The Patterns of Distribution of Organochlorine Pesticides in Sediment in the Letort Spring Run, Cumberland County, Pennsylvania.

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Abstract

The purpose of this study was to interpret the distribution through time and space of previously gathered and unanalyzed pesticide data in sediment from the Letort Spring Run, Cumberland County, Pennsylvania. The Letort Spring Run drains an area of 55.4 km^2 encompassing large parts of South Middleton, North Middleton, and Middlesex townships, a small area of Dickinson Township, and 65% of the borough of Carlisle. In its headwaters, the Letort is internationally renowned for its trout fly-fishing and is designated a high quality cold-water fishery by the Pennsylvania Department of Environmental Protection. The stream flows through an upstream agricultural area, an urban area (the borough of Carlisle), and finally a heavy trucking area (Middlesex Township) until its confluence with the Conodoguinet Creek. Environmental science students in Dr. Candie Wilderman's classes at Dickinson College collected pesticide data in sediment at sites within these three regions of the Letort in 1993, 1995, 1996, 1998, and 2006 as part of larger studies focusing on urban stormwater runoff. This study focuses on the organochlorine pesticides in these samples to determine temporal and spatial patterns. Data were examined to document sediment quality guideline exceedances and to determine if concentrations followed the expected degradation behavior of pesticides in sediment in aquatic systems over time. Based on this analysis of trends, the four most contaminated sites were resampled in the spring of 2008. Interpretation of these data will need to await further study.

DDT, DDE, gamma chlordane, endrin, and endrin aldehyde were the compounds most frequently detected in the samples. Hot and cold spots were determined by a site ranking system developed by the author. Most of the hot spots were found in the trucking reach, followed by the urban sites. The sites designated as hot spots exceeded sediment quality guidelines for three to five pesticides. The cold spots (no exceedances) were most common in the upstream area. DDT and its metabolites and endrin were found with greater frequency over time, while endosulfan, heptachlor, lindane, and methoxychlor were found less frequently over time. Pesticides found with greater frequency are still active in the aquatic system, either from previous concentrations becoming newly bioavailable or as a consequence of degradation. Pesticides found less often over time indicate that the chemicals are degrading and are being removed from the system. Aldrin/dieldrin and chlordane do not seem to follow any clear patterns in regards to frequency of detection. Transport of contaminated soil (possibly from urban and agricultural use) via stormwater runoff seems to be a major source of organochlorine insecticides to the Letort Spring Run. While limited fish tissue data showed a general decrease in pesticide concentration over time, the data suggest there are differences in the rate of degradation in sediment systems compared to biological systems, probably due to dissimilarity in the chemical properties of pesticides.

Since the sediment data were from different sites in different years, future studies would benefit from examining all of the sites in one sampling year. Extensive fish tissue studies or other biological assessments could be executed to more fully understand the extent of toxicology of the pesticides in the Letort. Lastly, analysis of historical land use would be useful to more accurately identify the sources of various pesticides to stream sediment.

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Figures and Tables

Introduction

This study focuses on interpreting previously gathered pesticide data in sediment from the Letort Spring Run, Cumberland County, Pennsylvania. The data, some of which are fifteen years old, have been used to supplement other studies, but have not been analyzed. The Letort Spring Run drains an area of 55.4 km^2 encompassing large parts of South Middleton, North Middleton, and Middlesex townships, a small area of Dickinson Township, and 65% of the Borough of Carlisle (Selan 2008, personal communication; Wilderman 2004). The Letort Spring Run begins in South Middleton Township, passes a watercress bog, a limestone quarry, Interstate 81, through Carlisle and four major stormwater outfalls, the US Army War College, farms, and the Middlesex Township trucking area very close to its confluence with the Conodoguinet, which is a tributary of the Susquehanna River (Wilderman 2004).

In its headwaters, the Letort is internationally renowned for its trout fly-fishing and is designated a high quality cold water fishery by the Pennsylvania Department of Environmental Protection (PA DEP) (Commonwealth of Pennsylvania 2005). Designated uses are determined by the Pennsylvania Department of Environmental Protection under the federal Clean Water Act, and are administered under the Commonwealth Chapter 93 Water Quality Standards (Commonwealth of Pennsylvania 2005). A portion of the Letort from the Route 34 bridge to the railroad bridge in Letort Park is classified as Exceptional Value by the PA DEP and the entire stream has been recognized as part of the Pennsylvania Scenic Rivers System since 1988 (LRA 2007). In February 2006, the Pennsylvania Fish and Boat Commission cited the 3 miles of the stream from Post Road to the confluence with the Conodoguinet as a Class A Wild Trout Stream (Cumberland Valley Trout Unlimited 2008).

Pesticides are common in urban streams like the Letort Spring Run. Often, pesticides are found at concentrations that exceed criteria set by government agencies to protect aquatic biota (Paul and Meyer 2001). Organochlorine pesticides found in urban stream sediments are known to frequently exceed the concentrations found in streams in intensive agricultural areas in the United States. Pesticide use in urban environments is responsible for 136,000 kg, or one third of US pesticide use (Hoffman et al. 2000; Paul and Meyer 2001). Urban pesticides largely result from household use. It is estimated that 70% to 97% of homes in the US apply pesticides. Commercial and industrial buildings, mosquito control, pet shampoos, and lawns and golf courses also use a large amount of pesticides (Hoffman et al. 2000; Paul and Meyer 2001). Golf courses are especially known for their very high pesticide application rate, which can exceed 35 pounds/acre/year compared to corn and soybean rotational fields that use 6 pounds/acre/year of pesticides. Insecticides are used more commonly in urban areas than herbicides (Hoffman et al. 2000).

It is difficult to draw clear comparisons between urban and agricultural use, as pesticide application is not well documented in urban areas. The high percentage of impermeable surfaces allows pesticide residues to be easily removed by stormwater runoff or sprinklers in urban environments (Hoffman et al. 2000). If a pesticide reaches an impermeable surface, there is a very high probability that it will be transported to a stream through the "continuous pathway" of paved surfaces found in developed areas (Hoffman et al. 2000).

Site Background and Study Design Rationale

Four previous studies have collected sediment data from the Letort Spring Run (Figures 1-4; Table 1). Three of these studies were led by Dr. Candie Wilderman, Professor

of Environmental Science at Dickinson College, in collaboration with her advanced aquatics classes. The first study on urban runoff in Carlisle during the spring of 1993 sampled the water chemistry, macroinvertebrate and fish populations, vegetation, and sediment at 10 sites along the Letort. Six of the sites had quantifiable concentrations of pesticides in sediment (Wilderman 1994). Pollutants found in the sediment seemed to correspond to the materials found in stormwater runoff. Many of the stormwater samples had concentrations of parameters that were "significantly elevated". On average however, Carlisle's stormwater was found to be similar to other urban areas (Wilderman 1994).

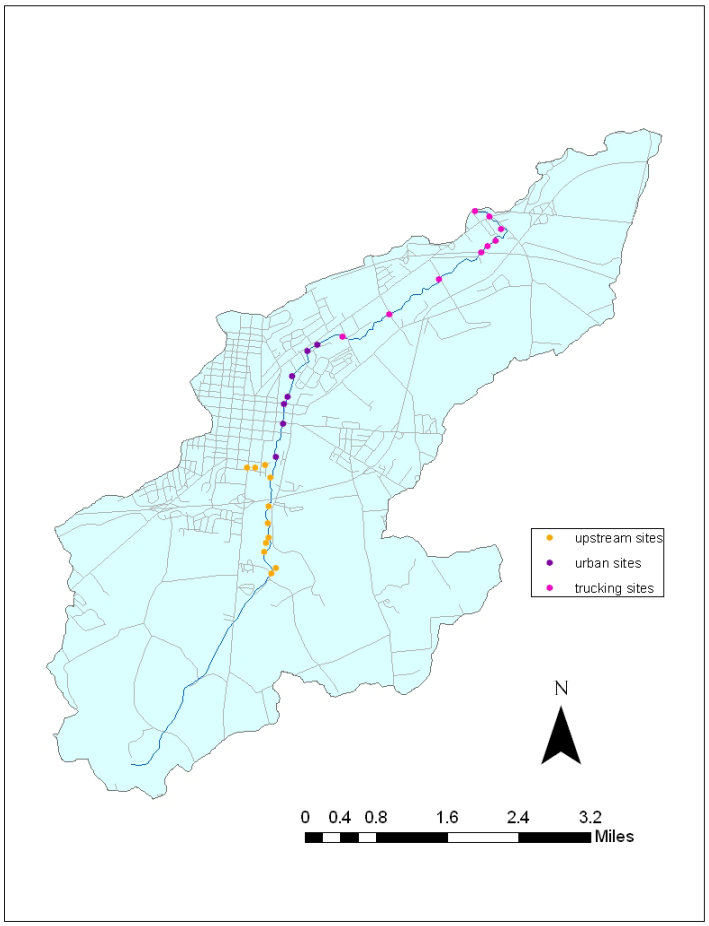


Figure 1. Site locations (1993-2006) in the Letort Spring Run watershed (Cioce 2008).

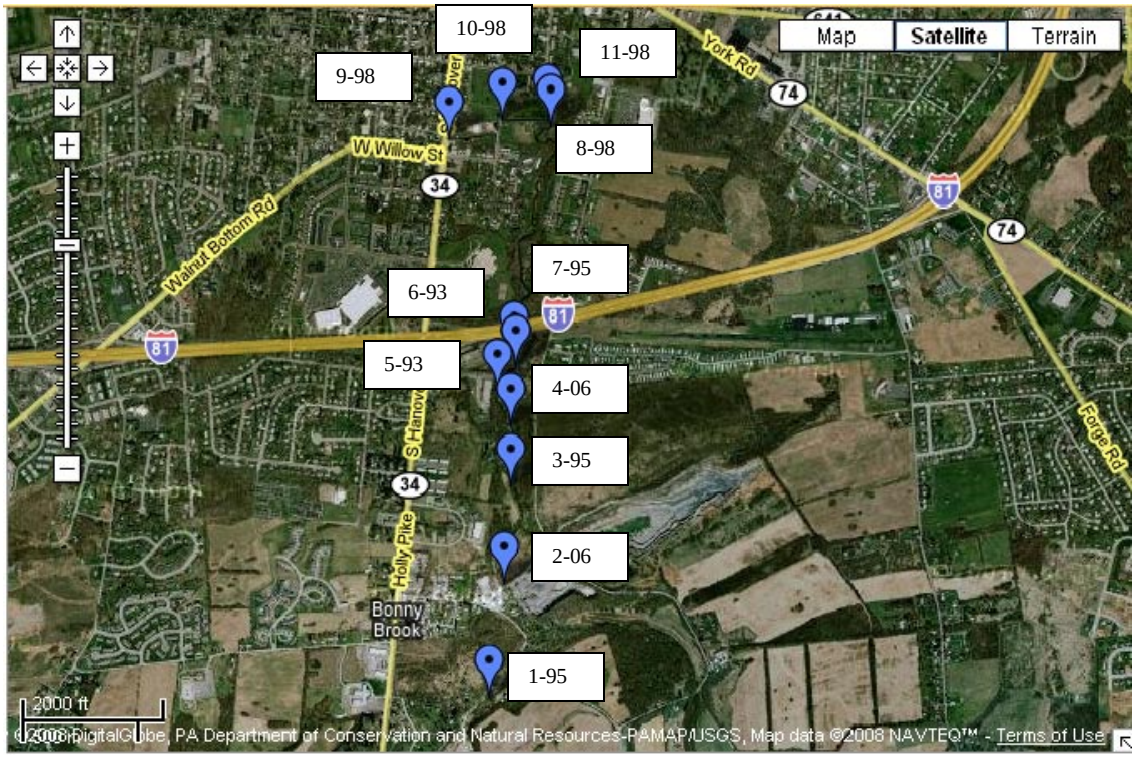


Figure 2. Upstream sample sites in the Letort Spring Run watershed (1993-2006). Map created in Google Maps.

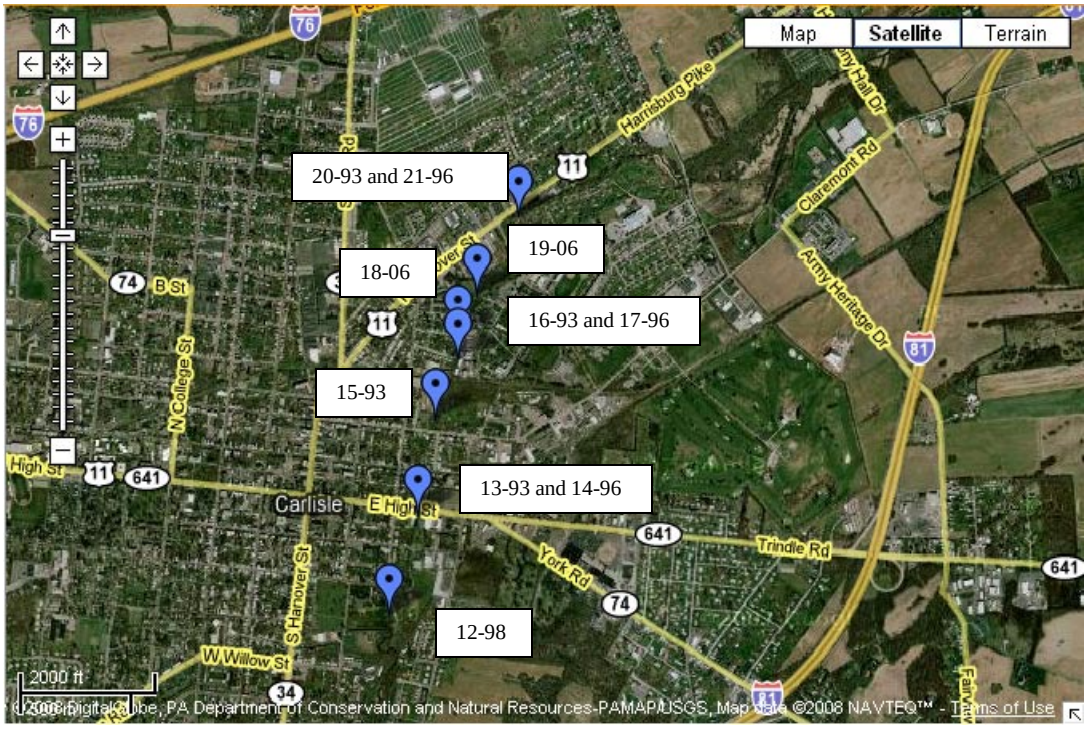


Figure 3. Urban sample sites in the Letort Spring Run watershed (1993-2006). Map created in Google Maps.

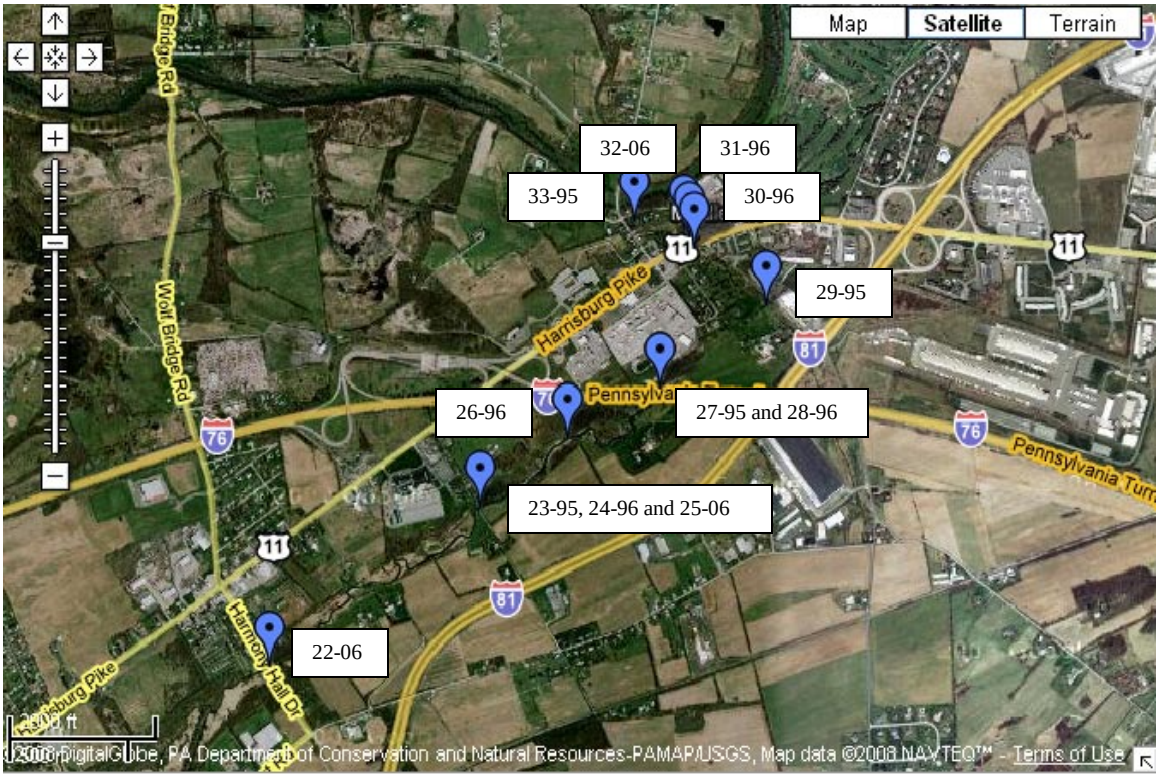


Figure 4. Trucking sample sites in the Letort Spring Run watershed (1993-2006). Map created in Google Maps.

Location	Site number and year	Site description
Upstream Reach	1-95	30m upstream from Bonnybrook Rd
	2-06	Letort along Spring Garden St., upstream of cress beds
	3-95	30m downstream from Quarry Outfall
	4-06	Letort approx 75 yds downstream from confluence of two branches
	5-93	Trout Unlimited-Vince's Meadow
	6-93	Just North of Borough Public Works Building
	7-95	Just upstream from Rt. 81 bridge
	8-98	Upstream of Mully Grub confluence
	9-98	Mully Grub, below Hanover St. outfall
	10-98	Mully Grub, below Bedford St.
	11-98	Mouth of Mully Grub
Urban Reach	12-98	Downstream of Mully Grub confluence
	13-93	Just below High St. storm sewer outfall
	14-96	Just below High St. storm sewer outfall
	15-93	Halfway down Biddle Mission Park
	16-93	Just below McKnight St. outfall
	17-96	Just below McKnight St. outfall
	18-06	Letort at Webster Street

	19-06	Letort upstream from War College entrance
	20-93	Just below Media St. outfall
	21-96	Just below Media St. outfall
Trucking Reach	22-06	Letort at Harmony Hall Rd.
	23-95	Just downstream from Shady Lane Bridge
	24-96	Just downstream from Shady Lane Bridge
	25-06	Letort at Shady Lane
	26-96	Upstream from mouth of Turnpike tributary
	27-95	In All American Retention Pond
	28-96	In All American Retention Pond
	29-95	At upper boundary of Sunday Farm
	30-96	Within oil boom at Rt. 11 outfall
	31-96	From Rt. 11 outfall pipe near Iron Kettle
	32-06	Letort at USGS gage below Rt. 11
	33-95	200m downstream from Rt. 11 overpass

Table 1. Sample sites between 1993 and 2006 grouped by land use.

A follow up study looked at the relationship between land use and stormwater runoff in the Letort Spring Run watershed in the trucking area (Wilderman 1997). Ten sites in four different land use areas (agriculture, suburban, urban, and trucking) were analyzed for water chemistry, macroinvertebrate and diatom populations, and sediment pollutants during the spring of 1995 and 1996. It was found that on a per-acre basis, the trucking land use contributes the most pollutants to the Letort, followed by urban, suburban, and agriculture areas. The Letort was negatively impacted from the pollutants, as measured through macroinvertebrate and diatom communities, vegetation, and sediment contamination.

The Mully Grub, a small tributary to the Letort, was the focus of an urban runoff study which led to a stream restoration and mitigation project (Wilderman 2004). The Mully Grub drains stormwater from the urban section of Carlisle into the Letort. Five stream sites in the Mully Grub were assessed for water chemistry, macroinvertebrate, diatom, and meiofaunal communities, sediment and habitat quality, and channel stability. Six street sites were also analyzed. The Mully Grub was found to be negatively impacted from stormwater runoff, based on increased concentrations of vehicular and organic pollutants during storm

events. Between storm events, the Mully Grub showed expected conditions based on its limestone geology. Concentrations of pesticides in sediment in the Mully Grub were similar to outfalls in the Letort and decreased with distance downstream. A restoration project was designed and implemented between 1999 and 2002 to improve the water quality in the Mully Grub that ultimately impacts the Letort Spring Run. The sediment in the Mully Grub has not been analyzed for pesticides since the restoration project has been completed.

Additional sediment data were gathered by Meghan Klasic '06, as part of her senior independent research project (Table 2). Klasic's research focused on the efficacy of using submerged aquatic vegetation as a bioindicator in the Letort (Klasic 2006). Sediment data were collected at six sites in the Letort and were processed by the PA DEP. For the purposes of this study, data collected at the Webster St. site was considered to be in the same location as the earlier McKnight St. samples, as Webster St. is only one block downstream from the McKnight St. outfall.

Site	1993	1995	1996	1998	2006
30m upstream from Bonnybrook Rd		X			
Letort along Spring Garden St., upstream of cress beds					X
30m downstream from Quarry Outfall		X			
Letort approx 75 yds downstream from confluence of two branches					X
Trout Unlimited-Vince's Meadow	X				
Just North of Borough Public Works Building	X				
Just upstream from Rt. 81 bridge		X			
Upstream of Mully Grub confluence				X	
Mully Grub, below Hanover St. outfall				X	
Mully Grub, below Bedford St.				X	
Mouth of Mully Grub				X	
Downstream of Mully Grub confluence				X	
Just below High St. storm sewer outfall	X		X		
Halfway down Biddle Mission Park	X				
Just below McKnight St. outfall	X		X		

Letort at Webster Street					X
Letort upstream from War College entrance					X
Just below Media St. outfall	X		X		
Letort at Harmony Hall Rd.					X
Just downstream from Shady Lane Bridge		X	X		X
Upstream from mouth of Turnpike tributary			X		
In All American Retention Pond		X	X		
At upper boundary of Sunday Farm		X			
Within oil boom at Rt. 11 outfall			X		
From Rt. 11 outfall pipe near Iron Kettle			X		
Letort at USGS gage below Rt. 11					X
200m downstream from Rt. 11 overpass		X			

Table 2. Timetable and description of locations of sites sampled over the sample period 1993-2006 as a result of four previous studies.

In all four studies, sediment was sampled for pesticides, metals, polychlorinated biphenyls (PCBs), and total petroleum hydrocarbons (TPHs). The scope of this study was limited to organochlorine pesticides, as these chemicals are the most toxic and are of the greatest concern due to their persistence in the environment. Concentrations found in stream sediment that are graphically represented in the Results section of this paper are shown below in Table 3.

Pesticide	**Site**	**Concentration (ug/kg)**
Aldrin	5-93- Vince's Meadow	90.00
Aldrin	16-93- McKnight St.	25.00
alpha-chlordane	13-93- High St. storm sewer	5.00
alpha-chlordane	15-93- Biddle Mission Park	3.00
alpha-chlordane	24-96- Shady Lane	13.60
gamma-chlordane	13-93- High St. storm sewer	4.60
gamma-chlordane	16-93- McKnight St.	11.00
gamma-chlordane	20-93- Media St.	24.00
gamma-chlordane	9-98- MG Hanover St.	48.00
gamma-chlordane	10-98- MG Bedford St.	4.10
gamma-chlordane	11-98- MG at Mouth	11.00
DDD	9-98- MG Hanover St.	31.00

DDD	19-06- US War Coll.	22.930
DDD	22-06- Harmony Hall Rd.	19.243
DDD	25-06- Shady Lane	18.835
DDE	9-98- MG Hanover St.	87.00
DDE	19-06- US War Coll.	26.882
DDE	20-93- Media St.	14.00
DDE	22-06- Harmony Hall Rd.	51.857
DDE	24-96- Shady Lane	45.80
DDE	25-06- Shady Lane	48.654
DDT	9-98- MG Hanover St.	50.00
DDT	11-98- MG at Mouth	9.80
DDT	12-98- DS MG Conf.	3.80
DDT	20-93- Media St.	20.00
DDT	21-96- Media St.	15.60
DDT	23-95- Shady Lane	17.00
DDT	24-96- Shady Lane	42.40
DDT	26-96- US TP Trib.	20.80
DDT	33-95- Rt. 11 overpass	29.00
Dieldrin	17-96- McKnight St.	24.20
Dieldrin	22-06- Harmony Hall Rd.	13.815
Dieldrin	25-06- Shady Lane	9.569
Endosulfan I	15-93- Biddle Mission Park	3.00
Endosulfan I	16-93- McKnight St.	32.00
Endosulfan I	20-93- Media St.	14.00
Endosulfan II	20-93- Media St.	4.95
Endosulfan sulfate	9-98- MG Hanover St.	290.00
Endosulfan sulfate	12-98- DS MG Conf.	36.00
Endosulfan sulfate	24-96- Shady Lane	28.20
Endrin	9-98- MG Hanover St.	120.00
Endrin	10-98- MG Bedford St.	15.00
Endrin	11-98- MG at Mouth	36.00
Endrin	20-93- Media St.	15.00
Endrin	21-96- Media St.	17.90
Endrin	24-96- Shady Lane	44.80
Endrin aldehyde	17-96- McKnight St.	47.80
Endrin aldehyde	21-96- Media St.	60.90
Endrin aldehyde	24-96- Shady Lane	149.00
Endrin aldehyde	26-96- US TP Trib.	41.30
Endrin aldehyde	28-96- AARP	11.60
Endrin aldehyde	31-96- Rt. 11 outfall	31.80

Endrin ketone	9-98- MG Hanover St.	240.00
Heptachlor	8-98- US MG Conf.	14.00
Heptachlor	10-98- MG Bedford St.	6.40
Heptachlor	16-93- McKnight St.	8.80
Heptachlor	23-95- Shady Lane	14.00
Heptachlor epoxide	17-96- McKnight St.	1.67
Heptachlor epoxide	24-96- Shady Lane	5.99
Heptachlor epoxide	30-96- Oil boom at Rt. 11	2.86
alpha-HCH	6-93- Public Works Bldg	9.00
beta-HCH	5-93- Vince's Meadow	14.00
gamma-HCH (Lindane)	17-96- McKnight St.	3.25
Methoxychlor	14-96- High St. storm sewer	46.20
Methoxychlor	17-96- McKnight St.	47.90
Methoxychlor	20-93- Media St.	53.00
Methoxychlor	24-96- Shady Lane	182.00

Table 3. Data from the sampling period 1993-2006 that are graphically depicted.

