detected in 8 of 20 human milk samples collected 20-90 days after parturition. Concentrations ranged from  $0.02$  to  $0.84 \text{ ppm}$  ( $20\text{-}840 \text{ ppb}$ ) in milk fat,

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with a mean concentration of 0.06 ppm (60 ppb) (Bordet et al. 1993). Higher levels of endrin were found in human milk in a study conducted in Jordan, where endrin has been widely used over the past 40 years (Alawi et al. 1992). In this study, endrin was detected in samples from 3 of 15 donors at concentrations ranging from 0.26 to 6.24 ppm (260-6,240 ppb) in milk fat. The median and maximum daily intakes of endrin for breast-fed infants were estimated to be 1.55 and 12.70 mg/kg (ppm) (1,550 and 12,700 ppb) body weight, respectively. The relevance of these findings to the U.S. population is unclear.

Although all uses of endrin in the United States were canceled by 1991 (Bishop 1984, 1985, 1986; EPA 1993e; USDA 1995), occupational exposures to endrin, endrin aldehyde, and endrin ketone may occur among workers involved in the handling and treatment of materials at hazardous waste sites, and among agricultural workers at sites formerly treated with endrin. No information was found in the available literature on current occupational exposures. In the past, exposures of agricultural workers were significant. Seasonal agricultural workers dusting potatoes with 1% endrin dust were calculated to be exposed to a dermal dose of 2.0 mg/kg (ppm) body weight/day and an inhalation dose of 0.04 mg/kg (ppm) body weight/day at a time when agricultural use of endrin was near its peak (Wolfe et al. 1963).

Occupational exposure to endrin was not evaluated during the National Occupational Exposure Survey (NOES) conducted from 1981 to 1983 or its predecessor, the National Occupational Hazard Survey (NOHS) conducted from 1972 to 1974. The surveys conducted by NIOSH were designed to provide data necessary to describe potential exposure agents and profile health and safety programs in United States workplaces. According to OSHA (1974), the g-hour TWA permissible exposure level (PEL) for endrin is 0.1 mg/m<sup>3</sup>. NIOSH (1992) advises that the recommended exposure limit for occupational exposure to endrin not exceed 0.1 mg/m<sup>3</sup> for a 10-hour TWA workday. In addition, the American Conference of Government Industrial Hygienists (ACGIH) recommended threshold limit value (TLV-TWA) for occupational exposure is 0.1 mg/m<sup>3</sup> (ACGIH 1988).

No information could be found in the available literature on general population or occupational exposures to endrin aldehyde or endrin ketone.

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### 5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Endrin has not been registered for use in the United States since voluntary cancellation of its final use as a toxicant on bird perches in 1991 (USDA 1995). All other uses of endrin were voluntarily canceled by 1986 (Bishop 1984, 1985, 1986; EPA 1993e; USDA 1995). Therefore, there are currently no population groups exposed to high levels of endrin associated with its application as a pesticide agent. Populations exposed to higher than background concentrations of endrin, endrin aldehyde, or endrin ketone include those living near hazardous waste sites where these compounds are present. Skin contact with or ingestion of endrin-contaminated soil may be an important source of exposure for children living near such hazardous waste sites. In addition, groundwater may be a source of exposure to endrin for adults and children if they consume drinking water from contaminated wells.

### 5.7 ADEQUACY OF THE DATABASE

Section 104(I)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of endrin is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of endrin.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

#### 5.7.1 Identification of Data Needs

**Physical and Chemical Properties.** The physical and chemical properties of endrin have been sufficiently documented to permit estimation of its environmental fate (ACGIH 1986; EPA 1981a, 1984a; HSDB 1995; Verschuere 1983). More complete information on the physical and chemical properties of endrin aldehyde and endrin ketone would be useful.

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**Production, Import/Export, Use, Release, and Disposal.** Endrin is no longer registered for use and is not likely to be imported into the United States (Bishop 1984, 1985, 1986; EPA 1993e; HSDB 1995; USDA 1995). Consequently, the risk of human exposure to endrin (and to endrin aldehyde and endrin ketone, which occur as impurities or transformation products of endrin) from these activities is expected to be minimal. However, recent information suggests that several organochlorine pesticides that have been banned from use or have been voluntarily cancelled in the United States are still being manufactured in large quantities for export abroad (FASE 1996). Unfortunately, only 25% of the pesticides exported from 1992 to 1994 could be definitively identified (FASE 1996). Information as to whether endrin is currently being produced and the export volumes for endrin are needed to evaluate existing routes of exposure for the general population and occupationally exposed individuals.