Organochlorine Pesticide Background

Pesticide use increased greatly since the beginning of the 20th century, but decreased beginning in the 1960s, as scientists learned of the harmful effects of some pesticides and worked to outlaw or restrict their use. Today, the United States uses about 1 billion pounds of pesticides each year, 80% of which is in agriculture, to control insects, weeds, and other organisms (USGS 2000). While most pesticides are used in agriculture, urban pesticides are used with a greater rate of application (Larson et al. 1999). This includes the use of pesticides for lawn/garden care, nuisance pest control, termite control, and industrial use (Nowell et al. 1999). In 1981, 85 million pounds of pesticides were applied to homes by homeowners compared to 47 million pounds applied by licensed commercial applicators (Nowell et al. 1999). However, the majority of insecticides (75%), including organochlorine insecticides, were applied by commercial applicators. While normally less than 2 percent of

pesticides applied to crops end up in waterways, many of these chemicals are still present in the environment, as the byproducts are persistent and do not break down easily (Battaglin and Fairchild 2002). It is not known what portion of urban pesticides reach waterways. It was found that some insecticides virtually disappear from the water column in 24 hours, as these compounds are soluble, while others are not as soluble in water (Edwards 1973). Scientists frequently sample streams for pesticides in both the water column and sediments. Some contaminants that cannot be detected in the water column are found in the sediment and within aquatic biota (USGS 2000). It is difficult to assess the toxicity of pesticides in the aquatic system since there is little information available about the synergistic effects of chemicals and there is not a lot of data for pesticides in stream sediment that will allow for long-term comparisons (USGS 2000).

One group of chemicals, the organochlorine pesticides, is known for their persistence in the environment. It has been said that "no other group of contaminants of anthropogenic origin has exacted such a heavy toll on the environment as have the organochlorine pesticides" (Blus 1995). The chemicals in this study are chlorinated hydrocarbon insecticides, a subgroup of the organochlorine pesticides (Matsumura 1985). Chlorinated hydrocarbon insecticides can be divided into three groups: DDT and related products, chlorinated cyclodiene insecticides (such as aldrin), and hexachlorocychlohexanes (HCHs, including lindane) (Walker et al. 1996). Chlorinated hydrocarbon insecticides are identified by the presence of carbon, chlorine, and hydrogen atoms; sometimes oxygen is present as well (Matsumura 1985). The carbon and chlorine atoms bond together. Cyclic carbon chains (such as benzene rings) also form in these chemicals (Matsumura 1985). The insecticides are nonpolar and are therefore hydrophobic (Table 4; Matsumura 1985). Generally, the

chlorinated hydrocarbons are chemically unreactive (low water solubility) and are highly lipophilic (Matsumura 1985; Walker et al. 1996). Organochlorines were first used in agriculture in the 1940s, and use peaked in the 1950s-60s (Nowell et al. 1999). While less than two percent of pesticides applied to crops end up in waterways, nearly half the amount of the organochlorine DDT may volatize and enter the atmosphere (Racke 1997).

Pesticide	Breakdown by microorganisms	Water Soluble	Sorbs to soil/sediment
Aldrin	No		
Dieldrin		No	Yes
Chlordane	No	No	Yes
DDD	Yes	No	Yes
DDE	Yes	No	Yes
DDT	Yes	No	Yes
Endosulfan		No	Yes
Endrin	No	No	Yes
Heptachlor	No		Yes
Lindane	Yes	Yes	No
Methoxychlor		No	Yes

Table 4. Key characteristics of the pesticides examined in this study. Behaviors are generalized and relative to other organochlorine pesticides. Missing data indicates unknown characteristics. (ATSDR Chlordane 1994; ATSDR DDT 2002; ATSDR Endosulfan 2007; ATSDR Endrin 1996; ATSDR Heptachlor 2007; ATSDR Methoxychlor 2002; Matsumura 1973; Matsumura 1985; Nowell et al. 1999; Walker et al. 1996; Willett et al. 1998).

Organochlorine pesticides are particularly harmful because they have a generally high solubility in lipids (fats). With a decrease in body weight, such as at a time of environmental stress, lipids and organochlorine residues move into the bloodstream, and can be transported to the brain and cause serious harm. Chlorinated hydrocarbons are effective insecticides due to their “ability to upset the nervous system” of organisms (Matsumura 1985). DDT, DDE, dieldrin, heptachlor, lindane and other HCH isomers, and methoxychlor are known endocrine disruptors (Nowell et al. 1999).

Organochlorine pesticides are very persistent in the environment and biomagnify. Because of this, many organochlorine insecticides were banned in the 1970s and were replaced by the use of organophosphates and carbamates, since these pesticides tend to be more water soluble and have shorter residence times (Nowell et al. 1999). Organochlorine half-lives can vary from months to years, but some chemicals may still be present for decades, or even centuries. Temperature, light, pH, and microorganism presence influence the breakdown of the pesticides (Blus 1995).

While organochlorine pesticides as a group are harmful, the toxicity within the group varies greatly. LD_{50} ranged from 1 mg/kg to greater than 2080 mg/kg for birds and from 8 mg/kg to 6000 mg/kg in laboratory rats (Brown 1978). The 96-h LC_{50} (estimated concentration in water that is lethal to 50% of exposed fish or other aquatic organisms within 96 hours) ranged from less than 1 ug/l to 4300 mg/l (Blus 1995). Endrin was the most toxic pesticide as measured with LD_{50} tests on stoneflies and rainbow trout (Table 5).

Pesticide	**LD_{50} in ug/L (ppb) for stonefly**	**LD_{50} in ug/L (ppb) for rainbow trout**
Aldrin	1.3	2.6-14.3
Chlordane	15.0	2.9-59.0
DDD	380.0	70.0
DDE		32.0
DDT	1.2-7.0	4.1-11.4
Dieldrin	0.50-0.58	1.2-2.3
Endosulfan	2.3	1.1-2.9
Endrin	0.076-0.540	0.74-2.40
Heptachlor	0.9-2.8	7.0-43.0
Heptachlor epoxide		20.0
Lindane	1.0-4.5	18.0-41.0
Methoxychlor	1.4-25.0	11.0-62.0

Table 5. Results of LD_{50} toxicity tests conducted on stoneflies and rainbow trout for organochlorine pesticides (Nowell et al. 1999). Missing data indicates unknown characteristics.

In a nationwide study conducted by the United States Geological Survey (USGS), organochlorines were found at greater concentrations in aquatic biota than in the sediment, which is problematic as contaminated food can lead to human health problems (USGS 2000). In the human body, tissues with high fat content store organochlorines, but these compounds can be released during lactation and starvation (USGS 2000).

The same USGS study also found that DDT, dieldrin, and chlordane (which are all organochlorines) are the pesticides that are most commonly found in sediment and aquatic biota at levels that can cause problems in the aquatic and terrestrial systems (USGS 2000). Another study found that aldrin, heptachlor, lindane, and dieldrin are the most threatening contaminants in the aquatic environment (Castillo 2000).

Sediment Background

Sediment is very important in aquatic systems. First off, it serves as "both a sink and source of organic and inorganic materials" (Burton and MacPherson 1995; Power and Chapman 1992). Most anthropogenic chemicals, including organochlorine pesticides, tend to sorb to sediments and organic materials, which allows chemicals to concentrate in the sediment. This is possible because organochlorine pesticides have a high n-octanol-water partition coefficient (k_{ow}) and a high soil organic carbon partition coefficient (k_{oc}) (Table 6; Nowell et al. 1999). Log k_{ow} is used as a measure of lipophilicity. A high k_{ow} value indicates that a substance will bioaccumulate. Water solubility and k_{ow} are inversely related. A k_{ow} value greater than three is characteristic of a substance that is moderately hydrophobic. All available k_{ow} values for organochlorine pesticides examined in this study exceed this benchmark (Table 6). Log k_{oc} is a measure of the extent of an organic substance to be adsorbed by soil and sediment. The amount of sorption is dependent on the size of the

molecule and the number and types of functional groups. Organochlorine pesticides are frequently found in sediments and biota, as their hydrophobic nature means they tend to sorb to carbon. Carbon is found on sediment as it accumulates on fine particles, and is present in aquatic biota due to chemical composition.

Pesticide	**log k_{ow}**	**log k_{oc}**
aldrin		4.24
chlordane	6	4.78
DDD	5.06-6.22	5.38
DDE	5.69-6.96	5.95
DDT	5.98-6.00	5.63
dieldrin	3.69-6.2	4.08
endosulfan	3.13	4.09
endrin	3.21-5.34	4
alpha HCH	3.8-3.81	3.28
heptachlor	4.4-5.5	4.38
heptachlor epoxide	3.65	3.89
lindane	3.24-3.61	3.13
methoxychlor	4.68	4.88

Table 6. Log k_{ow} and log k_{oc} values for organochlorine pesticides (Nowell et al. 1999). A k_{ow} value greater than three is characteristic of a substance that is moderately hydrophobic. Missing data indicates unknown characteristics.

It is expected that stream sediment will act as a source of persistent and hydrophobic organochlorine pesticides to surface water, at a diminishing rate over time, as concentrations of these chemicals degrade in the aquatic system (Nowell et al. 1999). Contaminated sediment can cause the alteration or loss of microbenthic and meiobenthic ecosystems, which impairs nutrient cycling capabilities (Gonzalez-Lopez et al. 2005). It is estimated that 1 gram of sediment contains 1 billion bacteria that aid in nutrient cycling. It is also possible for fish to become contaminated as they feed on benthic invertebrates that are associated with toxic sediment. This could be of concern in the Letort Spring Run, as the stream is internationally renowned for its native trout populations.

Sediments act as natural sorbents and therefore would be expected to contain the highest concentration and diversity of contaminants in most aquatic systems (Samoiloff

1989). Contaminants that are bound to sediment are “more persistent, less mobile, and occur at higher concentrations” than contaminants in water (Power and Chapman 1992). It has been shown that the likelihood of detecting pesticides in sediment is directly related to the amount of pesticides applied in the drainage area (Nowell et al. 1999). The contaminants in sediment can enter the biologic system in three ways: by adsorption of the contaminant by contact of an organism with the sediment, by ingestion of sediment, and desorption of the contaminant into the water column, where the organism uptakes the contaminant from the water (Figure 5; Nowell et al. 1999; Samoiloff 1989). Additionally, pesticides move through the hydrologic system in three ways: phase transfer processes (which control movement among different environmental media), transport processes (control movement through the surface/water system), and transformation processes (control the change of chemical structure) (Nowell et al. 1999). After the initial deposition, pesticides can be buried with sediment, transported downstream, resuspended and reintroduced into the water column, or ingested by aquatic biota (Nowell et al. 1999).

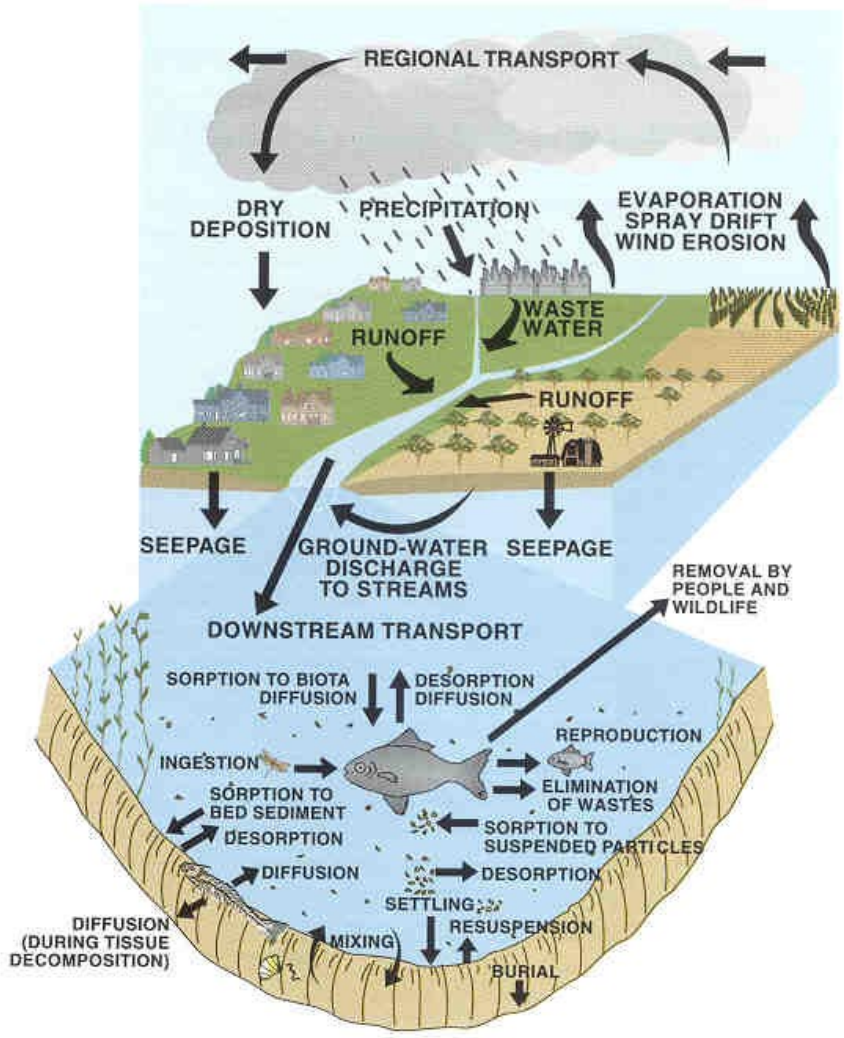


Figure 5. Diagram of pesticide movement in the hydrologic system (Water Resources of Oklahoma 2005). Modified figure from Majewski and Capel (1995).

Pesticides are broken down in sediment systems by biological and chemical means. Aquatic biota use enzymes to transform the chemicals. Biological processes are the only degradation methods that can completely mineralize a pesticide (turn it into water, carbon dioxide, and chloride ions). This is significant, as complete mineralization is the ideal fate for a pesticide since it renders it the least active. It is difficult for organisms to transform synthetic organochlorines as the necessary enzymes for degradation are unavailable. Biotransformation is eventually possible through the process of cometabolism, where

microorganisms use carbon sources for growth and energy. The pesticides enter this process and are transformed. Intermediate products are often formed and have toxicities that can be greater or less than the original parent compound. Products that are more toxic can decrease biotransformation (Nowell et al. 1999).

It is important to note that any toxins in sediment are not active until released. A high concentration of a contaminant can be present in the sediment, but it will not negatively affect aquatic organisms unless it is bioavailable (Power and Chapman 1992). This can occur when the pesticide is suspended in the water column (either in association with a soil particle or dissolved), when aquatic biota contaminated with pesticides die and release the pesticides back into the system or when such organisms excrete, and when contaminated groundwater enters the system (Nowell et al. 1999). In high flow conditions, pesticides enter an aquifer, and will leave the aquifer and enter the stream during low flow conditions (Nowell et al. 1999). In lake systems, it was found that once pesticides are buried past the first few centimeters of sediment, the chemicals are removed from most possibilities of entering the water column (Nowell et al.1999). Stream systems are more unpredictable, as flood conditions and high flows can resuspend materials that were previously deposited and carry the particles downstream.

The only way to measure bioavailability is to conduct biological assessments to contaminant response, for example, through bioassays (Power and Chapman 1992). Ideally, sediments would be assessed through analysis of community structure, sediment toxicity, tissue chemistry, pathology, and sediment chemistry, but most often only sediment chemistry is measured (Power and Chapman 1992). Additionally, the concentration of a pesticide in sediment is inversely related to sediment particle size (Edwards 1973). Fine sediments are

more biologically and chemically reactive due to a large surface area to volume ratio and the accompanying surface charges (Power and Chapman 1992). Chemical analysis is useful to explain toxic potential of the sediment, but a biological threat must also be present. Toxicological significance is hinged upon bioavailability of the substance (Samoiloff 1989). To this end, biomonitoring aquatic organisms for effects of contaminated sediment (normally in the laboratory) is the preferred method of testing toxicity.

There are issues associated with methods of collection and sample alteration for sediments. It is difficult to assess the quality of the sediment without disturbing the system (Power and Chapman 1992). When sediments are collected, transported to a laboratory, stored, and finally tested for toxicity, the original structure and characteristics are altered because of the fragility of the sediment. It is also likely that the surficial fine particle layer will be lost in collecting the sample. This is problematic as this layer is the most biologically active and may contain the highest concentrations of contaminants. It is recommended that a core sampler be used to limit the loss of a surficial layer. Dredge (grab) samplers are disruptive, lose the surficial layer, and destroy the stratified vertical gradients in the sediment column. If a dredge sampler is to be used, the Ekman is considered the least disruptive, but cannot be used in deep water. While it is known that sediments are altered during the collection process, the extent of disturbance while measuring toxicity is not clear. It is therefore recommended that testing begin soon after collection to preserve the microenvironments within the sediment, no longer than after 2 weeks storage at 4°C (Burton and MacPherson 1995).

It is also thought that polluted sediments can cause biological harm even if standards for water are not exceeded. This is problematic as there are not many established levels for

pesticides in sediment in the aquatic system. There are suggested sediment quality guidelines (SQGs) which classify sediment contamination using a two tiered system that consists of a threshold effects concentration (TEC) and a probable effects concentration (PEC). A violation of the TEC indicates moderate pollution, while levels below the TEC are considered unpolluted (Smith et al. 1996; Wilderman 2004). If the concentration also exceeds the PEC, the site is considered heavily polluted. Different agencies have established varying TEC and PEC criteria that often conflict with each other, making it difficult to categorize the extent of pollution (Table 7). In a report published under the United States Geological Survey in 1999, it was noted that "no single type of sediment guideline is generally accepted in the scientific literature" (Nowell et al. 1999).

Pesticide	**MacDonald consensus-based TEC**	**MacDonald consensus-based PEC**	**NOAA and CCME TEL**	**NOAA and CCME PEL**	**FL DEP TEL**	**FL DEP PEL**
DDT	4.16	62.9	1.19*	4.77*	1.2	4.8
Dieldrin	1.90	61.8	2.85	6.67	0.72	4.3
Endrin	2.22	207				
Heptachlor epoxide	2.47	16	0.6	2.74		

Table 7. Examples of conflicting sediment quality guidelines for organochlorine pesticides (CCME 2002, FL DEP 1994, MacDonald et al. 2000, NOAA 1999). No classification indicates that there are no sediment quality guidelines for that pesticide.
*= CCME guideline only.

Another challenge is that TEC and PEC values have not been established for all pesticides. The focus has been on developing standards to safeguard human health. For this reason, sediment quality guidelines have not been developed for pesticides with less environmental persistence. Guidelines have not been developed for some pesticides with more toxic properties, as based on LD_{50} (Table 8). Generally, pesticides with soil half-lives less than one year do not currently have established sediment quality guidelines.

Pesticide	LD_{50} in ug/L (ppb) for stonefly	LD_{50} in ug/L (ppb) for rainbow trout	Half-life (in soil)	Have SQGs?
Aldrin	1.3	2.6-14.3	20-100 days	**No**
Chlordane	15.0	2.9-59.0	1-4 years	**Yes**
DDD	380.0	70.0	730-5690 days	**Yes**
DDE		32.0	730-5690 days	**Yes**
DDT	1.2-7.0	4.1-11.4	2-15 years	**Yes**
Dieldrin	0.50-0.58	1.2-2.3	2.5-5 years	**Yes**
Endosulfan	2.3	1.1-2.9	35-150 days	**No**
Endrin	0.076-0.540	0.74-2.40	12 years	**Yes**
Heptachlor	0.9-2.8	7.0-43.0	0.75-2 years	**No**
Heptachlor epoxide		20.0	Several years	**Yes**
Lindane	1.0-4.5	18.0-41.0	191-423 days	**Yes**
Methoxychlor	1.4-25.0	11.0-62.0	57-300 days	**No**

Table 8. The extent of Sediment Quality Guidelines (SQGs) for organochlorine pesticides based on LD_{50} and half-life values (ATSDR; Nowell et al. 1999; PMEP 1993; UNEP 2002). Missing data indicates unknown characteristics.

Another regulatory problem exists in the quantification of a chemical's residence time in sediment. The commonly accepted way to make priorities among chemical pollutants in environmental systems is to evaluate persistence, potential for bioaccumulation, and toxicity (Webster et al. 1998). Persistence is measured through half-lives in different environmental media. The Canadian Environmental Modeling Centre has established general persistence levels above which guidelines should be established for chemicals shown in Table 9; these defining levels are considered typical and as of 1998, were being considered to be adopted internationally (Woodfine and Mackay 2001). The persistence criterion for sediment reflects the extent of existing sediment quality guidelines. Generally, pesticides with soil half-lives (persistence) greater than one year have established sediment quality guidelines (Table 9). It is significant to note that soil and sediment systems do not have the same criteria.

Medium	Persistence criteria
Air	≥ 2 days
Surface water	≥ 182 days (6 months)
Soil	≥ 182 days (6 months)
Sediment	≥ 365 days (1 year)

Table 9. Single medium persistence criteria developed by the Canadian Environmental Modeling Centre (Woodfine and Mackay 2001).

In soils, degradation can be influenced by soil type (which influences sorption), water content, and soil use. Sediment systems are more unpredictable due to their varying composition, and the presence of both aerobic and anaerobic processes at different rates and depths. It was previously thought that a chemical that was resistant in aerobic conditions would not degrade in an anaerobic environment (Hill and McCarty 1966). Studies have shown however that many pesticides degrade faster under biologically active anaerobic conditions, including lindane, heptachlor, DDT, DDD, aldrin, and endrin (Hill and McCarty 1966). Dieldrin and heptachlor epoxide were found to be very persistent in both aerobic and anaerobic conditions. These studies indicated that anaerobic environments can be very biologically active, and can cause significant degradation of pesticide compounds. Therefore, the half-life of a chemical in soil and sediment would not necessarily be the same.

Soil half-lives are measured in the laboratory under standardized conditions. These values can be used to effectively compare the relative differences in persistence of pesticides (Nowell 2008, personal communication). However, it is doubtful that soil half-lives are representative of sediment half-lives. For example, one study that analyzed DDT concentrations in soil and stream sediment indicated that DDT breaks down faster once it had entered the aquatic system (Agee 1986). A few studies have produced so called "sediment half-lives" for pesticides by measuring field dissipation half-lives. Field dissipation half-lives are site-specific and involve the "overall rate of change over time in the compound of

interest as a consequence of reduced input, chemical transformation, and dilution" (Barbash and Resek 1996; Nowell 2008, personal communication). These measures do not represent a specific fate process, but rather the combination of several processes (including transformation, volatilization, and transport away from the site) occurring at the same time (Barbash and Resek 1996). Because these half-lives are heavily site specific, it is challenging to use them to compare sampling locations that would have different environmental conditions.

Materials and Methods

Pesticide data in sediment were previously collected at 27 different sites in the Letort over the study period 1993-2006 (11 in the upstream section, 7 in the urban area and 9 in the trucking reach, Figures 1-4, Table 1). Table 10 shows the timeline for sampling throughout the study period. Pesticide data were analyzed according to sediment quality guidelines and interpreted through graphical analysis using Microsoft Excel and studies in the literature. The MacDonald consensus based TEC and PEC levels were used for this analysis since these levels are the result of a survey of numerous studies, and are therefore the most representative of the data available in the literature. Only sites with a positive concentration at any of the sample years were graphed in order to make the figures readable. Extensive background research was conducted to gather information on the toxicology and environmental fate of organochlorine pesticides in aquatic systems.

Site	1993	1995	1996	1998	2006	2008
30m upstream from Bonnybrook Rd		X				
Letort along Spring Garden St., upstream of cress beds					X	
30m downstream from Quarry Outfall		X				
Letort approx 75 yds downstream from confluence of two branches					X	

Trout Unlimited-Vince's Meadow	X					
Just North of Borough Public Works Building	X					
Just upstream from Rt. 81 bridge		X				
Upstream of Mully Grub confluence				X		
Mully Grub, below Hanover St. outfall				X		X
Mully Grub, below Bedford St.				X		
Mouth of Mully Grub				X		
Downstream of Mully Grub confluence				X		
Just below High St. storm sewer outfall	X		X			
Halfway down Biddle Mission Park	X					
Just below McKnight St. outfall	X		X			
Letort at Webster Street					X	
Letort upstream from War College entrance					X	
Just below Media St. outfall	X		X			X
Letort at Harmony Hall Rd.					X	X
Just downstream from Shady Lane Bridge		X	X		X	X
Upstream from mouth of Turnpike tributary			X			
In All American Retention Pond		X	X			
At upper boundary of Sunday Farm		X				
Within oil boom at Rt. 11 outfall			X			
From Rt. 11 outfall pipe near Iron Kettle			X			
Letort at USGS gage below Rt. 11					X	
200m downstream from Rt. 11 overpass		X				

Table 10. Sampling time table with sites resampled in 2008 in red.

A ranking system was developed by the author to determine the location of the most polluted sites (hot spots) compared to the least contaminated sites (cold spots) based on exceedances of the MacDonald consensus based sediment quality guidelines. Sites were assigned a rank using a numerical system (higher numbers indicate a more polluted site). Each site was ranked for each year it was sampled. A score of 0 was given if concentrations of a pesticide were 0, or below the TEC. A score of 0 was also given if there were no sediment quality guidelines established for a pesticide. A score of 3 was given for each time a pesticide exceeded the TEC, and a score of 5 was given each time a pesticide exceeded the

PEC. The four most contaminated sites were targeted for resampling during the spring of 2008. The samples were not processed in time for this report, and interpretation of the results will need to await further studies.

Sediment samples were collected at these sites in accordance with PA DEP's methods and were processed by PA DEP's Bureau of Laboratories. Sediments were collected using a stainless steel trowel and mixing bowl, prepared with FL-70 soap, methanol, deioinzed water, and wrapped in aluminum foil until sampling was to commence (Wilderman 2004). Sediments were collected at each site using the trowel, and were mixed to form a composite sample in the bowl. Samples were put into amber glass bottles provided by PA DEP. Sample bottles were iced and delivered to PA DEP for analysis. Analysis was conducted according to US EPA Method 608, "Methods for Chemical Analysis of Water and Wastes", Federal Register volume 49, number 209, October 26, 1984 (Wilderman 2004). Additionally, fish tissue data collected and analyzed by PA DEP for two sites on the Letort were examined to determine the bioavailability of pesticides at these sites. Data were graphically analyzed using Microsoft Excel.

Results and Interpretation

Analysis of all chemicals over time

It is clear that the distribution of pesticides found varies with time. While it is difficult to draw conclusions regarding changes over time from the data, as sites were not continuously sampled among all years, some trends can be seen. DDT, DDE, gamma chlordane, endrin, and endrin aldehyde were the compounds most frequently detected in the samples (Figure 6). Comparatively, the most commonly detected pesticides in sediment and aquatic biota in 400 monitoring studies and 140 reviews nationwide were DDT and its

metabolites, chlordane, and dieldrin (Nowell et al. 1999). Pesticides that are still being actively used (endosulfan, lindane, and methoxychlor) did not show a significant increase in detection compared to organochlorine insecticides that have been banned in the United States.

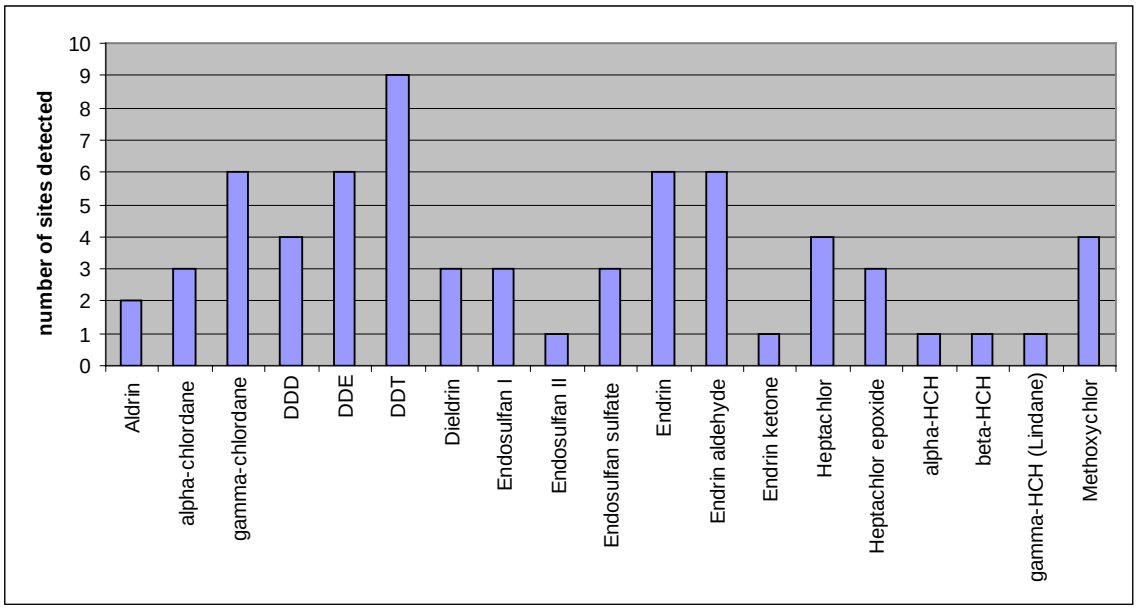


Figure 6. Number of sites where each pesticide was found over the sampling period 1993-2006.

DDT and its metabolites (DDD and DDE) were found more frequently over the sampling period from 1993-2006 (Figures 7-11). Pesticides found with greater frequency and that are no longer being used are still active in the aquatic system, either from previous concentrations becoming newly bioavailable or as a consequence of degradation. DDT increased in frequency mostly from sampling in the Mully Grub in 1998, but was no longer found in 2006. Instead, DDD and DDE were found in 2006, which seems to indicate the pesticide is in the process of being broken down. Endrin and its breakdown products also generally increase in frequency over time, but were not found at the small number of sites sampled in 2006. Endrin aldehyde was only found in 1996.

Endosulfan, heptachlor, gamma-HCH (Lindane), and methoxychlor were found less frequently over time. Generally, these pesticides degraded to their breakdown products (also measured in the sediment data from 1993-2006), which indicate their removal from the system over time.

Aldrin/dieldrin and chlordane do not follow any clear patterns. Dieldrin increases in 2006, but aldrin is only present in 1993. It is possible that aldrin became bioavailable at Harmony Hall and Shady Lane, which would explain the presence of dieldrin, as aldrin quickly degrades to this metabolite (ATSDR Aldrin/Dieldrin 2002; Matsumura 1985). Chlordane generally decreases in frequency, but it appears that the gamma isotope might be more persistent. This is very difficult to interpret, as little information is available on the fate of these isomers.

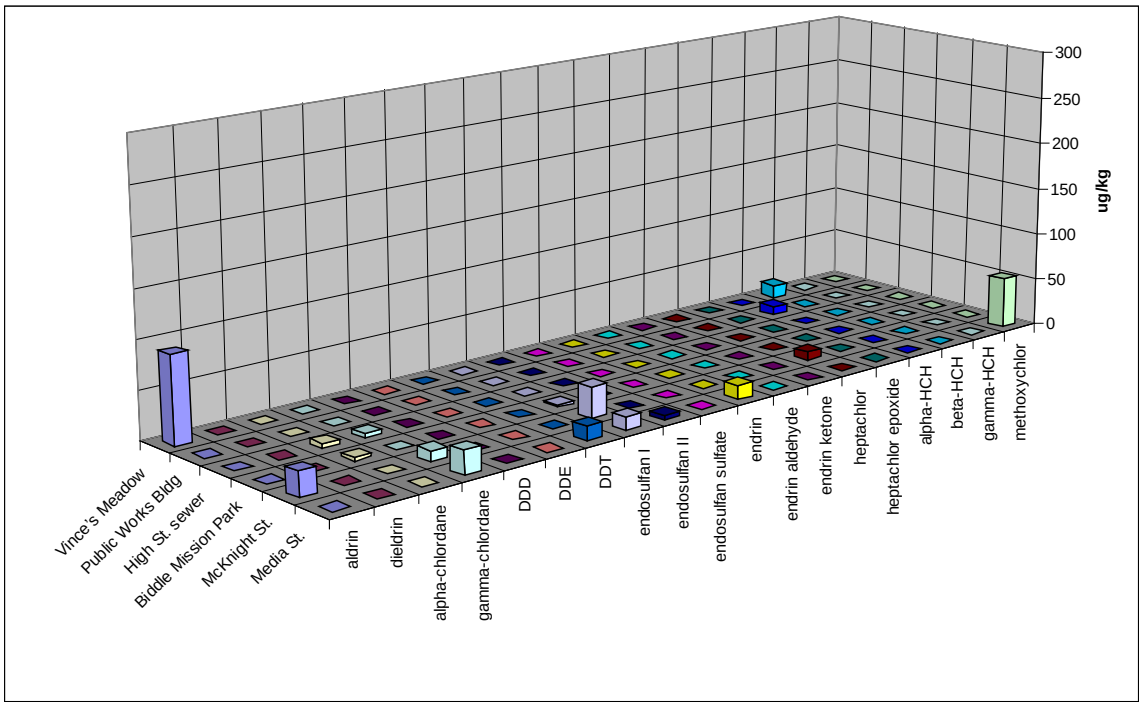


Figure 7. Concentrations of organochlorine insecticides found in 1993 in sample sites in the Letort Spring Run.

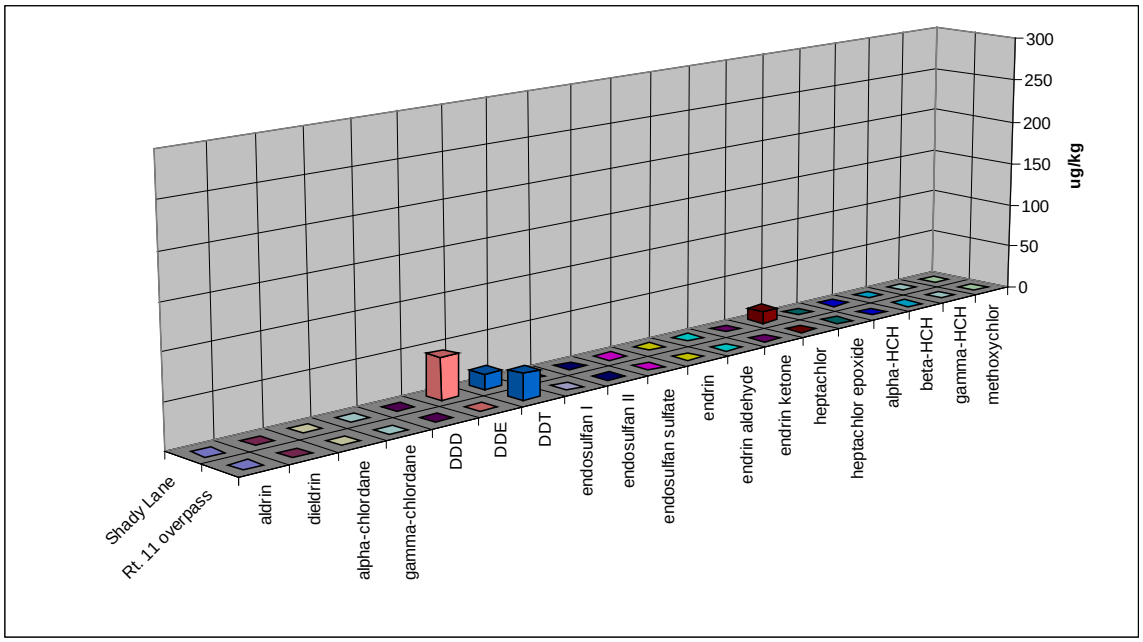


Figure 8. Concentrations of organochlorine insecticides found in 1995 in sample sites in the Letort Spring Run.

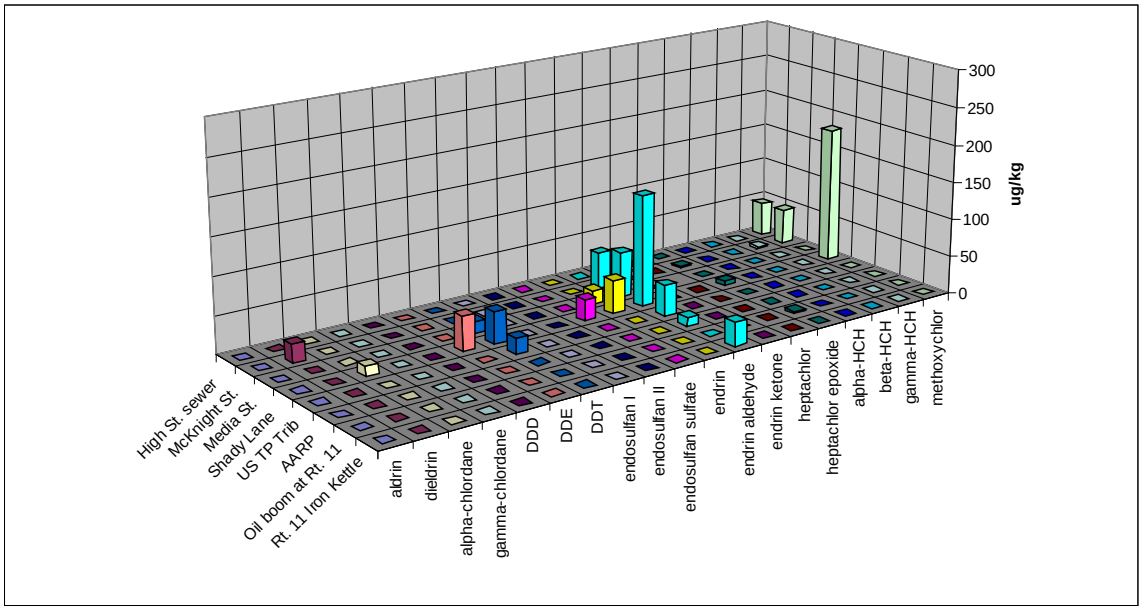


Figure 9. Concentrations of organochlorine insecticides found in 1996 in sample sites in the Letort Spring Run.

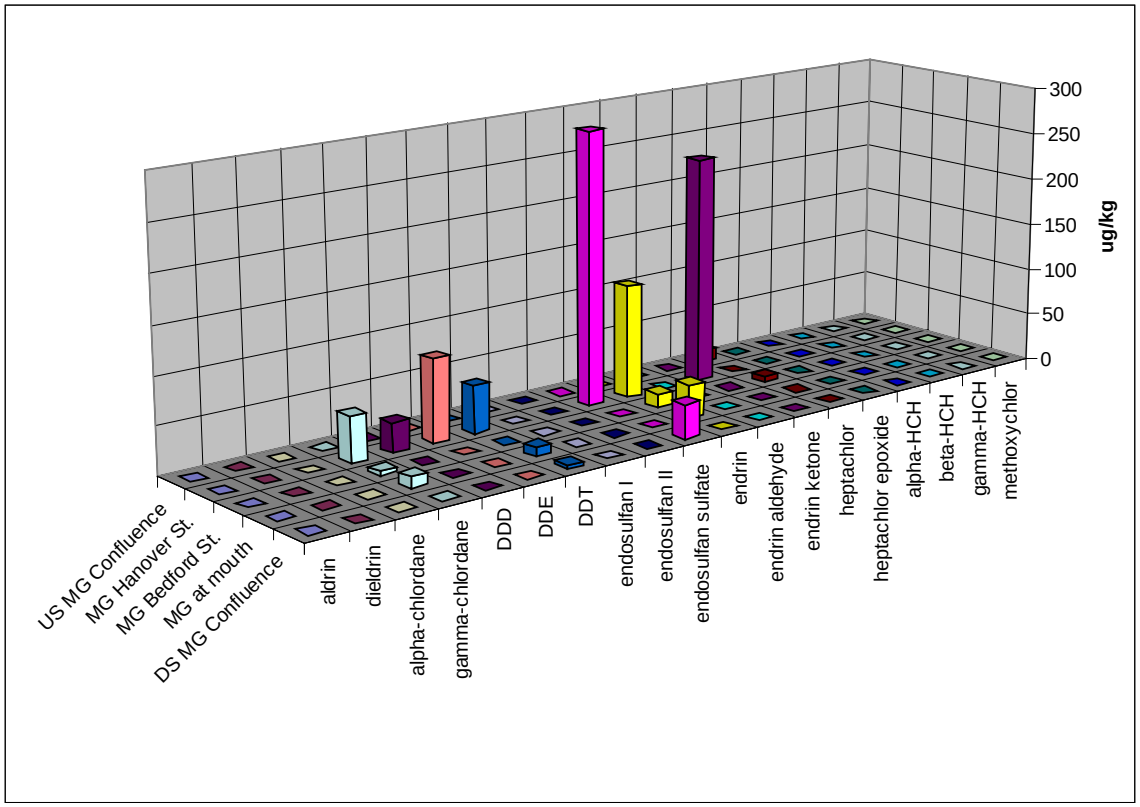


Figure 10. Concentrations of organochlorine insecticides found in 1998 in sample sites in the Letort Spring Run.

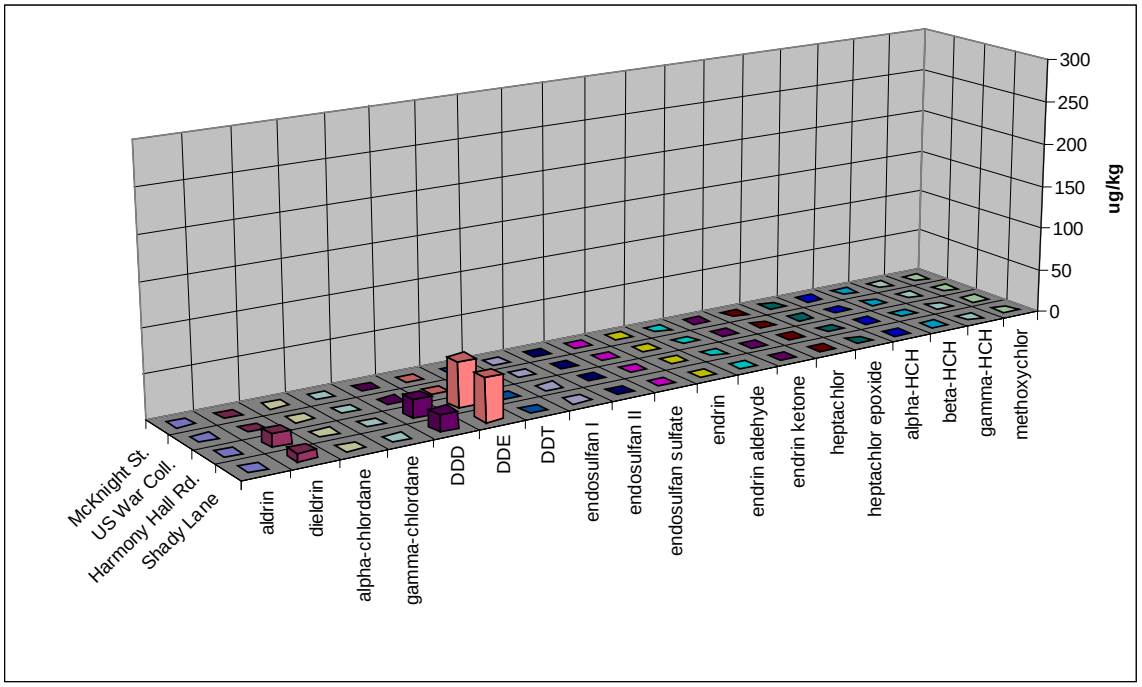


Figure 11. Concentrations of organochlorine insecticides found in 2006 in sample sites in the Letort Spring Run.

Analysis by site

A ranking system created by the author was used to evaluate contamination among the sites sampled. The five most polluted sample sites (known as "hot spots") as measured through the ranking system (described in Materials and Methods) are highlighted in red in Table 11. This ranking system was used as the justification to resample the Mully Grub below the Hanover Street outfall, and the Letort below the Media St. outfall, along Harmony Hall Road, and downstream from the Shady Lane bridge in the spring of 2008. Most of the hot spots were found in the trucking reach (3 out of 9 sites), followed by the urban sites (1 out of 10 sites) (Table 11). The sites designated as hot spots exceeded sediment quality guidelines for three to five pesticides, commonly chlordane, DDT and metabolites, and endrin (Table 12). The cold spots (no exceedances) were most common in the upstream area (5 out of 8 sites).

Site	Year	Ranking
Spring Garden St., upstream of cress beds	2006	0
75 yards downstream of two branches	2006	0
Vince's Meadow	1993	0
Just north of Boro Public Works building	1993	0
Upstream of Mully Grub confluence	1998	0
Mully Grub, below Hanover St. outfall	1998	**21**
Mully Grub, below Bedford St. outfall	1998	6
Mouth of Mully Grub	1998	9
Downstream of Mully Grub confluence	1998	0
Just below High St. storm sewer outfall	1993	6
	1996	0
Halfway down Biddle Mission Park	1993	0
Just below McKnight St. outfall	1993	3
	1996	6
	2006	0
Letort upstream from War College entrance	2006	6
Just below Media St. outfall	1993	**14**
	1996	6
Harmony Hall Rd.	2006	**11**
Just downstream from Shady Lane bridge	1995	3
	1996	**17**
	2006	**11**

Upstream from mouth of TP trib	1996	3
In All American retention pond	1996	0
Within oil boom at Rt. 11 outfall	1996	3
From Rt. 11 outfall pipe near Iron Kettle	1996	0
200 M. downstream from Rt. 11 overpass	1995	3

Table 11. Pollution ranking system. Higher numbers indicate a more polluted site. The five most polluted sites are highlighted in red.

Site	Year	Ranking	Pesticides that contributed to ranking
Mully Grub, below Hanover St. outfall	1998	**21**	Gamma chlordane, DDD, DDE, DDT, endrin
Mully Grub, below Bedford St. outfall	1998	6	Gamma chlordane, endrin
Mouth of Mully Grub	1998	9	Gamma chlordane, DDT, endrin
Just below High St. storm sewer outfall	1993	6	Alpha chlordane, Gamma chlordane
Just below McKnight St. outfall	1993	3	Gamma chlordane
	1996	6	Dieldrin, lindane
Letort upstream from War College entrance	2006	6	DDD, DDE
Just below Media St. outfall	1993	**14**	Gamma chlordane, DDE, DDT, endrin
	1996	6	DDT, endrin
Harmony Hall Rd.	2006	**11**	DDD, DDE, dieldrin
Just downstream from Shady Lane bridge	1995	3	DDT
	1996	**17**	Alpha chlordane, DDE, DDT, endrin, heptachlor epoxide
	2006	**11**	DDD, DDE, dieldrin
Upstream from mouth of TP trib	1996	3	DDT
Within oil boom at Rt. 11 outfall	1996	3	heptachlor epoxide
200 M. downstream from Rt. 11 overpass	1995	3	DDT

Table 12. Pesticides that contributed to nonzero rankings. See Table 3 for complete data.

Pesticides were classified as highly, moderately, or unpolluted based on exceedances of sediment quality guidelines established by various environmental agencies in Table 13. When the data were analyzed based on available TEC and PEC values, there was a substantial amount of conflict between the criteria. The MacDonald consensus-based PEC and the Florida Department of Environmental Protection (FL DEP) PEL (probable effects level, equivalent to PEC) for example are on the higher end (FL DEP 1994; MacDonald et al. 2000). When held to these standards, the concentrations of pesticides do not often breach these levels, and are therefore considered moderately polluted. The National Oceanic and Atmospheric Administration (NOAA) and the Canadian Council of Minister for the Environment (CCME) PELs tend to be more stringent (CCME 2002; NOAA 1999).

Additionally, each time a pesticide was found, the concentration was classified to a pollution level (Table 14). Often, a concentration of a pesticide was ranked at different pollution levels (most frequently there were conflicts between the moderately and heavily polluted categories). DDE was found at concentrations considered to be heavily polluted at more than 50% of sites sampled (Figure 12). Chlordane and DDD were also found to be heavily polluted at more than 20% of sites. The majority of pesticides were found to be moderately polluted in the sediment, with the exception of DDE. Chlordane, DDT, and heptachlor epoxide were at unpolluted concentration levels in a portion of their sites (~10% and 30%, respectively).