Endrin and endrin aldehyde are listed as hazardous wastes and disposal of wastes is controlled by a number of federal regulations. Past disposal methods have included landfills (EPA 1987c). Chemical treatment (reductive dechlorination) and incineration are possible disposal methods (HSDB 1995; IRPTC 1985). Existing information on disposal appears adequate. No information was found on disposal of endrin ketone; however, because endrin is no longer used in the United States, current levels of endrin ketone in wastes should be minimal and additional information on disposal is not needed.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxic Release Inventory (TRI), which contains this information for 1993, became available in 1995. This database will be updated yearly and should provide a list of industrial production facilities and emissions. No information was available from the Toxic Release Inventory (TRI) on production because endrin, endrin aldehyde, and endrin ketone are not among the chemicals that facilities are required to report (EPA 1995a).

**Environmental Fate.** Endrin released to the environment partitions to several environmental compartments; air (Chan et al. 1994; Eisenreich et al. 1981; Nash 1983), soil and sediment (Kenaga 1980; Sharom et al. 1980a; Swann et al. 1983), groundwater (Cohen 1986; EPA 1989; HazDat 1996) and biological organisms (ASTER 1995; EPA 1980a; Metcalf et al., 1973; Leblanc 1995). If released to soils, some endrin partitions to the atmosphere via volatilization from soil surfaces. Once in the

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atmosphere, endrin is associated primarily with particulate matter based on its low vapor pressure and high  $K_{oc}$  (Kenaga 1980). Small amounts of endrin in the atmosphere may also exist in the vapor phase (Eisenreich et al. 1981). In addition to volatilization, endrin may be lost via photodegradation and heat transformation from soil and plant surfaces exposed to bright sunlight (Burton and Pollard 1974; EPA 1979g; Knoevenagel and Himmelreich 1976; Phillips et al. 1962; Zabik et al. 1971). The remainder is adsorbed strongly to soil where it may persist for extended periods (half-life of months to years), depending on soil conditions (Nash and Woolson 1967). Leaching of endrin into groundwater is not expected to occur very rapidly under most circumstances, due to the compound's high sorption characteristics (Kenaga 1980; Swann et al. 1983).

Endrin released to water will adsorb to sediments or bioaccumulate in fish and other aquatic organisms. Both bioaccumulation and biomagnification of endrin were reported to occur in an aquatic laboratory microcosm system (Metcalf et al. 1973). In terrestrial ecosystems, endrin transformation products (endrin ketone, endrin aldehyde, and endrin alcohol) have been measured in plants grown on endrin-treated soil (Beall et al. 1972; Nash and Harris 1973).

Information on biodegradation of endrin in soil under aerobic conditions exists, but degradation products are not identified (Nash and Woolson 1967; Patil et al. 1970). Anaerobic biodegradation, which may occur in river bottoms and in Superfund sites, has been studied in the laboratory, but not under natural conditions (Gowda and Sethunathan 1976; Maule et al. 1987). Further information on these processes, including identification of degradation products, would be useful in determining potential mechanisms and the potential for contamination of groundwater by endrin released from soils.

No experimental data could be found in the available literature on the environmental fate of endrin aldehyde or endrin ketone, which occur as impurities in or degradation products of endrin. Estimated physical and chemical constants (see Table 3-2) allow some prediction of fate and transport processes for these compounds. However, additional experimental data on the physical and chemical properties of endrin aldehyde and endrin ketone would be useful in providing a clearer picture of their environmental fate.

**Bioavailability from Environmental Media.** Absorption of endrin following inhalation has been shown to occur in laboratory animals (Treon et al. 1955) and endrin can also be absorbed by humans

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following inhalation of contaminated air (Hoogendam et al. 1965). Since endrin has a low volatility, inhalation is probably not a major concern except for potential inhalation of contaminated dust at hazardous waste sites.

Endrin has also been shown to be absorbed after ingestion by humans (Coble et al. 1967; Curley et al. 1970; Kintz et al. 1992; Rowley et al. 1987; Runhaar et al. 1985; Waller et al. 1992; Weeks 1967); however, no studies were located on the rate or extent of absorption that occurs in orally exposed humans or animals. Exposure to endrin through ingestion of contaminated drinking water is not expected to be an important source of concern because the compound has only rarely been detected in drinking water (Schafer et al. 1969; Wnuk et al. 1987). Since endrin is tightly bound to soil particles, ingestion of endrin-contaminated soil, particularly by children, may be an important route of exposure near hazardous waste disposal sites that contain endrin.