Pesticide	Sites found	Concentration (ppb)	MacDonald consensus-based TEC	MacDonald consensus-based PEC	NOAA and CCME TEL	NOAA and CCME PEL	FL DEP TEL	FL DEP PEL
Aldrin	5-93- TU Vince's Meadow	90.00						
	16-93- Just below McKnight St Oufall	25.00						
alpha-HCH	6-93- Just north of Boro Public Works Bldg	9.00						
beta-HCH	5-93- TU Vince's Meadow	14.00						
gamma-HCH (Lindane)	17-96- Just below McKnight St Outfall	3.25	2.37	4.99	0.94	1.38	0.32	0.99
alpha-Chlordane	13-93- Just below High St storm sewer Outfall	5.00	3.24	17.6	4.5	8.9	2.3	4.8
	15-93- Halfway down Biddle Mission Park	3.00	total chlordane		total chlordane		total chlordane	
	24-96- Just downstream from Shady Lane Bridge	13.60	X	X	X	X	X	X
gamma-Chlordane	9.98- Mully Grub, below Hanover St. outfall	48.00	X	X	X	X	X	X
	10-98- Mully Grub, below Bedford St.	4.10	X	X	X	X	X	X
	11-98- Mouth of Mully Grub	11.00	X	X	X	X	X	X
	13-93- Just below High St storm sewer Outfall	4.60	X	X	X	X	X	X
	16-93- Just below McKnight St Oufall	11.00	X	X	X	X	X	X
	20-93- Just below Media Outfall	24.00	X	X	X	X	X	X
Chlorneb[+]	28-96- In All American Retention Pond	75.80						
Cyanazine[+]	16-93- Just below McKnight St Oufall	620.00						
	20-93- Just below Media Outfall	499.00						
4,4' DDD	9-98- Mully Grub, below Hanover St. outfall	31.00	4.88	28	3.54	8.51	1.2	7.8
	19-06- Letort upstream from War College entrance	22.93	X	X	X	X	X	X
	22-06- Letort at Harmony Hall Rd.	19.24	X	X	X	X	X	X
	25-06- Letort at Shady Lane	18.84	X	X	X	X	X	X

4,4’ DDE	9-98- Mully Grub, below Hanover St. outfall	87.00	3.16	31.3	1.42	6.75	2.1	374
	19-06- Letort upstream from War College entrance	26.88	X	X	X	X	X	X
	20-93- Just below Media Outfall	14.00	X	X	X	X	X	X
	22-06- Letort at Harmony Hall Rd.	51.86	X	X	X	X	X	X
	23-95- Just downstream from Shady Lane Bridge	45.80	X	X	X	X	X	X
	25-06- Letort at Shady Lane	48.65	X	X	X	X	X	X
4,4’ DDT	9-98- Mully Grub, below Hanover St. outfall	50.00	4.16	62.9	1.19*	4.77*	1.2	4.8
	11-98- Mouth of Mully Grub	9.80	X	X	X	X	X	X
	12-98- Downstream of Mully Grub confluence	3.80	X	X	X	X	X	X
	20-93- Just below Media Outfall	20.00	X	X	X	X	X	X
	21-96- Just below Media Outfall	15.60	X	X	X	X	X	X
	23-95- Just downstream from Shady Lane Bridge	17.00	X	X	X	X	X	X
	24-96- Just downstream from Shady Lane Bridge	42.40	X	X	X	X	X	X
	26-96- Upstream from mouth of TP Trib	20.80	X	X	X	X	X	X
	33-95- 200m downstream from Rt. 11 Overpass	29.00	X	X	X	X	X	X
Dieldrin	17-96- Just below McKnight St Outfall	24.20	1.90	61.8	2.85	6.67	0.72	4.3
	22-06- Letort at Harmony Hall Rd.	13.82	X	X	X	X	X	X
	25-06- Letort at Shady Lane	9.57	X	X	X	X	X	X
Endosulfan I	15-93- Halfway down Biddle Mission Park	3.00						
	16-93- Just below McKnight St Oufall	32.00						
	20-93- Just below Media Outfall	14.00						
Endosulfan II	20-93- Just below Media Outfall	4.95						
Endosulfan sulfate	9-98- Mully Grub, below Hanover St. outfall	290.00						
	12-98- Downstream of Mully Grub confluence	36.00						
	24-96- Just downstream from Shady Lane Bridge	28.20						
Endrin	9-98- Mully Grub, below Hanover St.	120.00	2.22	207				

	outfall							
	10-98- Mully Grub, below Bedford St.	15.00	X	X				
	11-98- Mouth of Mully Grub	36.00	X	X				
	20-93- Just below Media Outfall	15.00	X	X				
	21-96- Just below Media Outfall	17.90	X	X				
	24-96- Just downstream from Shady Lane Bridge	44.80	X	X				
Endrin aldehyde	17-96- Just below McKnight St Outfall	47.80						
	21-96- Just below Media Outfall	60.90						
	24-96- Just downstream from Shady Lane Bridge	149.00						
	26-96- Upstream from mouth of TP Trib	41.30						
	28-96- In All American Retention Pond	11.60						
	31-96- From Rt. 11 Outfall Pipe near Iron Kettle	31.80						
Endrin ketone	9-98- Mully Grub, below Hanover St. outfall	240.00						
Heptachlor	8-98- Upstream of Mully Grub confluence	14.00						
	10-98- Mully Grub, below Bedford St.	6.40						
	16-93- Just below McKnight St Oufall	8.80						
	23-95- Just downstream from Shady Lane Bridge	14.00						
Heptachlor epoxide	17-96- Just below McKnight St Outfall	1.67	2.47	16	0.6	2.74		
	24-96- Just downstream from Shady Lane Bridge	5.99	X	X	X	X		
	30-96- Within oil boom at Rt. 11 Outfall	2.86	X	X	X	X		
Hexachlorobenzene[+]	9-98- Mully Grub, below Hanover St. outfall	300.00						
Methoxychlor	14-96- Just below High St. storm sewer Outfall	46.20						
	17-96- Just below McKnight St Outfall	47.90						
	20-93- Just below Media Outfall	53.00						
	24-96- Just downstream from Shady Lane Bridge	182.00						
Metolachlor[+]	3-95- 30m downstream from quarry outfall	220.00						

	15-93- Halfway down Biddle Mission Park	235.00						
	24-96- Just downstream from Shady Lane Bridge	337.00						
	30-96- Within oil boom at Rt. 11 Outfall	225.00						
C-permethrin+	24-96- Just downstream from Shady Lane Bridge	431.00						
	31-96- From Rt. 11 Outfall Pipe near Iron Kettle	76.60						
Propachlor+	1-95-30m downstream from Bonnybrook Rd.	3700.00						
	14-96- Just below High St. storm sewer Outfall	102.00						
	26-96- Mouth of TP Trib	3900.00						
	27-95- In All American Retention Pond	2300.00						
	29-95- At upper boundary of Sunday Farm	4200.00						
	30-96- Within oil boom at Rt. 11 Outfall	52.80						
Trifluralin+	7-95- Just upstream from 81 bridge	24.00						

Table 13. Sediment quality guidelines for samples taken from 1993- 2006.
Red highlighting indicates a violation of the standard, while green indicates a pesticide concentration below the standard (CCME 2002, FL DEP 1994, MacDonald et al. 2000, NOAA 1999). 'X' indicates the number above applies. No classification indicates that there are no sediment quality guidelines for that pesticide.
* CCME guideline only. +=Not analyzed in this study.

Pesticide	Sites found	Concentration (ppb)	MacDonald consensus-based TEC	MacDonald consensus-based PEC	NOAA and CCME TEL	NOAA and CCME PEL	FL DEP TEL	FL DEP PEL
Aldrin	5-93- TU Vince's Meadow	90.00						
	16-93- Just below McKnight St Oufall	25.00						
alpha-HCH	6-93- Just north of Boro Public Works Bldg	9.00						
beta-HCH	5-93- TU Vince's Meadow	14.00						
gamma-HCH (Lindane)	17-96- Just below McKnight St Outfall	3.25	M		H		H	
alpha-Chlordane	13-93- Just below High St storm sewer Outfall	5.00	M		M		H	
	15-93- Halfway down Biddle Mission Park	3.00	U		U		M	
	24-96- Just downstream from Shady Lane Bridge	13.60	M		H		H	
gamma-Chlordane	9-98- Mully Grub, below Hanover St. outfall	48.00	H		H		H	
	10-98- Mully Grub, below Bedford St.	4.10	M		U		M	
	11-98- Mouth of Mully Grub	11.00	M		H		H	
	13-93- Just below High St storm sewer Outfall	4.60	M		M		M	
	16-93- Just below McKnight St Oufall	11.00	M		H		H	
	20-93- Just below Media Outfall	24.00	H		H		H	
Chlomeb[+]	28-96- In All American Retention Pond	75.80						
Cyanazine[+]	16-93- Just below McKnight St Oufall	620.00						
	20-93- Just below Media Outfall	499.00						
4,4' DDD	9-98- Mully Grub, below Hanover St. outfall	31.00	H		H		H	
	19-06- Letort upstream from War College entrance	22.93	M		H		H	
	22-06- Letort at Harmony Hall Rd.	19.24	M		H		H	
	25-06- Letort at Shady Lane	18.84	M		H		H	
4,4' DDE	9-98- Mully Grub, below Hanover St. outfall	87.00	H		H		M	

	19-06- Letort upstream from War College entrance	26.88	M	H	M
	20-93- Just below Media Outfall	14.00	M	H	M
	22-06- Letort at Harmony Hall Rd.	51.86	H	H	M
	23-95- Just downstream from Shady Lane Bridge	45.80	H	H	M
	25-06- Letort at Shady Lane	48.65	H	H	M
4,4' DDT	9-98- Mully Grub, below Hanover St. outfall	50.00	M	H*	H
	11-98- Mouth of Mully Grub	9.80	M	H	H
	12-98- Downstream of Mully Grub confluence	3.80	U	M	M
	20-93- Just below Media Outfall	20.00	M	H	H
	21-96- Just below Media Outfall	15.60	M	H	H
	23-95- Just downstream from Shady Lane Bridge	17.00	M	H	H
	24-96- Just downstream from Shady Lane Bridge	42.40	M	H	H
	26-96- Upstream from mouth of TP Trib	20.80	M	H	H
	33-95- 200m downstream from Rt. 11 Overpass	29.00	M	H	H
Dieldrin	17-96- Just below McKnight St Outfall	24.20	M	H	H
	22-06- Letort at Harmony Hall Rd.	13.82	M	H	H
	25-06- Letort at Shady Lane	9.57	M	H	H
Endosulfan I	15-93- Halfway down Biddle Mission Park	3.00			
	16-93- Just below McKnight St Oufall	32.00			
	20-93- Just below Media Outfall	14.00			
Endosulfan II	20-93- Just below Media Outfall	4.95			
Endosulfan sulfate	16-96- Just downstream from Shady Lane Bridge	28.20			
Endrin	9-98- Mully Grub, below Hanover St. outfall	120.00	M		
	10-98- Mully Grub, below Bedford St.	15.00	M		
	11-98- Mouth of Mully Grub	36.00	M		
	20-93- Just below Media Outfall	15.00	M		
	21-96- Just below Media Outfall	17.90	M		

	24-96- Just downstream from Shady Lane Bridge	44.80	M					
Endrin aldehyde	17-96- Just below McKnight St Outfall	47.80						
	21-96- Just below Media Outfall	60.90						
	24-96- Just downstream from Shady Lane Bridge	149.00						
	26-96- Upstream from mouth of TP Trib	41.30						
	28-96- In All American Retention Pond	11.60						
	31-96- From Rt. 11 Outfall Pipe near Iron Kettle	31.80						
Endrin ketone	9-98- Mully Grub, below Hanover St. outfall	240.00						
Heptachlor	8-98- Upstream of Mully Grub confluence	14.00						
	10-98- Mully Grub, below Bedford St.	6.40						
	16-93- Just below McKnight St Oufall	8.80						
	23-95- Just downstream from Shady Lane Bridge	14.00						
Heptachlor epoxide	17-96- Just below McKnight St Outfall	1.67	U		M			
	24-96- Just downstream from Shady Lane Bridge	5.99	M		H			
	30-96- Within oil boom at Rt. 11 Outfall	2.86	M		H			
Hexachlorobenzene[+]	9-98- Mully Grub, below Hanover St. outfall	300.00						
Methoxychlor	14-96- Just below High St. storm sewer Outfall	46.20						
	17-96- Just below McKnight St Outfall	47.90						
	20-93- Just below Media Outfall	53.00						
	24-96- Just downstream from Shady Lane Bridge	182.00						
Metolachlor[+]	3-95- 30m downstream from quarry outfall	220.00						
	15-93- Halfway down Biddle Mission Park	235.00						
	24-96- Just downstream from Shady Lane Bridge	337.00						
	30-96- Within oil boom at Rt. 11 Outfall	225.00						
C-permethrin[+]	24-96- Just downstream from Shady Lane	431.00						

	Bridge							
	31-96- From Rt. 11 Outfall Pipe near Iron Kettle	76.60						
Propachlor+	1-95-30m downstream from Bonnybrook Rd.	3700.00						
	14-96- Just below High St. storm sewer Outfall	102.00						
	26-96- Mouth of TP Trib	3900.00						
	27-95- In All American Retention Pond	2300.00						
	29-95- At upper boundary of Sunday Farm	4200.00						
	30-96- Within oil boom at Rt. 11 Outfall	52.80						
Trifluralin+	7-95- Just upstream from 81 bridge	24.00						

Table 14. Individual pollution classification based on sediment quality guidelines for samples taken from 1993-2006.
H indicates a site that is heavily polluted, M indicates moderately polluted, and U indicates unpolluted (CCME 2002, FL DEP 1994, MacDonald et al. 2000, NOAA 1999). No classification indicates that there are no sediment quality guidelines for that pesticide.
*= CCME guideline only. += Not analyzed in this study.

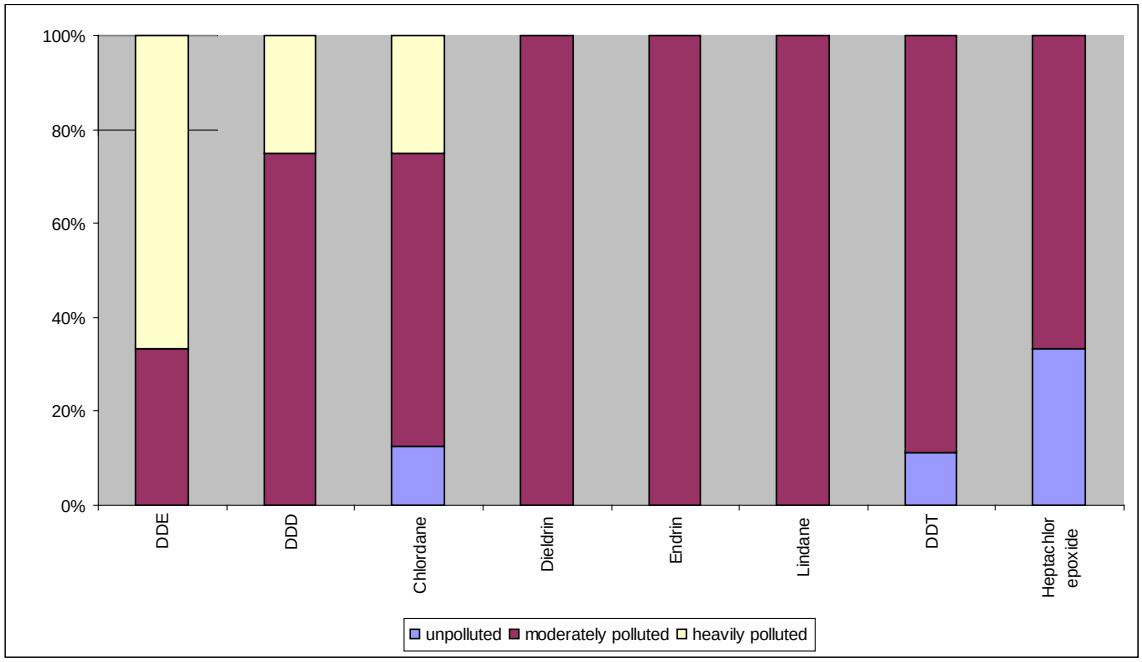


Figure 12. The percentages of unpolluted, moderately polluted, and heavily polluted sites based on sediment data from the 1993-2006 study period, arranged in general order of pollution. Each positive incidence of a pesticide was included. Note: aldrin, endosulfan, heptachlor, and methoxychlor are not included, as sediment quality guidelines have not been established to date.

Analysis of individual chemicals over space and time

Aldrin/Dieldrin: Background

Aldrin and dieldrin were widely used from the 1950s to the 1970s on cotton, corn, and citrus crops (ATSDR Aldrin/Dieldrin 2002; Nowell et al. 1999). Because of human and environmental health concerns, the EPA banned these pesticides in 1974, except to control termites; all uses were banned in 1987 (ATSDR Aldrin/Dieldrin 2002).

Aldrin is a soil insecticide that is applied in the field and breaks down to dieldrin (an epoxide) quickly in the body and the environment (ATSDR Aldrin/Dieldrin 2002; Matsumura 1985). For this reason, aldrin is only found in areas near application sites (Blus 1995). While aldrin is a cyclodiene insecticide (almost insoluble in water) and as such is considered stable and not widely capable of breakdown by microorganisms, aldrin is less

persistent than other organochlorine pesticides, with a soil half-life of 20-100 days (Table 15; Matsumura 1973; Matsumura 1985). Organisms focus their degradation processes on the non-chlorinated rings, which lets the chlorine-containing rings persist. An epoxidation reaction allows aldrin to be converted to dieldrin. Dieldrin was used in soil to control insects (for both agriculture and public health) and termites (Nowell et al. 1999). It is also possible for organisms to reduce dieldrin to create aldrin.

Pesticide	**Half-life (in soil)**
Aldrin	20-100 days
Dieldrin	2.5-5 years
Chlordane	1-4 years
DDD	730-5690 days
DDE	730-5690 days
DDT	2-15 years
Endosulfan I	35 days
Endosulfan II	150 days
Endrin	12 years
Heptachlor	0.75-2 years
Lindane	191-423 days
Methoxychlor	57-300 days

Table 15. Half-lives of pesticides in soil (ATSDR; Nowell et al. 1999; PMEP 1993; UNEP 2002). This information must be used for relative comparisons of persistence since no analogous information exists for sediments.

Dieldrin, however, is even more persistent in the environment. Dieldrin is considered the most toxic commercial insecticide (Nyangababo et al. 2005). While concentrations for dieldrin in the water column are low due to a decreased ability to break down in water, the pesticide strongly sorbs to soil and sediment and has a strong tendency to bioaccumulate (Nowell et al. 1999). This means that sediment may serve as a sink for the toxin, which would allow traces of dieldrin to pass into the water column over time (Nyangababo et al. 2005). Dieldrin is slowly transformed by soil microbes in aerobic or anaerobic conditions. For example, only 10 out of 600 soil microbes were able to degrade dieldrin in a previous

study (Nowell et al. 1999). Decomposition of dieldrin is only known to occur in the presence of strong acids or strong ultraviolet light (Matsumura 1985).

There is great concern about the effect of these chemicals on the mortality of wildlife, especially birds. Aldrin-treated rice feed caused the death of birds and invertebrates in Texas (Nyangababo et al. 2005). When dieldrin was used to control Japanese beetles in Illinois, it resulted in extreme mortality of most terrestrial mammals in the area (Nyangababo et al. 2005). The EPA has imposed a drinking water limit of 0.001 ppm and 0.002 ppm for aldrin and dieldrin, respectively (ATSDR Aldrin/Dieldrin 2002).

Aldrin/Dieldrin: Results

With a half-life of 20-100 days in soil, aldrin quickly breaks down to dieldrin (Table 15). The data indicate that aldrin became available in areas close to McKnight St. in 1993 and Vince's Meadow in 1993 (Figure 13). This could be possible through the introduction of soil contaminated with aldrin into the hydrologic system from stormwater runoff, from the disruption of previously buried contaminated stream sediment, or from continued use of the pesticide after it was banned. Dieldrin is very persistent in the environment, with a half-life of about 2.5-5 years in soil (Table 15; Nowell et al. 1999). The data follow this expected degradation behavior, most closely at McKnight St. (Figure 14; ATSDR Aldrin/Dieldrin 2002; Matsumura 1985). Inconsistencies in sampling make it difficult to determine patterns of breakdown at other sites. For example, Vince's Meadow was only sampled in 1993, and Harmony Hall Rd. was sampled only in 2006. Also, there was a ten year period without sampling at McKnight St. and Shady Lane.

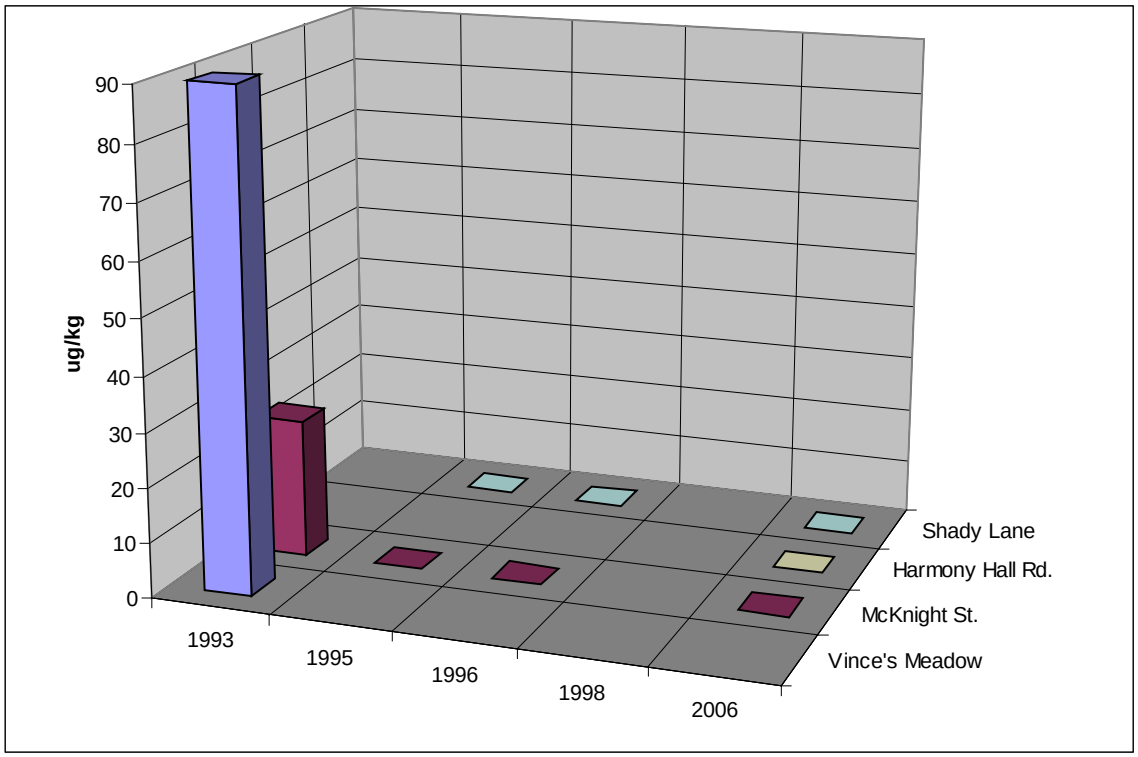


Figure 13. Concentrations of aldrin found in sites in the Letort Spring Run.

Sediment quality guidelines have been established for dieldrin, but not for aldrin (Table 13). All three instances of dieldrin found in the study sites (McKnight St. in 1996, Harmony Hall 2006, and Shady Lane 2006) were classified as moderately polluted in sediment, as concentrations exceeded the TEC, but did not exceed the PEC (Table 13). While dieldrin was moderately polluted at McKnight St. in 1996, no dieldrin was detected in 2006 (Figure 14). It is possible that dieldrin is coming from the urban area of Carlisle, as it is found at sites just downstream of this region. It is also feasible that aldrin was used along Harmony Hall and Shady Lane in previous years (possibly from agricultural applications), and now the persistent breakdown product of dieldrin is left in the sediment. A housing development has been under construction at Harmony Hall Rd. for the last few years. It is possible that soil contaminated with aldrin or dieldrin is being disturbed in this process and has been transported to the Letort. Additionally, Cumberland Valley Trout Unlimited

conducted a restoration project along a 1000 foot stretch of the Letort at Shady Lane in early 2002 (Cumberland Valley Trout Unlimited 2008). The project involved reshaping the channel, installing gravel spawning areas, and doing riparian buffer zone plantings. Sediment and soil were likely disturbed in this process, which could have added aldrin contaminated soil to the aquatic system at this site, accounting for the presence of dieldrin in 2006. In summary, degradation patterns are seen as aldrin disappears from Vince's Meadow while at McKnight St. aldrin moves to dieldrin and then disappears. The appearance of dieldrin in 2006 at Harmony Hall and Shady Lane may be due to land disturbances at these sites.

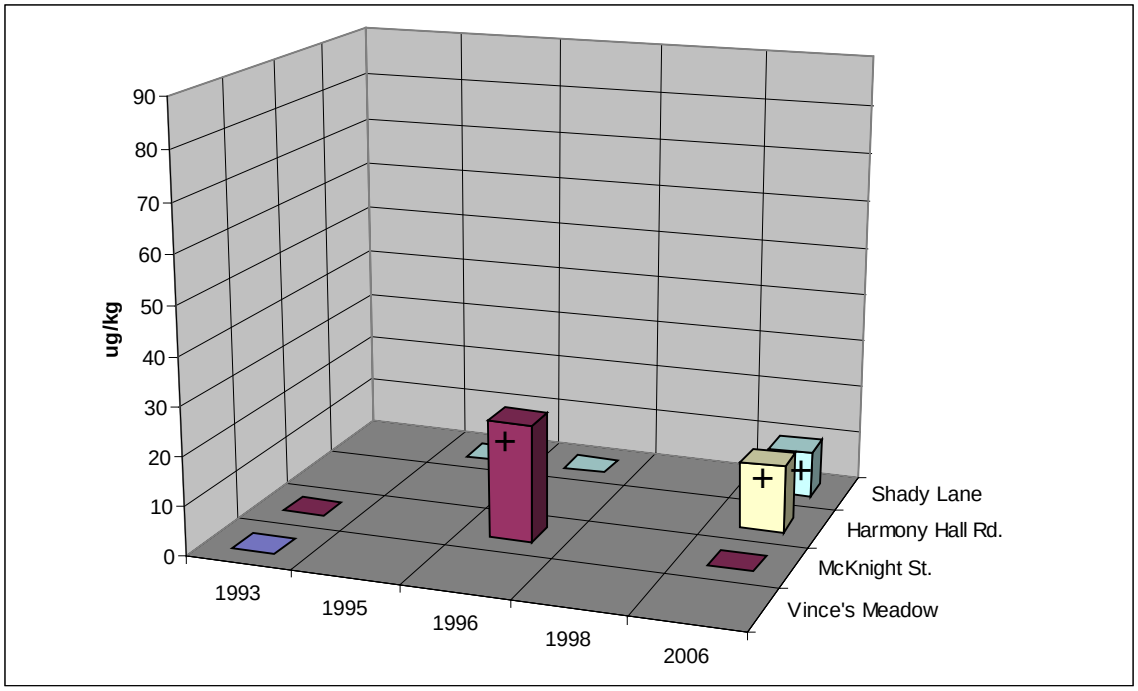


Figure 14. Concentrations of dieldrin found in sites in the Letort Spring Run. +indicates a violation of the TEC.

Chlordane: Background

Chlordane was used as an insecticide on corn and citrus crops, as well as home lawns and gardens, beginning in 1948 (ATDSR Chlordane 1994). Chlordane is not a single

chemical; rather, it is a mixture of two isomers (alpha chlordane and gamma chlordane) plus at least 120 other chemical compounds derived from cyclopentadiene and hexachlorocyclopentadiene (Nowell et al. 1999; UNEP 2002). Chlordane and its metabolites are frequently found in low concentrations in environmental samples (Blus 1995). Chlordane was used on lawns, golf courses, and some crops before being limited to use for termite control in 1983, with all uses banned in 1988 (ATDSR Chlordane 1994). Gamma chlordane is known to be more persistent in the environment, and alpha chlordane can hydrolyze under alkaline conditions (Nowell et al. 1999). The pesticide has been known to cause decreases in bird populations, and bioaccumulates in fish, birds, and mammals (ATSDR Chlordane 1994; Blus 1995). These effects are still being seen today, most likely related to its past uses.

Chlordane is also a cyclodiene insecticide and is considered stable and not widely capable of breakdown by microorganisms (Matsumura 1973). Chlordane binds tightly to soil particles, and can remain in soil for 20 years (ATSDR Chlordane 1994). A very slow breakdown process via evaporation to the air occurs from these soil particles (ATSDR Chlordane 1994). Chlordane is not likely to enter groundwater and does not break down easily in the water column (ATSDR Chlordane 1994). The EPA has set a limit for drinking water at 0.002 ppm (ATSDR Chlordane 1994).

Chlordane: Results

Sediment quality guidelines have been established for the total amount of chlordane (Table 13). Chlordane has varied widespread uses, and is therefore a commonly detected pesticide in stream sediment (Nowell et al. 1999). Five sites are moderately polluted for chlordane in sediment (High St. storm sewer in 1993, McKnight St. in 1993, Shady Lane in 1996, Mully

Grub at Bedford St. in 1998, and the Mully Grub at the mouth in 1998), two sites are heavily polluted (Media St. in 1993 and the Mully Grub at Hanover St. in 1998), and one site (Biddle Mission Park in 1993) had unpolluted sediment (Figure 15). The two heavily polluted sites are located at major stormwater outfalls that drain portions of the urban area of Carlisle. Most of the moderately polluted sites are located in the urban section of Carlisle, as well as the only unpolluted site along Biddle Mission Park. It is possible that chlordane entering the stream at the High St. storm sewer is diluted downstream at Biddle Mission Park, and increases again at McKnight St. due to the stormwater outfall located at the site.

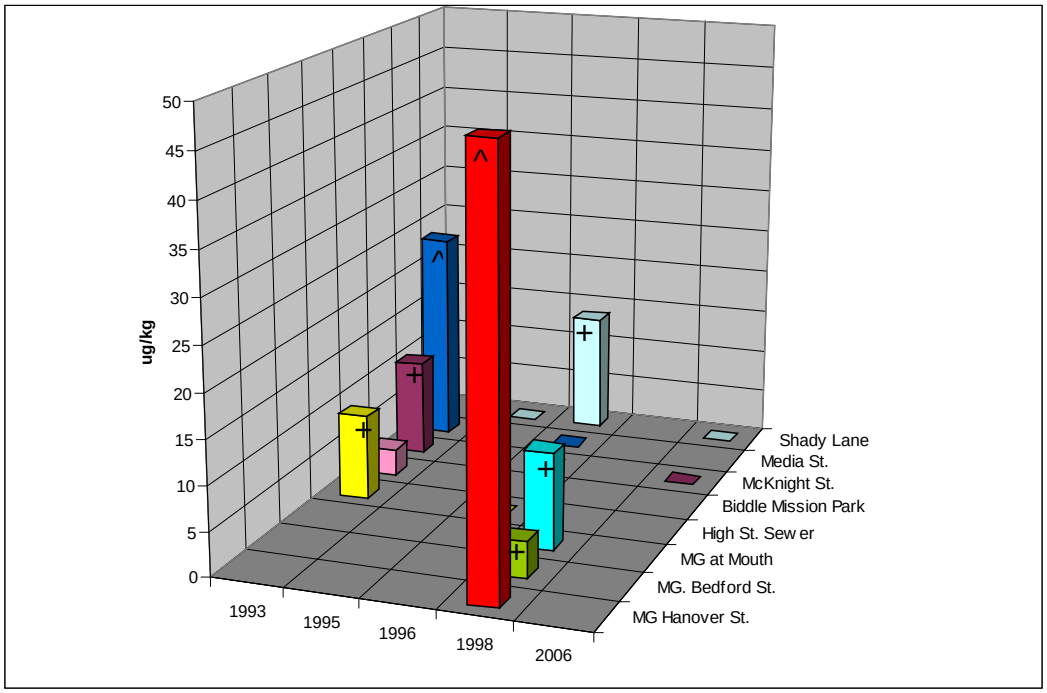


Figure 15. Concentrations of total chlordane (alpha + gamma) found in sites in the Letort Spring Run. + indicates a violation of the TEC, and ^ indicates a violation of the PEC.

While Shady Lane was moderately polluted in 1996, chlordane was undetected in 1995 and 2006. This indicates an addition of chlordane at this site between 1995 and 1996, possibly from the runoff of contaminated soil or an unknown disturbance. It is also possible that chlordane was used after it was banned in this area. Chlordane appears to break down

very quickly in the Letort, which is in accordance with its soil half-life that ranges from 1 to 4 years (Table 15). In the 2006 samples at all sites, chlordane was not found. Chlordane was found to have a mean sediment half-life ranging from 7.7 to 17 years in one study (TNRCC 2001). Even though chlordane may have a long half-life in sediment as shown in one study, it does not seem to follow this trend in the Letort. At Media St, the concentration of chlordane disappeared faster than expected (from 24 ug/kg in 1993 to 0 ug/kg in 1996). Based on the lowest end of the soil half-life for this pesticide, a concentration of 3 ug/kg would have been expected. This again highlights the challenges in using soil half-lives to predict degradation behavior in stream sediment. The concentrations of alpha and gamma chlordane vary in the Letort, with both isomers being found together at only one site (Figures 16 and 17; High St. storm sewer in 1993). Gamma chlordane tends to be found closer to major stormwater outfalls, compared to alpha chlordane. There is little to no literature available about the differences in fate between these two isomers, and sediment quality criteria have only been established for total chlordane. In summary, chlordane was commonly found in urban areas and seems to break down faster than expected in the Letort. Alpha and gamma chlordane vary, with gamma chlordane being found more frequently in the Letort.

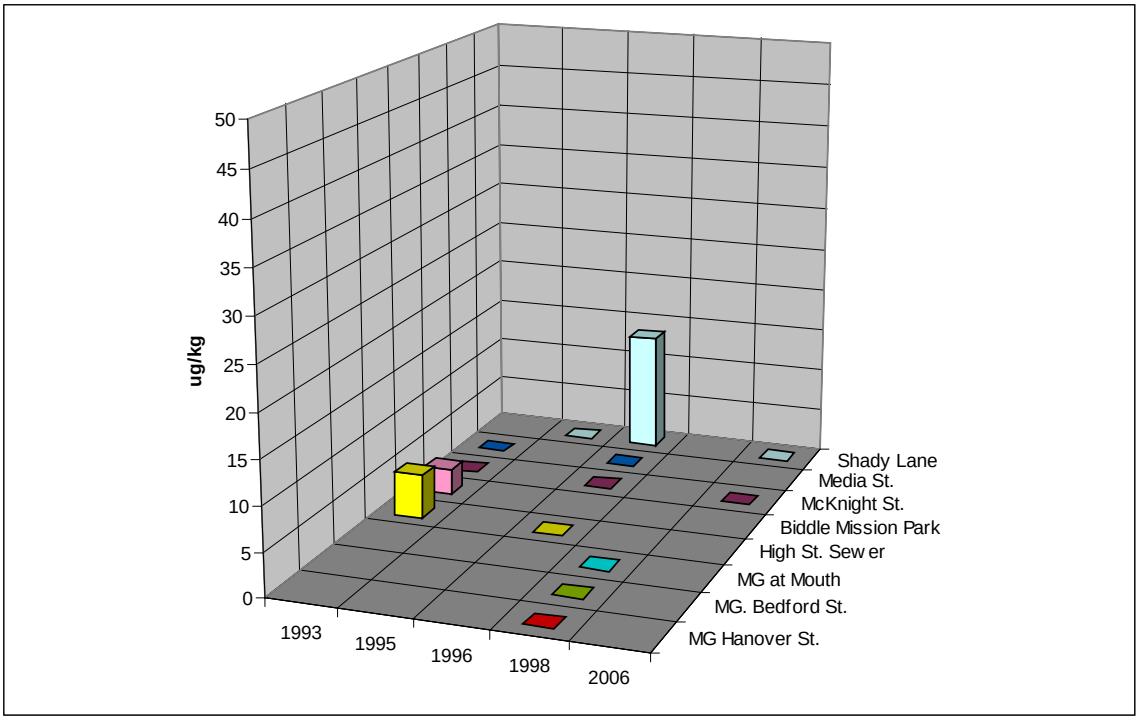


Figure 16. Concentrations of alpha chlordane found in sites in the Letort Spring Run.

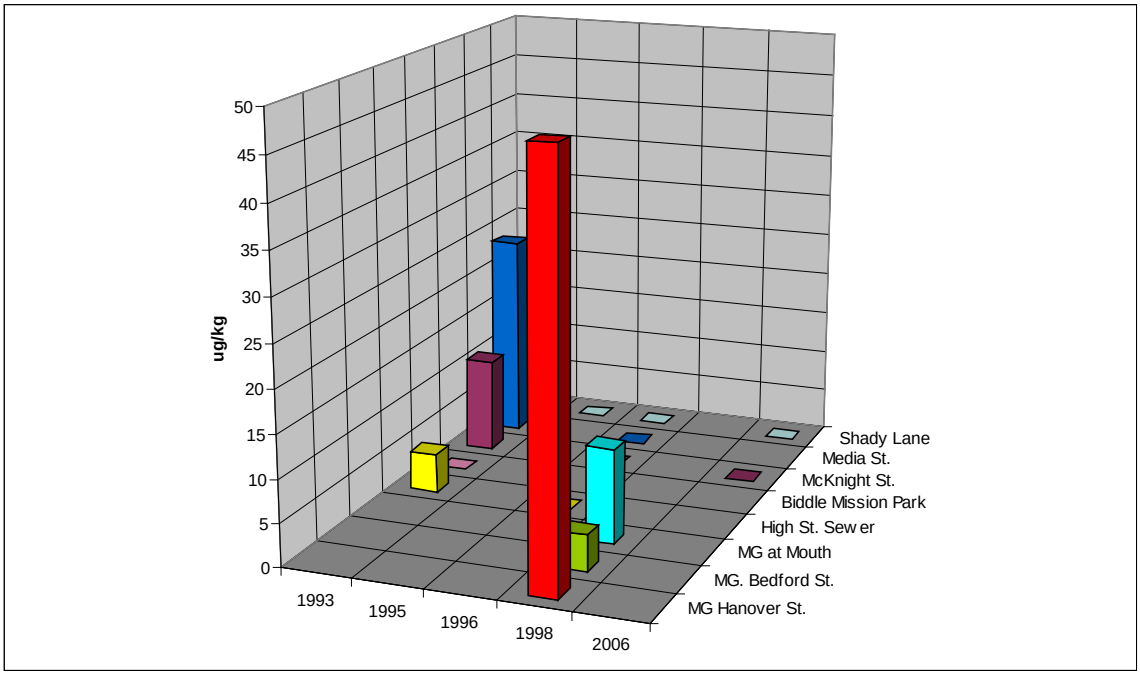


Figure 17. Concentrations of gamma chlordane found in sites in the Letort Spring Run.

DDT and metabolites (DDD and DDE): Background

DDT (dichlorodiphenyltrichloroethane) is an insecticide first synthesized in 1874 that is known to lead to decreases in bird populations due to its tendency to bioaccumulate (Blus 1995). DDE (dichlorodiphenyldichloroethylene), a metabolite of DDT, is largely responsible for the negative effect on avian communities, as it causes eggshell thinning and reproductive problems. DDE residues are normally found in the highest concentration compared to other metabolites as well as in higher trophic levels. After DDT is applied, DDE increases due to a breakdown of the parent compound. DDD (dichlorodiphenyldichloroethane), another breakdown product of DDT, was also used as a pesticide, but has since been banned (ATSDR DDT 2002). DDD is only known to have caused declines in two species: the western grebe (*Aeschmorphorus occidentalis*) and the common loon (*Gavia immer*) (Edwards 1973).

DDT usage peaked in the United States at 80 millions pounds in 1959, but decreased to 12 million by 1972 due to the development of resistance among target species (Nowell et al. 1999). Between 1970 and 1972, DDT was mostly used on cotton, soybean, and peanut crops (Nowell et al. 1999). DDT was also used in urban environments for control of residential pests and municipal control of disease vectors and nuisance insects (Nowell et al. 1999). DDT is of particular concern because it is known to quickly concentrate into the bottom sediment upon entering an aquatic system and bioaccumulate (Edwards 1973). The EPA banned the chemical in 1972, but it continues to be used to control malaria in some countries (ATSDR DDT 2002). DDT is not currently manufactured in the United States, but the federal government does not currently have the authority to prohibit a company from choosing to produce the chemical in the future (CEC 2001). As recently as 1990, it was

found to be on hand (and presumably still being used) in a survey of American households (Nowell et al. 1999).

DDT, DDD, and DDE in air are rapidly broken down by sunlight and have an atmospheric half-life of 2 days (ATSDR DDT 2002). The chemicals bind tightly to soil where DDT is degraded to DDD and DDE by microorganisms. DDT initially breaks down rapidly, but as time passes, the rate of evaporation from soil slows. Some DDT moves into areas in soil that are too small for microorganisms to break it down. If the soil is disturbed and DDT is moved out from these small areas, the chemical will become available in the system again, even after the initial decrease in concentration (ATSDR DDT 2002). DDT is degraded by microorganisms to form chlorinated analogues including DDD (TDE), DDMS (2,2-dichlorodiphenyl-1-monochlorinated saturated ethane), and DDNS (2,2-dichlorodiphenyl-1-nonechlorinated saturated ethane) in a process known as reductive dechlorination reaction (hydrogen atoms replace chlorine) and oxidative system (Matsumura 1973). Later enzymatic reactions occur to form either dicofol (an organochlorine miticide) and FW-152 (2,2-dichloro-1,1-bis(4-chlorophenyl)ethanol, a metabolite) or DDE, DDMU (2,2-dichlorodiphenyl-1-monochlorinated unsaturated ethylene), and DDNU. Dehydrochlorination (removal of chlorine atom from the original molecule and a hydrogen atom from the adjacent carbon) also takes place, where DDT changes to become DDE (Matsumura 1985). The presence of iron, aluminum, or chromium salts catalyzes the reaction. (Matsumura 1985). It is of interest to note that DDE is nontoxic to insects (Matsumura 1985). Smaller fish are more sensitive to DDT than larger fish (Extoxnet 1996). DDT and DDD also have greater toxicity in colder temperatures (Mayer et al. 1994). The

chemicals do not dissolve easily in water, and the EPA has not established drinking water criteria (ATSDR DDT 2002).

In soil, DDT has a half-life ranging from 2-15 years (varying with soil type) based on lab and field plot estimates (Table 15; ATSDR DDT 2002). More recent studies indicate that the half-life in soil may be 15 years or greater (Nowell et al. 1999). The half-lives of DDD are DDE are estimated to be 730-5690 days (2-15.5 years) in soil (Nowell et al. 1999). Additionally, DDT was found to have a mean sediment half-life of 7.2-18.8 years in one study (ATSDR DDT 2002; TNRCC 2001). Another study that analyzed DDT concentrations in soil and stream sediment indicates that DDT breaks down faster once it has entered the aquatic system (Agee 1986). The composition of total DDT was 60% DDT and <10% DDD in contaminated soils and <20% DDT and >20% DDD in the river downstream from the area of contamination.

DDT and metabolites (DDD and DDE): Results

Sediment quality guidelines have been established for DDD, DDE, and DDT (Table 13). Eight of nine sediment sites were moderately polluted for DDT, and one site (downstream of the Mully Grub confluence in 1998) was unpolluted, likely due to dilution as the Mully Grub meets the Letort (Figure 18). DDD was moderately polluted in sediment at three sites in the Letort (Upstream of the War College in 2006, Harmony Hall Rd. in 2006, and Shady Lane in 2006) (Figure 19). One site, the Mully Grub at Hanover St. in 1998, was heavily polluted. Four of the sites with DDE are heavily polluted (Shady Lane in 1995 and 2006, Mully Grub at Hanover St. in 1998, and Harmony Hall in 2006) and 2 sites (Media St. in 1993 and upstream of the War College in 2006) are moderately polluted (Figure 20). Mully Grub at Hanover Street may be heavily polluted with DDD and DDE since it is a

major stormwater outfall for a portion of urban Carlisle. As previously stated, development and restoration projects at Harmony Hall and Shady Lane in 2006 may explain the heavy contamination of DDE in sediment at these sites.

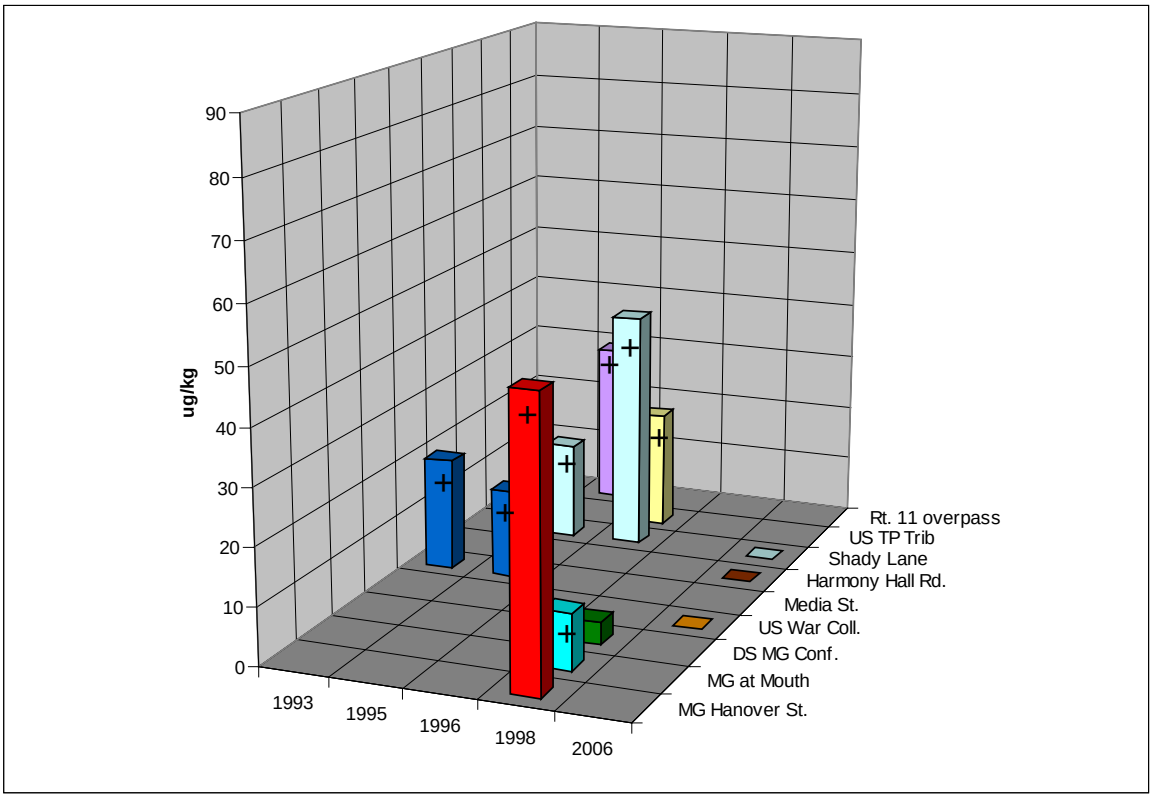


Figure 18. Concentrations of DDT found in sites in the Letort Spring Run. + indicates a violation of the TEC, and ^ indicates a violation of the PEC.

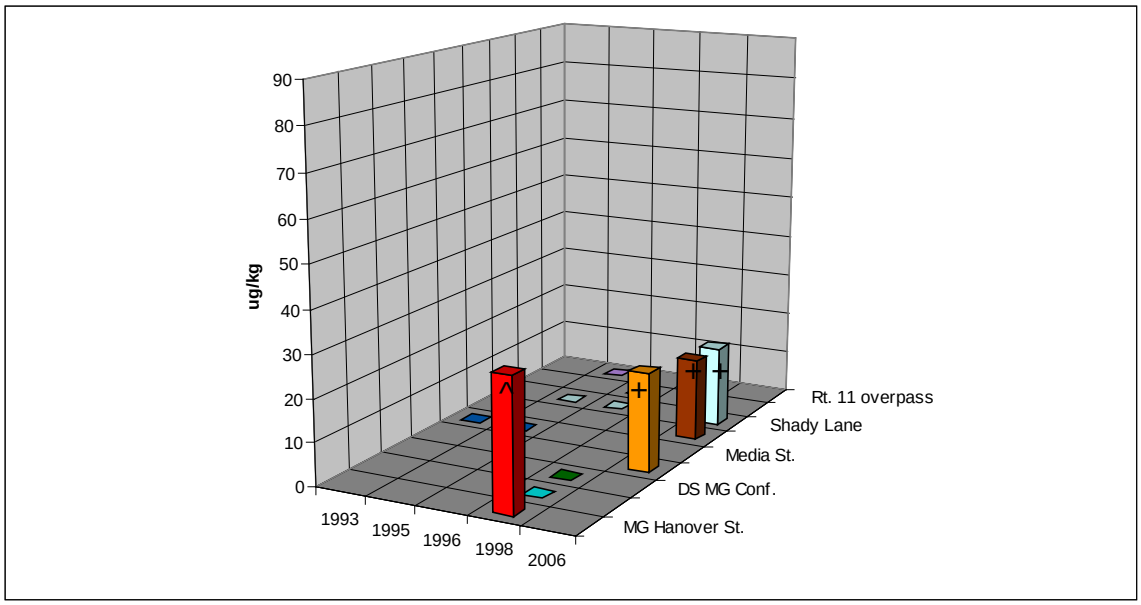


Figure 19. Concentrations of DDD found in sites in the Letort Spring Run. + indicates a violation of the TEC, and ^ indicates a violation of the PEC.