Little information was available regarding the absorption of endrin following dermal exposure. Agricultural worker exposure studies demonstrated that dermal exposure was significantly greater than inhalation exposure (Wolfe et al. 1963). Dermal exposure of rats and rabbits to endrin indicates that percutaneous absorption of endrin occurs (Gaines 1960; Treon et al. 1955). Information regarding the bioavailability of endrin from both ingestion of soil-bound endrin and dermal contact with endrin-contaminated soils would be helpful, particularly for population living near hazardous waste sites.

No information could be found in the available literature on the bioavailability of endrin aldehyde or endrin ketone. This information would be useful for assessing the potential for exposure to these compounds from various environmental media, particularly in the vicinity of hazardous waste sites where endrin ketone has been found in surface water, groundwater, leachate, soil, and sediment (HazDat 1996).

**Food Chain Bioaccumulation.** Endrin has been shown to bioaccumulate significantly in a variety of aquatic organisms (Argyle et al. 1973; ASTER 1995; Hanson et al. 1977; Jarvinen and Tyo 1978; Lowe 1966; Mason and Rowe 1976; Metcalf et al. 1973; Mount and Putnicki 1966; Schimmel et al. 1975; Tyler-Schroeder 1979; Vance and Drummond 1969). The results of an aquatic ecosystem study suggest that biomagnification of endrin is relatively low compared to other organochlorine pesticides (Metcalf et al. 1973). Data on bioaccumulation and bioconcentration of endrin generally appear to be adequate, particularly since endrin has not been used in the United States since the

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mid-1980s. Information on its bioconcentration by additional snail species would be useful as the pouch snail exhibited the highest BCF value and may serve as an environmental indicator of endrin contamination.

No experimental information could be found in the available literature on bioconcentration or bioaccumulation of endrin aldehyde or endrin ketone. Estimated BCFs indicate some potential for bioaccumulation for both compounds. No information was found on concentrations of either of these compounds in aquatic systems, but it would be expected that levels would be nondetectable or very low, and that they would continue to decline. Therefore, additional information is not needed at this time.

**Exposure Levels in Environmental Media.** Endrin has been reported to occur at very low levels in food (Davies 1988; FDA 1988, 1989, 1990, 1991, 1992, 1993, 1994, 1995; KAN-DO Office and Pesticides Team 1995; Minyard and Roberts 1991; Roy et al. 1995; Schattenburg and Hsu 1992; Trotter and Dickerson 1993; Yess et al. 1993) and air (Bidleman 1981; Kutz et al. 1976; Nash 1983). It has only rarely been detected in a number of national and regional surveys of drinking water supplies (Schafer et al. 1969; Wnuk et al. 1987). Because endrin is no longer commercially used in the United States, future levels of endrin, endrin aldehyde, and endrin ketone in environmental media are expected to be low. There are possibilities of exposure from foodstuffs imported from countries that still use endrin (Hundley et al. 1988). There may also be some localized risks from exposures near waste disposal sites or from groundwater contaminated with endrin (Cohen 1986; EPA 1989; HazDat 1996; Plumb 1987). Additional data on environmental concentrations of endrin, endrin aldehyde, and endrin ketone from these possible sources of exposure would be useful.

Reliable monitoring data for the levels of endrin, endrin aldehyde, and endrin ketone in contaminated media at hazardous waste sites are needed so that the information obtained on levels of these substances in the environment can be used in combination with their known body burdens to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

**Exposure Levels in Humans.** Metabolism of endrin in humans is relatively rapid compared with other organochlorine pesticides. Thus, levels in human blood and tissue may not be reliable estimates of exposure except after very high occupational exposures or acute poisonings (Runhaar et al. 1985).



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Endrin was not found in adipose tissue samples of the general U.S. population (Stanley 1986), or in adipose breast tissue from breast cancer patients in the United States (Djordjevic et al. 1994). Endrin has been detected in the milk of lactating women (Alawi et al. 1992; Bordet et al. 1993; Dewailly et al. 1993), but no data from the United States could be located. Data on the concentrations of endrin in breast milk from U.S. women would be useful. No information was found on levels of endrin, endrin aldehyde, or endrin ketone in blood and other tissues of people near hazardous waste sites. This information is necessary for assessing the need to conduct health studies on these populations.

**Exposure Registries.** No exposure registries for endrin, endrin aldehyde, or endrin ketone were located. These substances are not currently among the compounds for which a subregistry has been established in the National Exposure Registry. These substances will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to these substances.

### 5.7.2 Ongoing Studies

A search of the Federal Research in Progress database (FEDRIP 1995) indicates that no research studies are in progress to fill the data needs identified in Section 5.7.1.