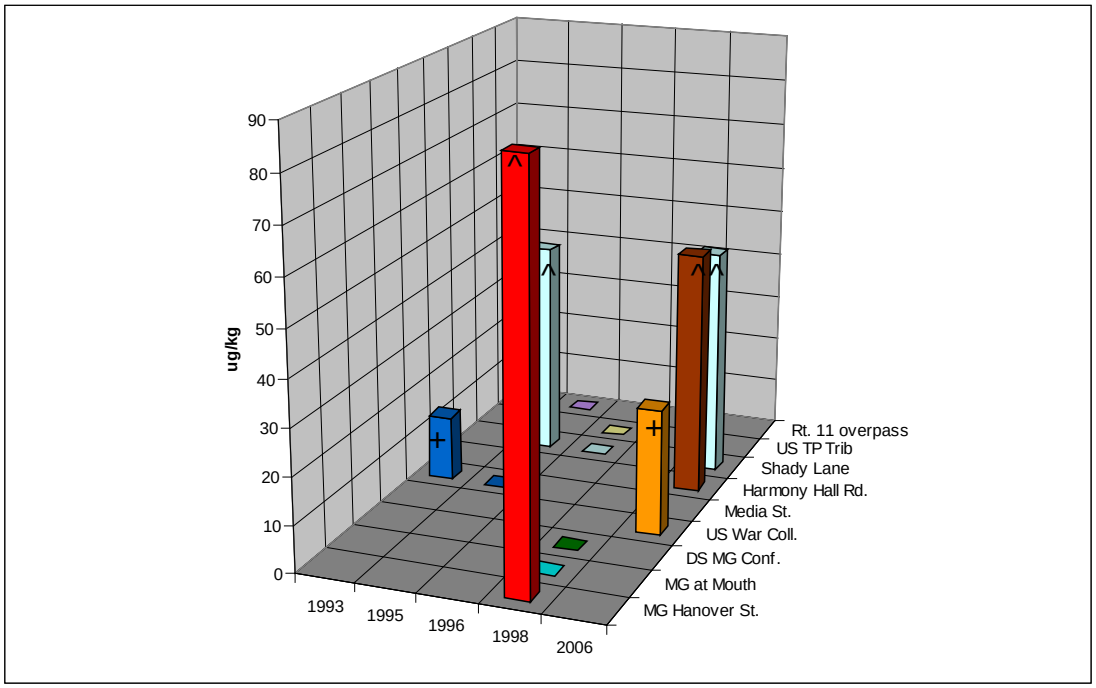
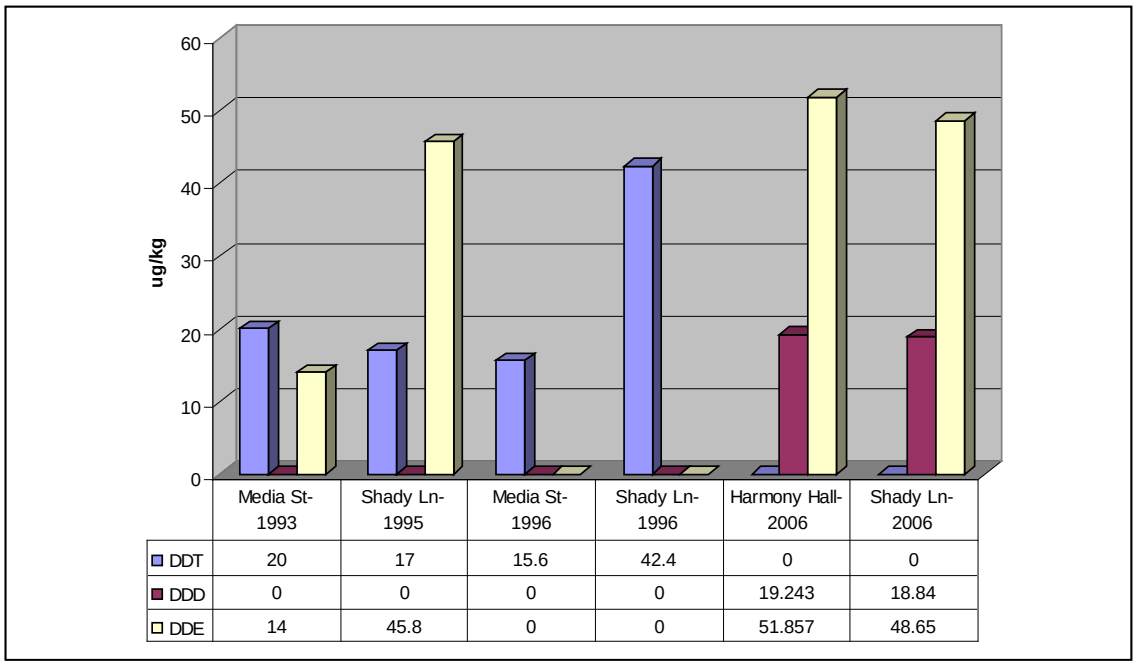


Figure 20. Concentrations of DDE found in sites in the Letort Spring Run. + indicates a violation of the TEC, and ^ indicates a violation of the PEC.

Media St. and Shady Lane seem to follow the same pattern of degradation over time. First, DDT and DDE are present (in 1993 at Media St., and in 1995 at Shady Lane), followed by DDT (at 1996 in both sites), and lastly DDD and DDE remain in the system (in 2006 at Shady Lane) (Figure 21). While Media St. was not sampled in 2006, the similarities with Shady Lane over time indicate that the concentrations of DDT and its metabolites might be similar to those at Shady Lane in 2006. The persistence of DDT at the 1996 samples may be due to DDT moving to small areas in sediment. This limits the efficacy of breakdown that can be performed by microorganisms (ATSDR DDT 2002). It is not known why only the parent compound (DDT) is present in the intermediate years. In 2006, DDD and DDE were present at Harmony Hall and Shady Lane (Figure 21). The concentrations at Harmony Hall are very similar to those at Shady Lane. This suggests that 1995 and 1996 concentrations at Harmony Hall (not measured) could have been similar to the readings at Shady Lane from 1995 and 1996. In summary, there is evidence that DDT is degrading into its breakdown products of DDD and DDE. These metabolites were found at concentrations that are considered to be heavily contaminated. Similar degradation patterns can be seen between sites, notably Media St., Shady Lane, and Harmony Hall.



	Media St-1993	Shady Ln-1995	Media St-1996	Shady Ln-1996	Harmony Hall-2006	Shady Ln-2006
DDT	20	17	15.6	42.4	0	0
DDD	0	0	0	0	19.243	18.84
DDE	14	45.8	0	0	51.857	48.65

Figure 21. DDT, DDD, and DDE concentrations found exhibiting the same degradation behavior at three sites in the Letort. Data are grouped by year to show similar degradation over time. Harmony Hall was used as a surrogate sample for Media St. to illustrate similar behavior (as Media St. was not sampled in 2006).

Endosulfan: Background

Endosulfan is a cyclodiene pesticide that is effective against insects and mites and is used on various crops including citrus, small fruit, coffee, grains, vegetables, and tobacco (Nowell et al. 1999; PMEP 1993). Endosulfan is also known to be very toxic to fish, and has been used as a piscicide (Nowell et al. 1999). This is worrisome since the Letort is a prized trout stream. Endosulfan use is not restricted in the United States at this point, although it is banned in the European Union. In February 2008, several groups, including the National Resources Defense Council, the Organic Consumers Association, and the United Farm Workers asked the EPA to consider banning the toxic chemical in the United States (Sass 2008). Endosulfan is composed of two isomers: endosulfan I (alpha) and endosulfan II (beta). Endosulfan does not readily breakdown in water and tends to stick to soil particles.

The breakdown of the chemical in acidic water is slower than under neutral conditions. In soil, endosulfan I has a half-life of 35 days, while endosulfan II has a half-life of 150 days based on the activity of fungi and bacteria (Nowell et al. 1999).

The pesticide breaks down into endosulfan sulfate. Endosulfan sulfate is known to be more persistent in the environment than its parent product, but has the same toxicity to rats and insects as technical endosulfan (Fukuto and Sims 1971; Nowell et al. 1999). More endosulfan sulfate forms when temperature increases. It is also thought that sunlight might contribute to starting the endosulfan sulfate formation process. The EPA currently recommends that endosulfan does not exceed 0.074 ppm in surface water (ATSDR Endosulfan 2007).

Endosulfan: Results

Sediment quality guidelines have not been established for endosulfan or endosulfan sulfate (Table 13). Again, concentrations are highest at stormwater outfalls that drain portions of urban Carlisle (Figure 22). Endosulfan appears to break down quickly in the Letort. Endosulfan I has a shorter half-life than endosulfan II, but when sites have been resampled in 2006, concentrations of zero were found for both isomers (Figures 23 and 24). Endosulfan II was only found at Media St. in 1993. The majority of endosulfan in the Letort was endosulfan I, the less persistent isomer. Even though endosulfan sulfate is more persistent than endosulfan, the concentration present in Shady Lane sediment in 1996 had fully broken down when resampled in 2006 (Figure 25). In summary, endosulfan was found in the highest concentrations close to stormwater outfalls in the urban section of the Letort. Endosulfan seems to quickly be removed from the system through its degradation to

endosulfan sulfate. Since the pesticide is still in use, concentrations may be found in sediment in the future (though there is a movement to ban the pesticide).

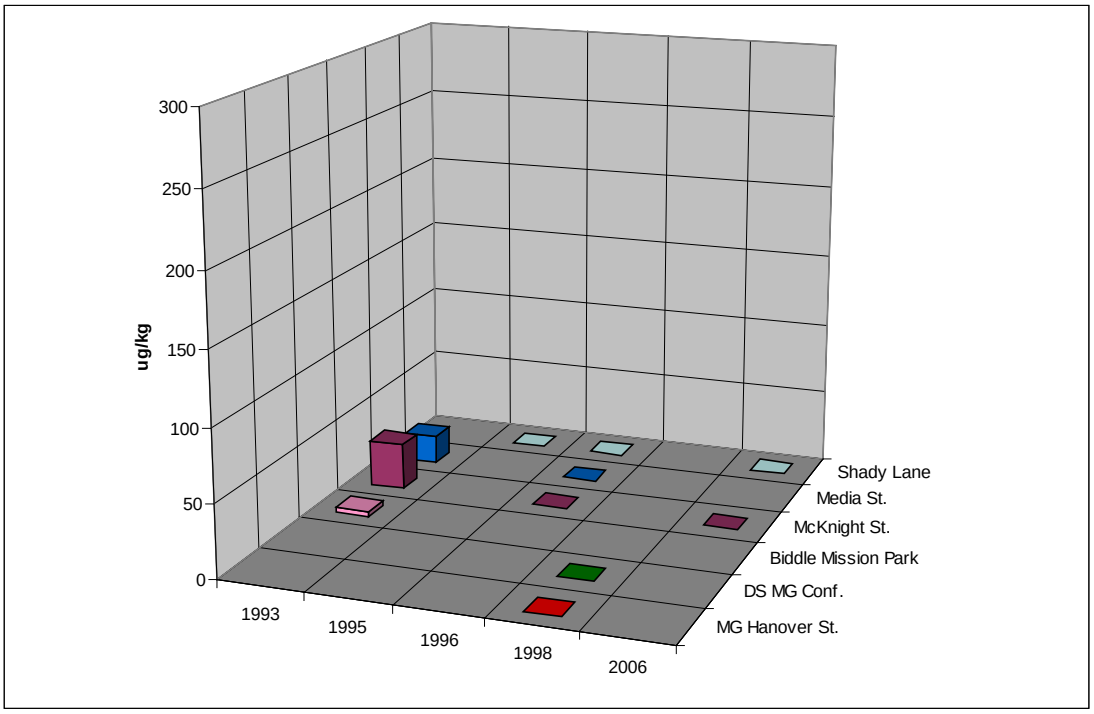


Figure 22. Concentrations of total endosulfan (I + II) found in sites in the Letort Spring Run.

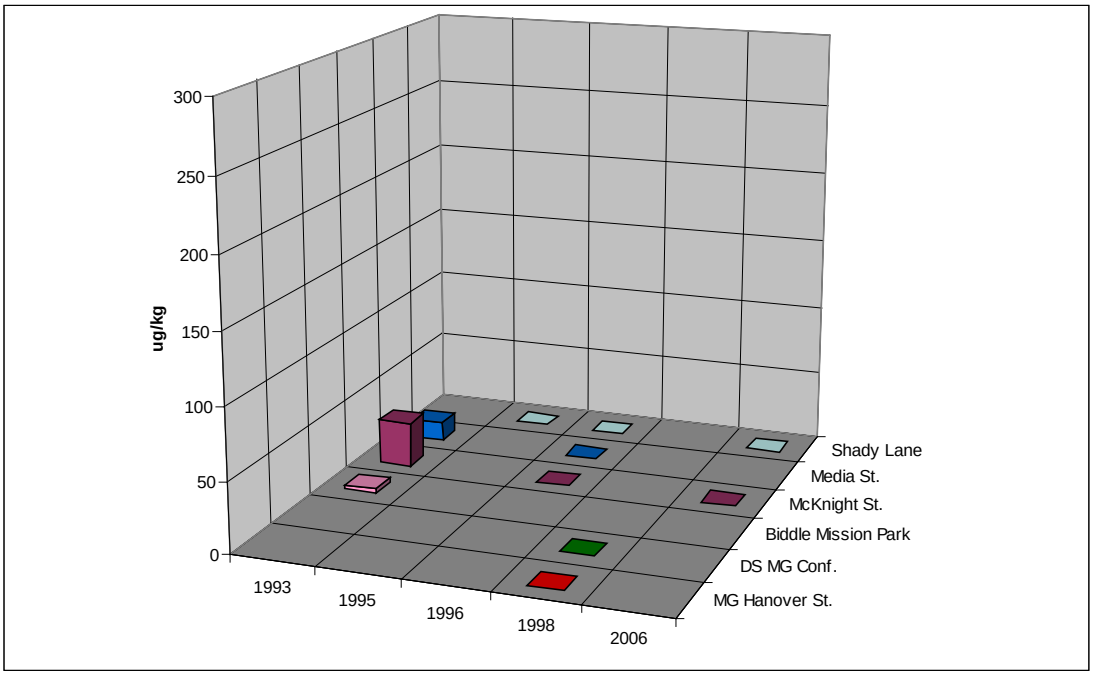


Figure 23. Concentrations of endosulfan I found in sites in the Letort Spring Run.

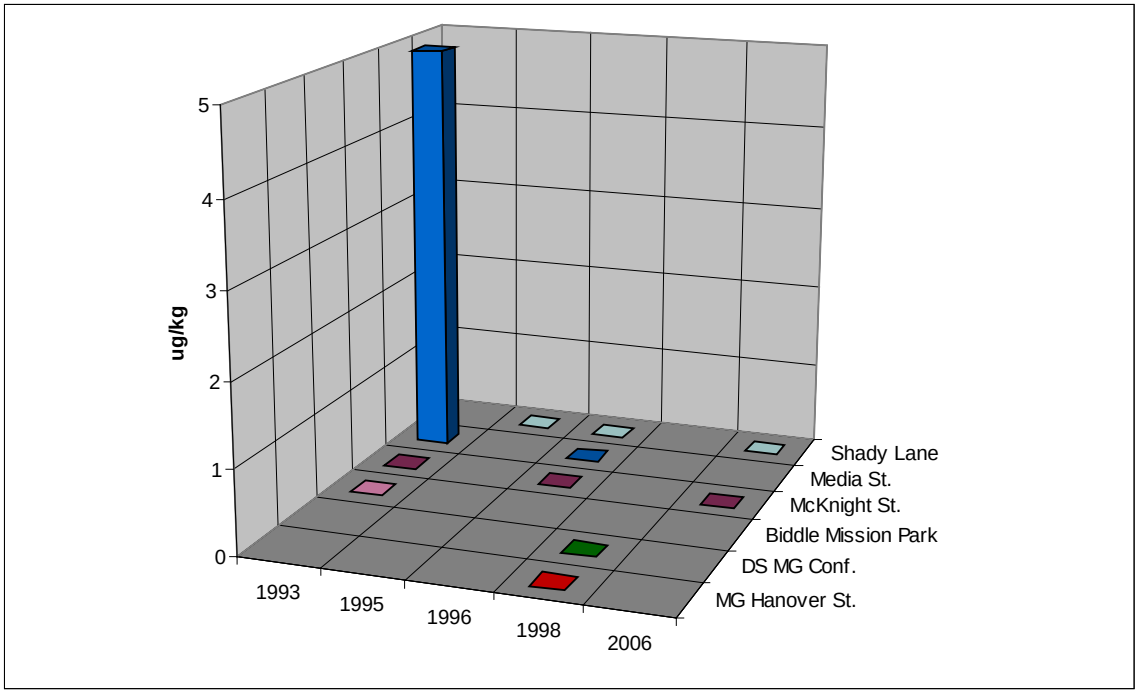


Figure 24. Concentrations of endosulfan II found in sites in the Letort Spring Run. Note that scale is different from other endosulfan graphs.

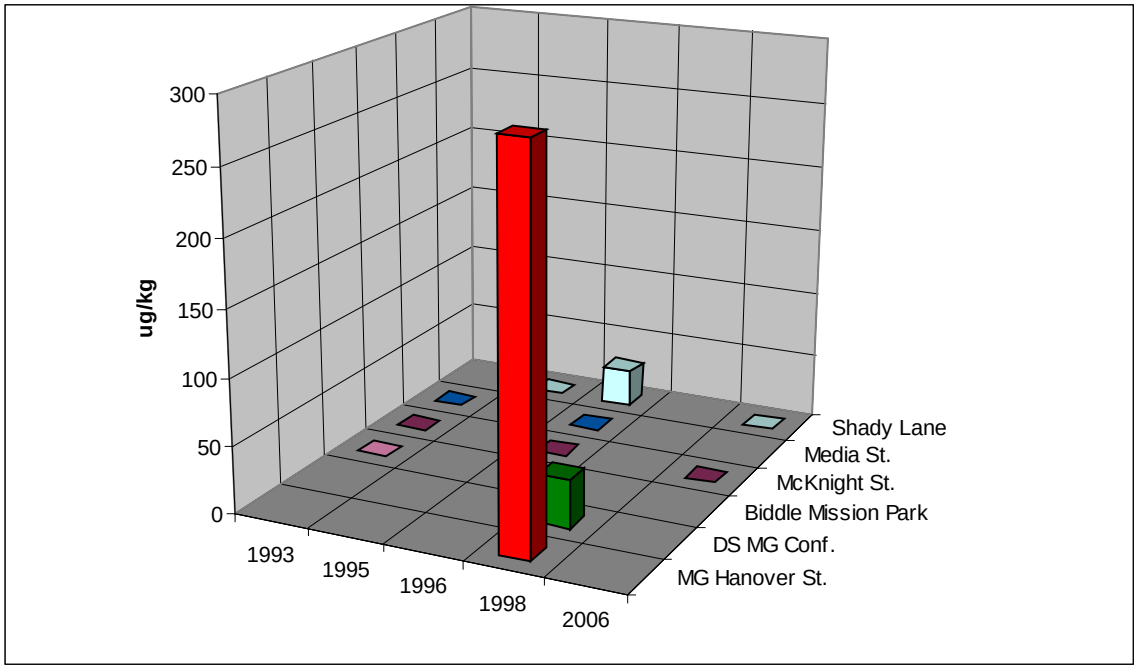


Figure 25. Concentrations of endosulfan sulfate found in sites in the Letort Spring Run.

Endrin: Background

Endrin (an isomer of dieldrin) was used to control insect, rodent, and bird populations (ATSDR Endrin 1996; Matsumura 1985). Endrin has a shorter half-life than other organochlorine pesticides in mammal and bird tissues (Blus 1995). Along with telodrin, it is considered the most acutely toxic organochlorine pesticide. In mammals, sometimes endrin is metabolized to 12-ketoendrine, which is more toxic than the parent chemical (Blus 1995). Endrin has not been made or sold in the United States for general use since 1986 (ATSDR Endrin 1996).

Endrin is also a cyclodiene insecticide and is considered stable and not widely capable of breakdown by microorganisms, but is easily degraded by heat and light (Matsumura 1973; Matsumura 1985). Endrin does not readily dissolve in water and is more likely to be found in sediment (ATSDR Endrin 1996). The half-life of endrin in soil varies, but it has been suggested that the chemical can persist for 10-12 years in soil (Table 15; ATSDR Endrin 1996). Epoxidation reactions convert isodrin (an organochlorine insecticide) to endrin. Epoxy rings are also rearranged in the breakdown of this chemical, which leads to the formation of ketones, aldehydes, and alcohols in the presence of high temperatures and sunlight. The significance of this step is not known, but it is possible that the rearrangements could allow the microbes to break the compound down further. Little is known about how endrin aldehyde (an impurity and breakdown product) and endrin ketone (a breakdown product when endrin is exposed to light) behave in the environment (ATSDR Endrin 1996). Endrin also has greater toxicity in warm water compared to cold water (Mayer 1994). The EPA has set a maximum drinking water limit at 0.0002 ppm (ATSDR Endrin 1996).

Endrin: Results

Sediment quality guidelines have been established only for endrin. All six instances of endrin found in the study sites (Media St. in 1993 and 1996, Shady Lane in 1996, Mully Grub at Hanover St. in 1998, Mully Grub at Bedford St. in 1998, and Mully Grub at the mouth in 1998) were classified as moderately polluted in sediment (Figure 26). Most of these sites are near urban stormwater outfalls, with the exception of Shady Lane. This site had a higher concentration of endrin in 1996 than Media St., which is located at an outfall. Endrin therefore entered the system somewhere between these two sites, possibly as runoff from contaminated soil, an event that disturbed sediment or soil, or the continued use of the chemical after it was banned.

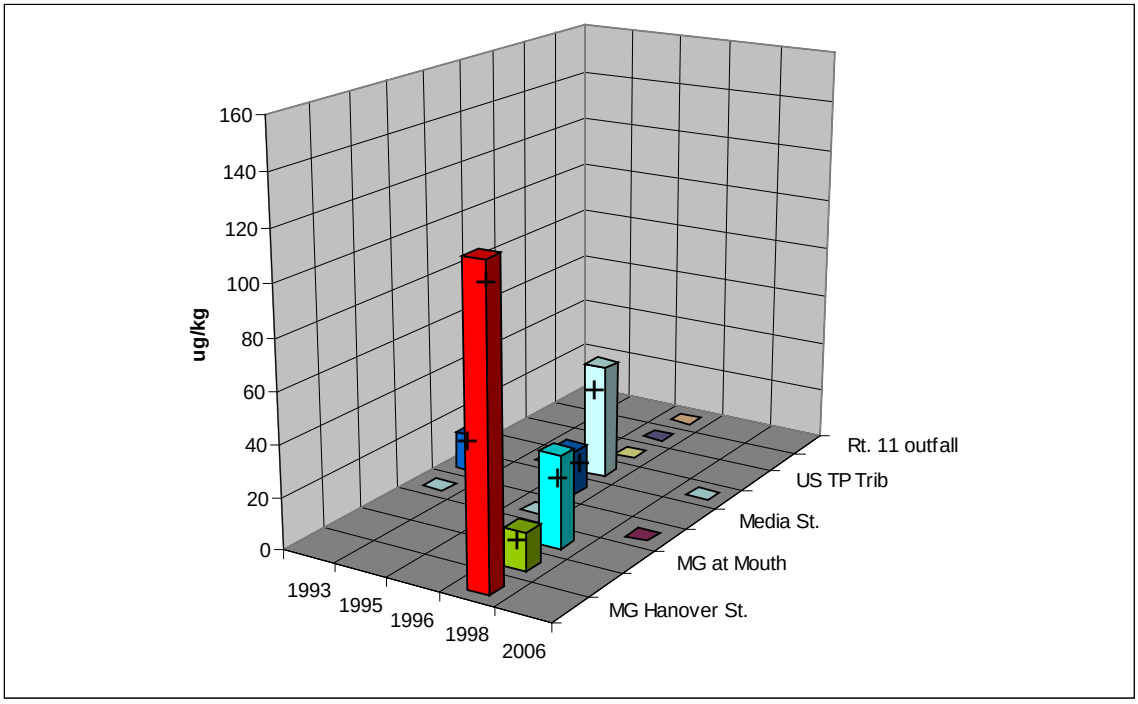


Figure 26. Concentrations of endrin found in sites in the Letort Spring Run. + indicates a violation of the TEC.

Endrin and endrin aldehyde are both absent in 2006 samples at Media St. and Shady Lane (Figures 26 and 27). Endrin aldehyde occurs more frequently than endrin in the Letort,

and this is a positive sign as it is a breakdown product of endrin. It is interesting to note that endrin aldehyde appears only in 1996 and downstream of High Street and the majority of the urban area of Carlisle. It is unknown why endrin aldehyde was only found in 1996. Two sites that had positive results for endrin aldehyde (McKnight St. and Shady Lane) both had concentrations of 0 ug/kg when resampled in 2006. It would be expected that the endrin aldehyde from 1996 would be broken down by now at other sites that have not been resampled. Endrin ketone appears only once, in the Mully Grub below the Hanover St. outfall, in 1998 (Figure 28). Unfortunately, very little is known about the fate of endrin aldehyde and endrin ketone. In summary, endrin was found at levels of moderate contamination in the Letort, mostly near stormwater outfalls. There is evidence that degradation is occurring, as endrin aldehyde is more common in sediment samples than its parent compound. Endrin breaks down quickly, as seen at McKnight St. and Shady Lane.

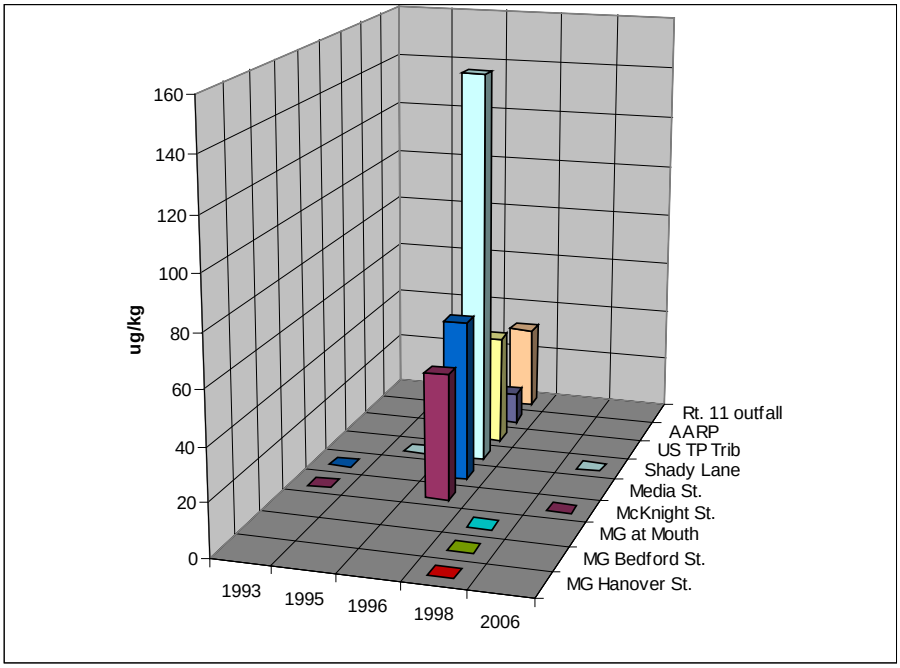


Figure 27. Concentrations of endrin aldehyde found in sites in the Letort Spring Run.

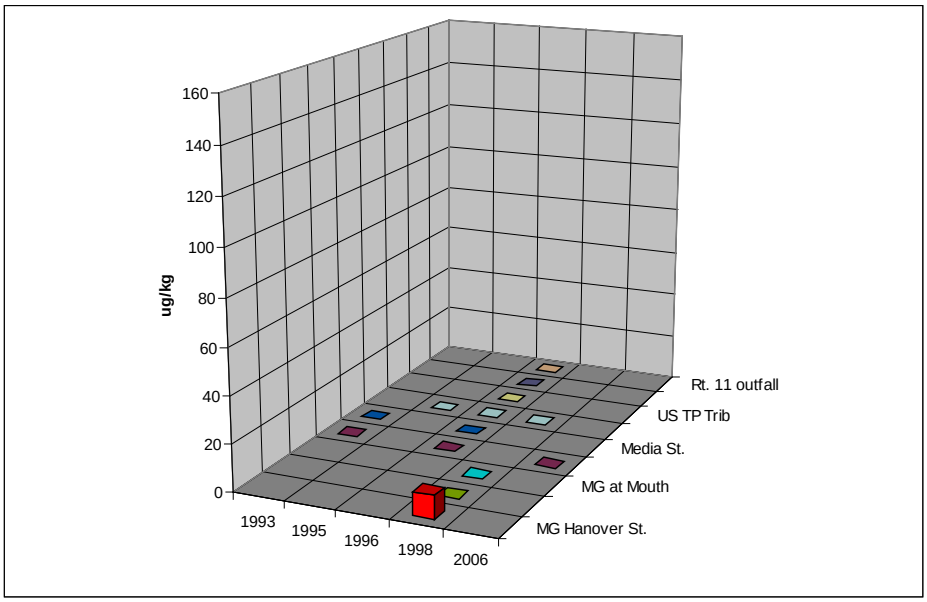


Figure 28. Concentrations of endrin ketone found in sites in the Letort Spring Run.

Heptachlor/heptachlor epoxide: Background

Heptachlor was a widely used insecticide in homes and on crops. The chemical rapidly breaks down by bacteria and animals to heptachlor epoxide once in the body and the environment (ATSDR Heptachlor 2007; Blus 1995). Heptachlor epoxide is persistent in the environment and more common and toxic than its parent compound (ATSDR Heptachlor 2007; Matsumura 1985). This chemical was used to control the imported red fire ant in the southeastern United States, but led to mortality among non-target birds and invertebrates (Nowell et al. 1999). Most uses of the pesticide were phased out by 1988, and currently heptachlor can only be used to control fire ants in underground power transformers (ATSDR Heptachlor 2007).

Heptachlor is also a cyclodiene insecticide that is a derivative of chlordane and is considered stable and not widely capable of breakdown by microorganisms (Matsumura 1973; Matsumura 1985). Epoxidation reactions convert heptachlor to heptachlor epoxide. Heptachlor is stored in biological systems as heptachlor epoxide (Matsumura 1985). A

hydrolysis reaction occurs, that when combined with microbial action forms 1-hydroxy-2,3-epoxy-chlordane from heptachlor epoxide. Hydrolysis is a reaction of the pesticide with water, which results in splitting the molecule into smaller, more water soluble portions (Nowell et al. 1999). The rate of this reaction can be affected by pH, temperature, and the presence of various metal ions. Heptachlor also can undergo photolysis in water (Nowell et al. 1999). Different wavelengths of sunlight are absorbed when the pesticide is sorbed to soil and sediment compared to water. The photolysis reaction is only important when water is shallow enough to allow for sunlight to penetrate to the sediment/water interface (Nowell et al. 1999). Both chemicals tend to stick tightly to soil particles and slowly evaporate to the air (ATSDR Heptachlor 2007). Heptachlor epoxide is capable of bioaccumulating in plants, fish, and cattle (ATSDR Heptachlor 2007). Heptachlor epoxide is more water soluble than heptachlor, slightly less bioaccumulative, and very persistent (Nowell et al. 1999). The EPA has established drinking water limits of 0.0004 ppm for heptachlor and 0.0002 ppm for heptachlor epoxide (ATSDR Heptachlor 2007).

Heptachlor/heptachlor epoxide: Results

Heptachlor breaks down quickly in the Letort, as seen at McKnight St. and Shady Lane, echoing its soil half-life of 0.75-2 years (Figure 29).

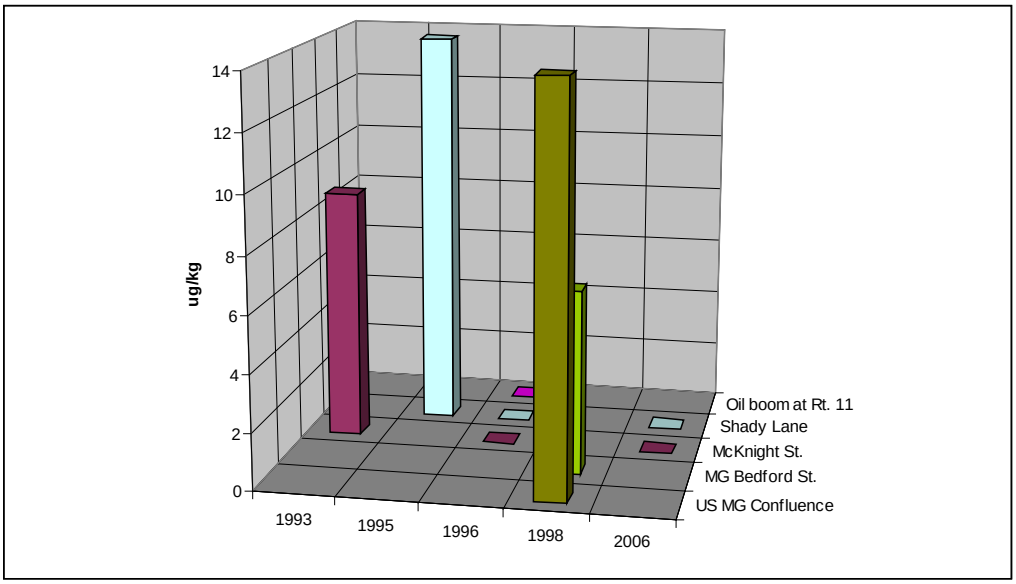


Figure 29. Concentrations of heptachlor found in sites in the Letort Spring Run.

Sediment quality guidelines have been established for heptachlor epoxide only (Table 13). Unfortunately, a soil half-life for heptachlor epoxide is not known, but has been estimated to be several years long (Nowell et al. 1999). Two of the three instances of heptachlor epoxide in sediment were classified as moderately polluted (Shady Lane in 1996 and within the Oil boom at Rt. 11 in 1996), and one site (McKnight St. in 1996) was unpolluted (Figure 30). It is not known what causes heptachlor epoxide contamination at these sites. Heptachlor epoxide is the more persistent and toxic form of the chemical, and interestingly, was only found in 1996 and downstream of High Street. Endrin aldehyde also followed this same pattern. It is not known what caused these chemicals to follow the same behavior. While heptachlor epoxide is present at McKnight St. and Shady Lane in 1996, it disappears by 2006. The concentration at the Oil boom at Rt. 11 in 1996 is interesting, as it is very far downstream in the trucking area and in a different landscape compared to McKnight St. and Shady Lane. It would be reasonable to assume that the oil boom at Rt. 11 would follow the trend seen at McKnight St. and Shady Lane, and the heptachlor epoxide

would be gone at this site by now (though unsampled). In summary, heptachlor is seen to be degrading in the Letort, as can be seen in Shady Lane. Heptachlor epoxide was found only in 1996 and downstream of High Street. It is unknown what caused this pattern of distribution.

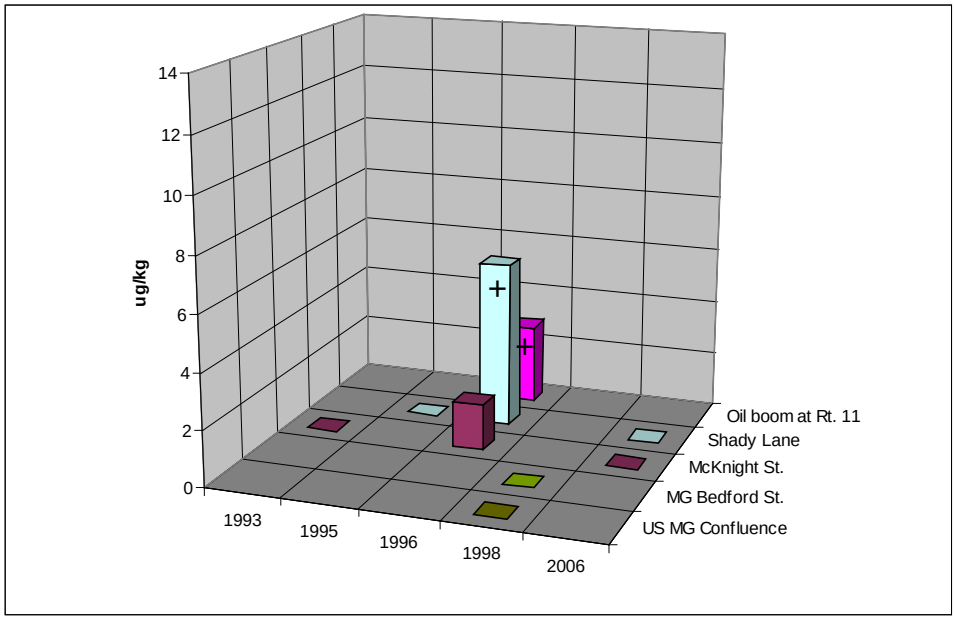


Figure 30. Concentrations of heptachlor epoxide found in sites in the Letort Spring Run. + indicates a violation of the TEC.

Lindane: Background

Lindane (gamma-HCH) is the main insecticide in a mixture of five isomers called hexachlorocyclohexane (HCH) which was previously mistakenly called benzene hexachloride (BHC) (Blus 1995; Willett et al. 1998). Lindane is about 50-10,000 times more effective than other isomers of HCH when used as a pesticide (Matsumura 1985; Willet et al. 1998). Some isomers of HCH crops and poultry products were consumed by humans, which led to the voluntary cancelling of its manufacture in the United States in 1976, but it is still imported for domestic use (ATSDR HCH 2005; Blus 1995). Lindane does not pose a substantial threat to wildlife, as it is metabolized to water-soluble chlorophenols and chlorobenzes that are quickly excreted. Alpha and beta isomers have some wildlife

repellency when used as a seed treatment. Lindane is currently in widespread use in the United States as an insecticide on fruits, vegetables, rice paddies, Christmas trees, and as a seed dressing (Willett et al.1998). It is also frequently used in shampoos to cure head lice and as a treatment for scabies (ATSDR HCH 2005; Willett et al. 1998).

HCH degrades faster in anaerobic conditions compared to an aerobic environment and has been known to disappear relatively quickly in soil (Matsumura 1973). HCH is more water soluble and volatile than other organochlorine insecticides, which explains its presence in all environmental mediums (Nowell et al. 1999; Walker et al. 1996; Willett et al. 1998). Dehydrochlorination of lindane leads to the formation of gamma-pentachlorocyclohex-1-ene (gamma-PCCH). It is possible that 1,2,3,5-tetrachlorobenzene could form if there is a lot of microbial activity. HCH is broken down in soil, sediments, and water by organisms such as algae, fungi, and bacteria to less dangerous compounds and it known to biodegrade under anaerobic conditions (ATSDR HCH 2005; Nowell et al. 1999). HCH has been shown to bioaccumulate in fish (ATSDR HCH 2005).

Beta-HCH accumulated in soil, rice straws, and milk in a Japanese study. Beta-HCH is thought to be the isomer of most toxicological concern, as it has been shown to have estrogenic effects on fish, and mammalian cells, and is found most frequently in human fat, blood, and breast milk (Willett et al. 1998). It is also the most persistent to microbial degradation and is the least volatile (Willett et al. 1998). Therefore, it is likely that the presence of beta-HCH in soil or sediment indicates a local contamination of HCH, and the alpha and gamma isomers are more common in the environment (Willett et al. 1998). The EPA has suggested that water children drink for up to 10 days should not have more than 1 ppm of lindane (ATSDR HCH 2005).

Lindane: Results

Sediment quality guidelines have been established for gamma-HCH (lindane) only (Table 13). Sediment was moderately polluted with lindane at the one site (McKnight St. in 1996) where it was found (Figure 31). However, lindane was not found when the site was resampled in 2006. It is unknown why lindane was found only at McKnight St. in 1996. Since lindane is still in widespread use in the US, it is possible that this level could increase in the future. Based on the chemical properties of the pesticide (a half-life in soil of 191 days) however, any lindane present would have been added to the system relatively recently. The presence of other isomers of HCH (alpha-HCH at the Public Works building in 1993 and beta-HCH at Vince's Meadow in 1993) suggests that lindane was used in these areas, but was in the process of breaking down (Figures 32 and 33). These two sites have not been resampled since 1993, so more recent concentrations are not known. In summary, lindane was found once in the sampling period and was found to be gone from the system in McKnight St. in its most recent sampling. Since the pesticide is still in use, concentrations may be found in sediment in the future (though the chemical has a shorter half life than most organochlorine insecticides).

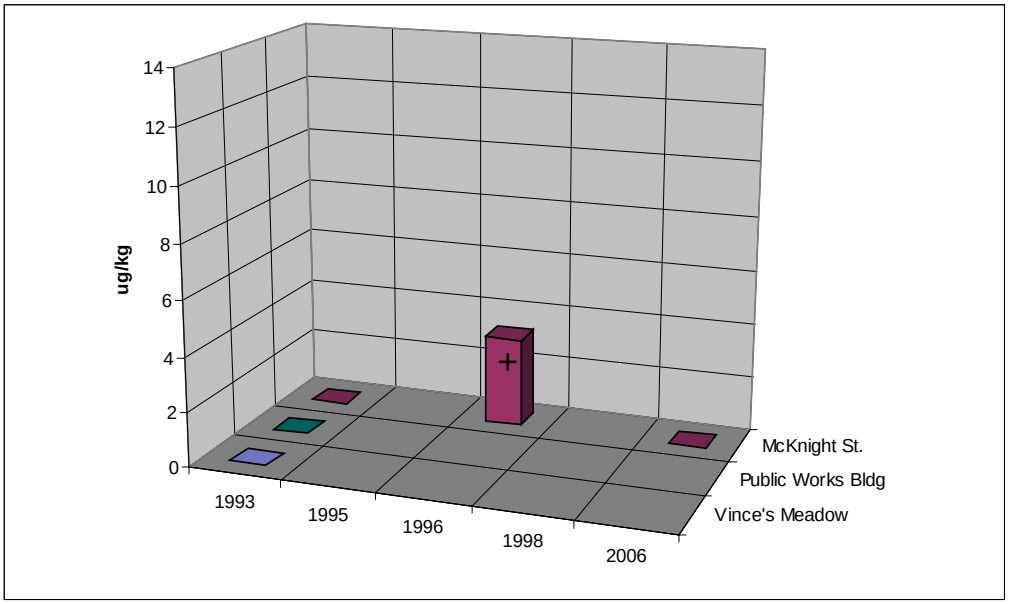


Figure 31. Concentrations of gamma-HCH (lindane) found in sites in the Letort Spring Run. + indicates a violation of the TEC.

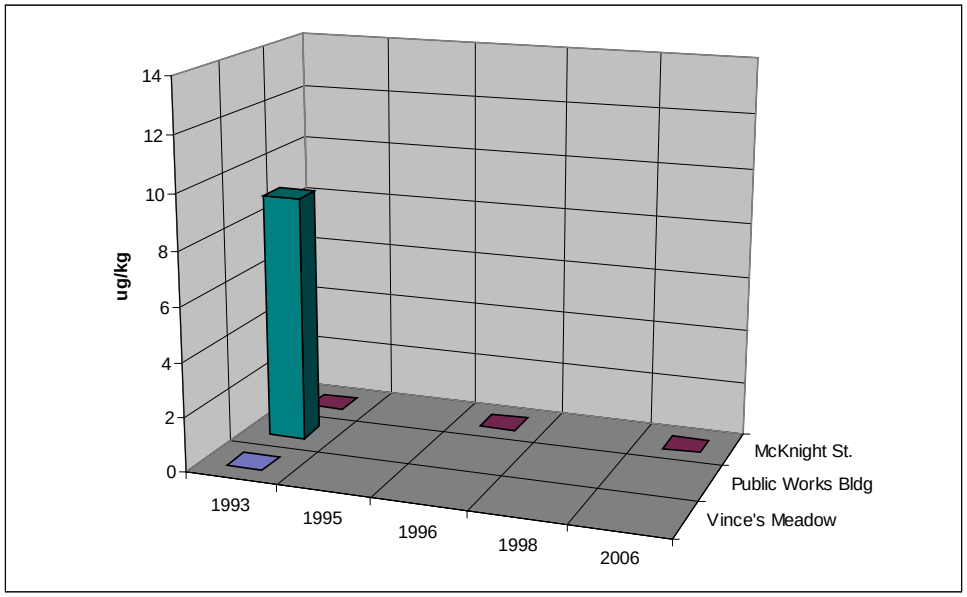


Figure 32. Concentrations of alpha-HCH found in sites in the Letort Spring Run.

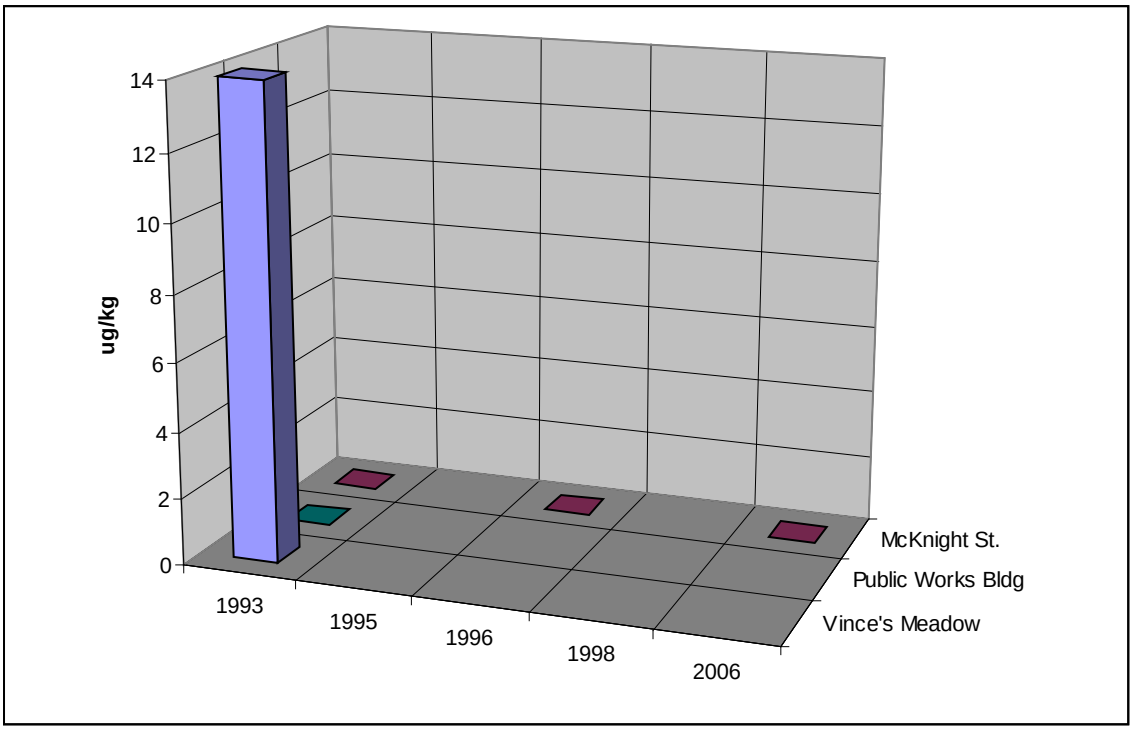


Figure 33. Concentrations of beta-HCH found in sites in the Letort Spring Run.

Methoxychlor: Background

Methoxychlor is an insecticide used currently to control house flies, black flies, mosquitoes, cockroaches, and chiggers. It is also used on food crops and livestock (ATSDR Methoxychlor 2002; Nowell et al. 1999). The pesticide binds strongly to soil and sediment particles, and does not dissolve easily in water (ATSDR Methoxychlor 2002). This chemical largely replaced DDT for control of Dutch elm disease in American elms, as it is less hydrophobic and persistent than other organochlorines (Blus 1995; Nowell et al. 1999). It is rapidly broken down in mammals and little residue has been found among bird species (Blus 1995). Methoxychlor also has greater toxicity in colder temperatures (Mayer et al. 1994). While this chemical normally does not bioaccumulate up the food chain, some of the breakdown products are just as toxic as the parent compound (ATSDR Methoxychlor 2002).

Methoxychlor has a soil half-life of 120-300 days (Table 15). The drinking water limit established by the EPA is 0.04 ppm (ATSDR Methoxychlor 2002).

Methoxychlor: Results

Sediment quality guidelines have not been established for methoxychlor (Table 13). Methoxychlor is present at Media St. in 1993, but is undetectable in 1996 (Figure 34). The 1996 concentrations at Shady Lane and McKnight St. are gone by 2006. It is expected that concentrations of methoxychlor at High St. storm sewer would follow this same pattern, and the methoxychlor would be completely broken down by now (though unsampled). In summary, there is evidence that methoxychlor is degrading as seen in concentrations at McKnight St., Media St., Shady Lane. Since the pesticide is still in use, concentrations may be found in sediment in the future (though the chemical has a shorter half life than most organochlorine insecticides).

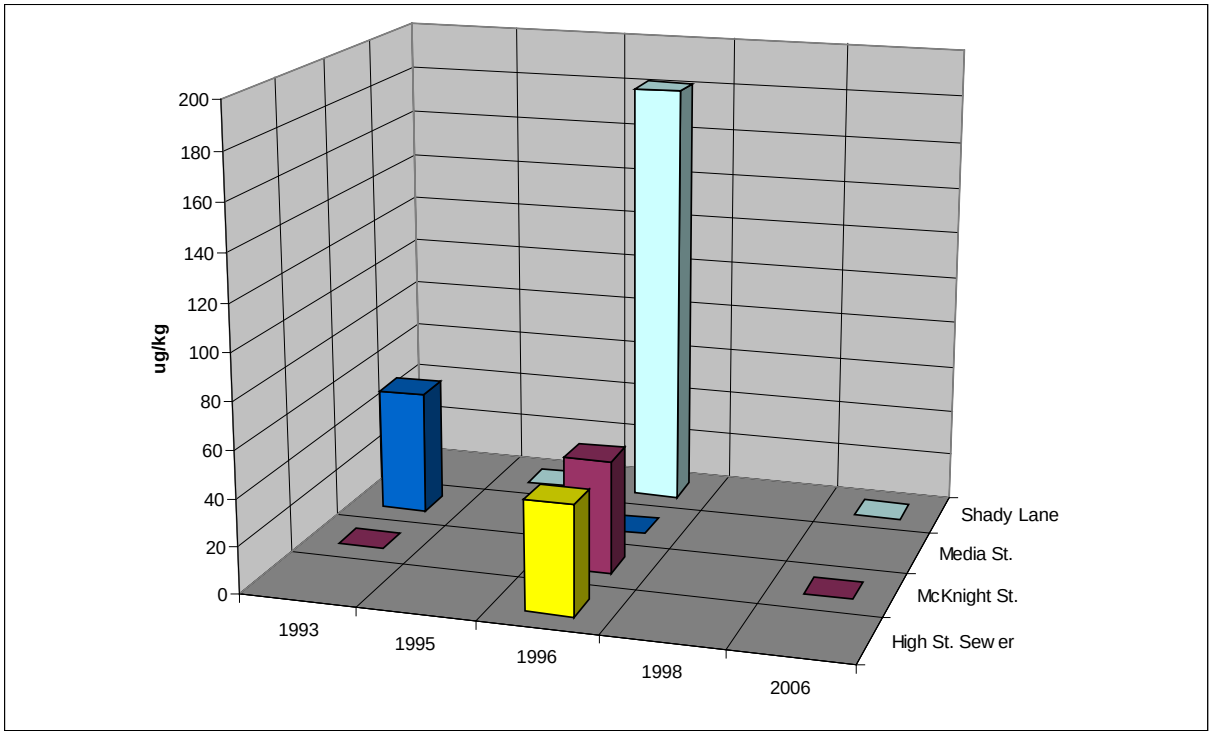


Figure 34. Concentrations of methoxychlor found in sites in the Letort Spring Run.

Fish tissue analysis

Pesticides contaminate aquatic biota by sorption to the surface of the organism, often through diffusion at gills along the lining of the mouth, at the gastrointestinal tract, or through the body surface (Nowell et al. 1999). The compounds are then bioaccumulated, biotransformed, or excreted. Organochlorine pesticides are known to biotransform slowly in fish. The concentrations increase with body size and age, and have a positive correlation with lipid content. The lipid content of fish changes with age and with the seasons.

Fish tissue data were taken in the Letort at two sites as part of separate studies conducted by the PA DEP. Fish tissue data are valuable in toxicological studies because it sheds light on the bioavailability of the chemical in the biological system. The War College was sampled in 1993 and Shady Lane was sampled in 2001 and 2005. White suckers and brown trout filets (five each) were collected at the War College, and five brown trout filets were analyzed at Shady Lane in both 2001 and 2005. For consistency, brown trout filet data are examined below. All of the filets were ground up, and a portion of the total was analyzed for pesticides (Schott 2008, personal communication).

Generally, concentrations of pesticides in fish tissue are declining (Figure 35). Guidelines from the Food and Drug Administration (FDA) and the EPA were rarely exceeded (Table 16). The FDA action levels are enforceable regulatory limits that focus on the unavoidable pesticide residues on food or animal feed (Nowell et al. 1999). The action levels specifically aim to protect the general public from contamination that might occur when fish are shipped via interstate commerce. The FDA action levels were not exceeded in any of the samples. Alternatively, the EPA screening values are designed to be at

concentrations that are of potential human health concern. As such, the screening values are set at the low end and indicate the possibility of effects on human health.

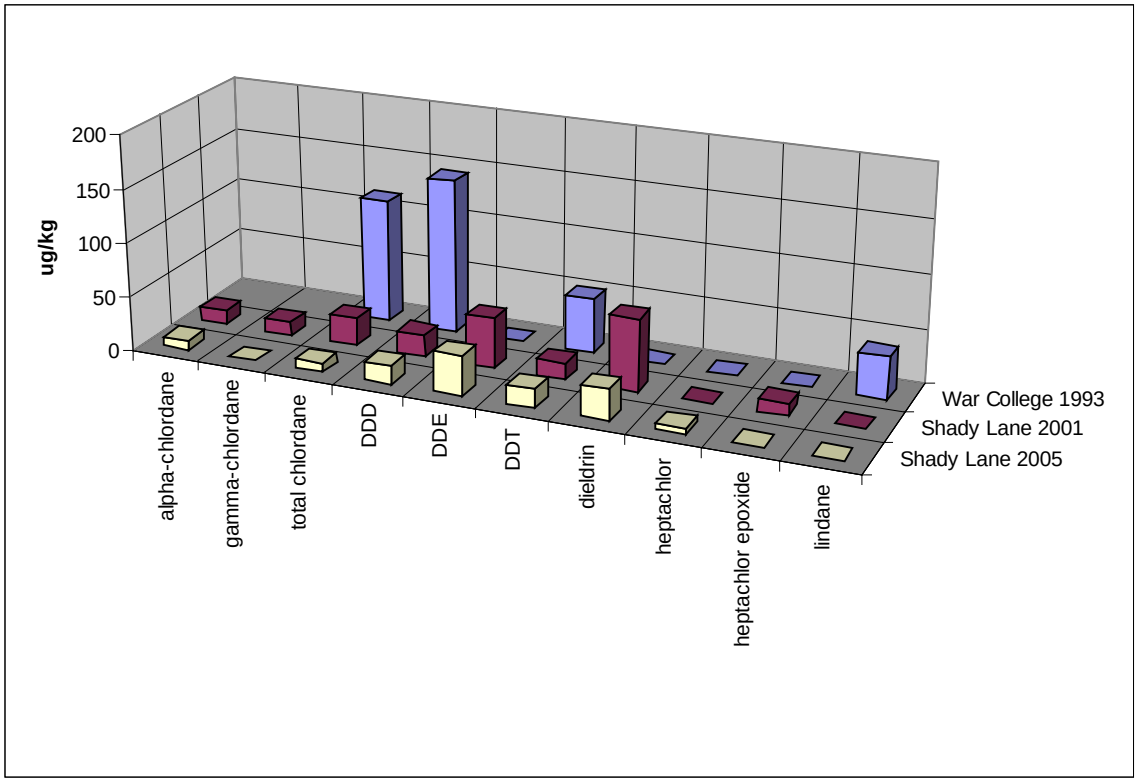


Figure 35. Available fish tissue data for brown trout (filets) from the Letort Spring Run (Schott 2008, personal communication).

Pesticide	Sites found	Concentration (ug/kg)	FDA action level 1989 (ug/kg)	EPA Screening Value 1995 (ug/kg)
alpha-chlordane	War College 1993	0	300 [1]	80 [1]
	Shady Lane 2001	13.529	X	X
	Shady Lane 2005	8.695	X	X
gamma-chlordane	War College 1993	0	X	X
	Shady Lane 2001	12.566	X	X
	Shady Lane 2005	0	X	X
total chlordane	War College 1993	115	X	X
	Shady Lane 2001	12.566	X	X
	Shady Lane 2005	8.695	X	X
DDD	War College 1993	143	5000 [2]	300 [3]
	Shady Lane 2001	20.398	X	X
	Shady Lane 2005	16.582	X	X
DDE	War College 1993	0	X	X

	Shady Lane 2001	46.743	X	X
	Shady Lane 2005	36.872	X	X
DDT	War College 1993	51	X	X
	Shady Lane 2001	15.622	X	X
	Shady Lane 2005	17.666	X	X
dieldrin	War College 1993	0	300 [4]	7
	Shady Lane 2001	66.506	X	X
	Shady Lane 2005	28.476	X	X
heptachlor	War College 1993	0	300 [5]	
	Shady Lane 2001	0	X	
	Shady Lane 2005	4.779	X	
heptachlor epoxide	War College 1993	0	300 [5]	10
	Shady Lane 2001	11.626	X	X
	Shady Lane 2005	0	X	X
lindane	War College 1993	39		80
	Shady Lane 2001	0		X
	Shady Lane 2005	0		X

Table 16. Pesticide concentration in fish tissue at three sites in the Letort Spring Run. Red highlighting indicates a violation, and green indicates compliance (Nowell et al. 1999).

[1] applies to total chlordane (alpha-chlordane + gamma-chlordane)
[2] applies to residues of DDD, DDE, and DDT, either singly or in combination
[3] applies to total DDT (DDD+DDE+DDT)
[4] applies to aldrin + dieldrin
[5] applies to heptachlor + heptachlor epoxide

The EPA screening value was exceeded for total chlordane at the War College in 1993. This corresponds to sediment heavily polluted with gamma-chlordane at Media St. (approximately the same location) in 1993. However, DDD and lindane were not detected in sediment samples at McKnight St. or Media St. (the two closest sites) in 1993, but these pesticides were found in fish tissue (Figure 36). This could likely be attributed to the differences in chemical behavior. For example, lindane is more water soluble than other organochlorine pesticides (Walker et al. 1996; Willett et al. 1998). This would make it easier for the chemical to become incorporated into the body of fish.

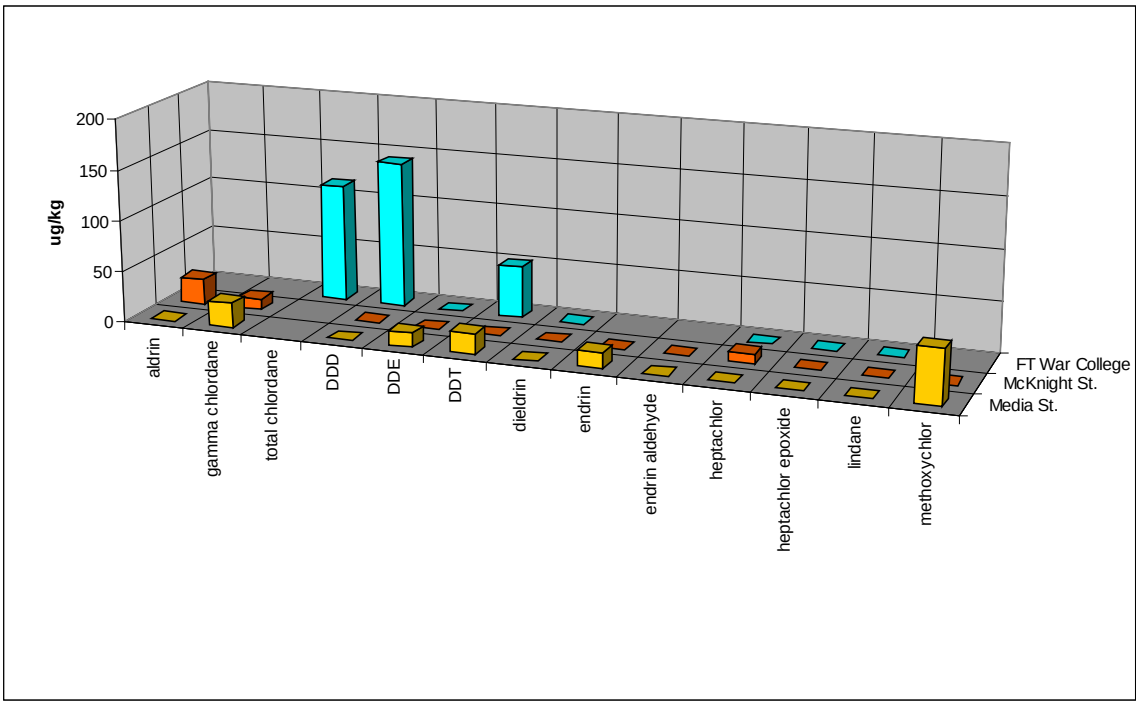


Figure 36. Pesticides concentrations found in sediment at Media St. and McKnight St. (the two closest sites) compared to pesticide concentrations found in fish tissue at the War College. All data are from 1993.

Additionally, the screening value for dieldrin was exceeded at Shady Lane in both 2001 and 2005, and the heptachlor epoxide value was breached (just barely) at Shady Lane in 2001. Since the Letort is a catch and release trout fishing stream, there is little cause for human health concern from the ingestion of these fish. Dieldrin was not found in sediment at Shady Lane until 2006 (Figure 37). This indicates that aldrin was previously added to the system, which has allowed for its breakdown product (dieldrin) to become incorporated into the biota. Heptachlor epoxide was found at Shady Lane in 1996. Heptachlor epoxide is more water soluble that heptachlor and is known for its bioaccumulation potential, which helps to explain its presence in fish tissue (ATSDR Heptachlor 2007). It is worthwhile to note that endosulfan was not found in fish tissue. This is a good sign, as endosulfan is a known piscicide (Nowell et al. 1999).

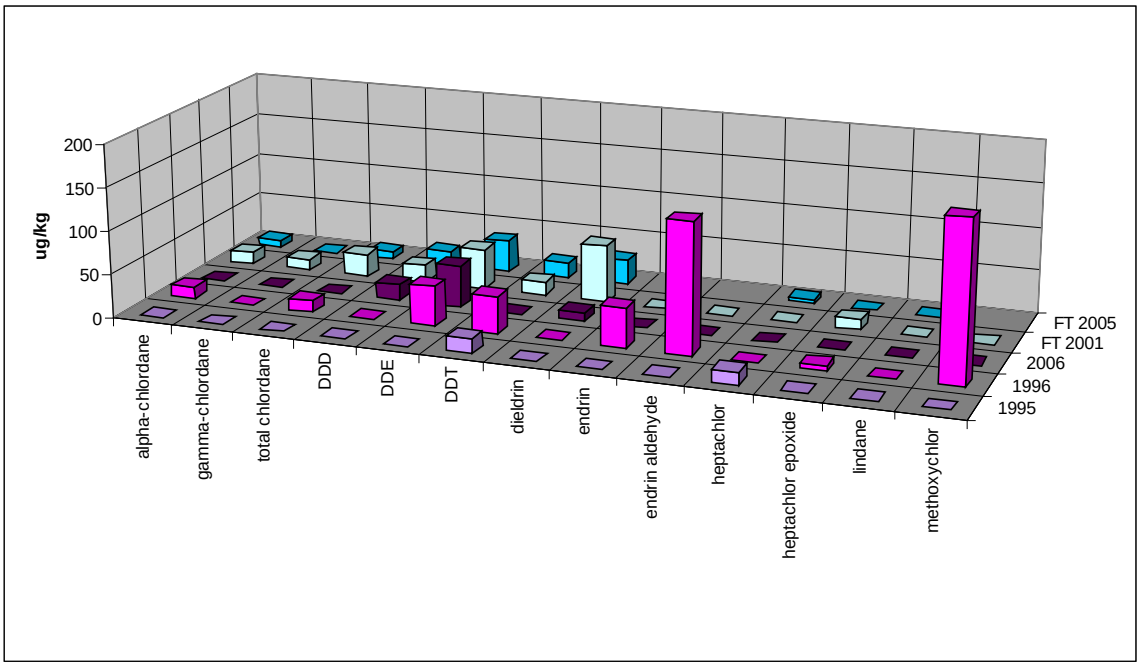


Figure 37. Pesticides concentrations found in sediment at Shady Lane in 1995, 1996, and 2006 compared to pesticide concentrations found in fish tissue at the same site in 2001 and 2005.

Overall assessment of pesticides in the Letort Spring Run

The majority of organochlorine pesticides found in sediment in the Letort are no longer used in this country. Transport of contaminated soil (possibly from urban and agricultural use) via stormwater runoff seems to be a major source of organochlorine insecticides to the Letort. The highest concentrations of the majority of chemicals were found at urban stormwater outfalls. This corresponds to the majority of hot spots being in the trucking reach (which includes Harmony Hall and Shady Lane), followed by the urban sites, with cold spots most frequently occurring in the upstream portion of the Letort. It is thought that disturbances of sediment due to development and restoration projects at Harmony Hall and Shady Lane likely led to the higher concentrations of pesticides at these sites, not trucking activity. It is likely that the pesticides found are from historic agricultural use at Harmony Hall and Shady Lane. If these two sites are removed from the ranking system, the

most contaminated sites are found in the urban area. Activities that might increase soil erosion or cause disturbance of soil should be carefully monitored to protect the aquatic system. Even though some of these pesticides have been banned for more than thirty years, the chemicals are still present in stream sediment. Concentrations of pesticides in the Letort are generally decreasing over time. Chemicals that are increasing are either in the middle of the degradation process, or appear to be increasing as an artifact of the sampling technique, due to limited resampling of sites (especially in the Mully Grub in 1998). It is predicted that pesticides will continue to become more available to aquatic systems over time from contaminated soil, but at a decreasing rate.

Suggestions for Future Studies

Further studies would benefit from more consistent sampling by examining all of the sites in this study within one sampling year. Also, there should be consistency in the sampling methods. Research could be done in order to determine the best place to sample stream sediment (across a transect, from the center or the banks, etc.). Since sediment systems vary so much, this would help to minimize variation caused by sampling methodology. Other ways to sample sediment could be employed to get a more accurate picture of the system. This could include analysis of community structure, sediment toxicity, tissue chemistry, pathology, or sediment chemistry. Additionally, a core sampler could be used when collecting sediment samples to limit the loss of the surficial layer, which normally has the highest levels of contaminants as it is the most biologically active layer. Studies could be expanded to compare the concentration of pesticides to sediment particle size, as an inverse relationship is known to exist (Edwards 1973).

The Mully Grub was sampled only in 1998, and was found to have high concentrations of several pesticides. Future studies could examine this tributary in depth to understand why concentrations were so much higher in the Mully Grub when compared to other stormwater outfalls in the urban section of Carlisle.

Extensive fish tissue studies or other biological assessments could be executed to more fully understand the bioavailability of pesticides in sediment to aquatic organisms. Ideally, whole fish should be analyzed and the samples should be separated so that concentrations of pesticides could be correlated back to a specific fish (and its weight and lipid percentage). This would help to determine the influence of age and fat content on the uptake of organochlorine insecticides by fish in the Letort Spring Run.

Historical analysis of land use patterns in the Letort watershed would be useful to more accurately identify the causes of various pesticides to stream sediment. The water column and soil close to the sites (even stream banks) could be sampled for pesticides to better understand the extent of pesticide distribution in the Letort Spring Run. Analysis could be expanded to include concentrations of metals, PCBs, and TPHs in stream sediment as well. Additionally, more research is needed on sediment systems in general, and specifically more work is needed to develop a complete set of sediment quality guidelines. Guidelines for endosulfan would be especially useful in the Letort, since the chemical is a known piscicide.

Conclusions

The results of this study show that the sites that are most polluted with organochlorine pesticides are found in the trucking and urban reaches of the Letort. Transport of contaminated soil (possibly from urban and agricultural use) via stormwater runoff seems to

be a major source of organochlorine insecticides to the Letort. The highest concentrations of the majority of chemicals were found at urban stormwater outfalls. While most pesticides were found at levels considered to be moderately polluted, DDE was heavily polluted at more than 50% of sites sampled.

DDT, DDE, gamma chlordane, endrin, and endrin aldehyde were the pesticides most frequently detected. There is evidence that DDT and endrin are degrading in the sediment as their breakdown products have become more frequently detected over time. Endosulfan, heptachlor, gamma-HCH (lindane), and methoxychlor, were found less frequently over time. There are no clear trends for chlordane within the data. Heptachlor epoxide and endrin aldehyde were only found in 1996 and downstream of High Street. It is not known what caused these chemicals to follow the same unique behavior. Development and restoration projects at Harmony Hall Rd. and Shady Lane a few years prior to 2006 may help explain the contamination of dieldrin, DDT, and DDD in sediment at these sites, as contaminated soil may have been disturbed.

Fish tissue analysis showed that generally the concentrations of pesticides in fish tissue are decreasing over time and fish tissue guidelines were rarely exceeded. There seem to be differences in the rate of degradation in sediment systems compared to biological systems, probably due to dissimilarity in the chemical properties of pesticides for different media. This would alter the chemical's behavior in biological systems.

The science of pesticides in sediment is in its infancy. More scientific studies on the fate of various compounds in sediment systems would be helpful to determine the extent of degradation in the Letort Spring Run. Currently, soil half-lives are the best estimation of residence time for pesticides in stream sediment. Sediment systems have highly variable

biological systems that change with depth. As such, sediment can be very unpredictable. It is thought that the half-life of a chemical in soil and sediment would not necessarily be the same, as the degradation processes would be affected differently by biological and chemical means in soil and sediment systems.

Even though some of these pesticides have been banned for more than thirty years, the chemicals are still present in stream sediment in the Letort Spring Run. While generally pesticides are degrading and decreasing in concentration, caution should be exercised when using chemicals that are persistent in the environment.

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References

Agee, B.A. 1986. DDT in the Salinas Valley: A special report on the probable source of technical grade DDT founding the Blanco Drain near Salinas, California. California Water Resources Control Board, Division of Water Quality. Water Quality Monitoring Report 86-2.

Agency for Toxic Substances and Disease Registry (ATSDR). 1994. Toxicological profile for Chlordane. United States Department of Health and Human Services, Public Health Service. Available online at: http://www.atsdr.cdc.gov/tfacts31.html. Accessed 23 Nov 2007.

Agency for Toxic Substances and Disease Registry (ATSDR). 1996. Toxicological profile for Endrin. United States Department of Health and Human Services, Public Health Service. Available online at: http://www.atsdr.cdc.gov/tfacts89.html. Accessed 23 Nov 2007.

Agency for Toxic Substances and Disease Registry (ATSDR). 2002. Toxicological profile for Aldrin/Dieldrin. United States Department of Health and Human Services, Public Health Service. Available online at: http://www.atsdr.cdc.gov/tfacts1.html. Accessed 23 Nov 2007.

Agency for Toxic Substances and Disease Registry (ATSDR). 2002. Toxicological profile for DDT, DDE, and DDD. United States Department of Health and Human Services, Public Health Service. Available online at: http://www.atsdr.cdc.gov/tfacts35.html. Accessed 23 Nov 2007.

Agency for Toxic Substances and Disease Registry (ATSDR). 2002. Toxicological profile for Methoxychlor. United States Department of Health and Human Services, Public Health Service. Available online at: http://www.atsdr.cdc.gov/tfacts47.html. Accessed 23 Nov 2007.

Agency for Toxic Substances and Disease Registry (ATSDR). 2005. Toxicological profile for Alpha-, Beta-, Gamma-, and Delta-Hexachlorocyclohexane. United States Department of Health and Human Services, Public Health Service. Available online at: http://www.atsdr.cdc.gov/tfacts43.html. Accessed 23 Nov 2007.

Agency for Toxic Substances and Disease Registry (ATSDR). 2007. Toxicological profile for Heptachlor and Heptachlor Epoxide. United States Department of Health and Human Services, Public Health Service. Available online at: http://www.atsdr.cdc.gov/tfacts12.html. Accessed 23 Nov 2007.

Agency for Toxic Substances and Disease Registry (ATSDR). 2007. Toxicological profile for Endosulfan. United States Department of Health and Human Services, Public Health Service. Available online at: http://www.atsdr.cdc.gov/tfacts41.html. Accessed 9 Feb 2008.

Barbash, J.E. and Resek, E.A. 1996. Pesticides in Groundwater: Distribution, Trends, and Governing Factors. Pesticides in the Hydrologic System. Volume 2. National Water Quality Assessment Program, United States Geological Survey. Ann Arbor Press, Inc., Chelsea, MI.

Battaglin, W. and Fairchild, J. 2002. Potential toxicity of pesticides measured in Midwestern streams to aquatic organisms. *Water Science and Technology*, 45 (9), 95-103.

Blus, L. J. 'Organochlorine Pesticides'. In Hoffman, D.J., Rattner, B.A., Burton, G.A. Jr., and Cairns, J. Jr. 1995. Handbook of Ecotoxicology. Lewis Publishers, Boca Raton.

Brown, A.W.A. 1978. Ecology of Pesticides. Wiley-Interscience Publications, New York.

Burton, G.A., Jr. and MacPherson C. 'Sediment Toxicity Testing Issues and Methods'. In Hoffman, D.J., Rattner, B.A., Burton, G.A. Jr., and Cairns, J. Jr. 1995. Handbook of Ecotoxicology. Lewis Publishers, Boca Raton.

Canadian Council of Ministers of the Environment. 2002 (updated). Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Summary tables. In: Canadian Environmental Quality Guidelines, 1999. Publication No. 1299, Canadian Council of Ministers of the Environment, Winnipeg. Available online at: http://www.ccme.ca/assets/pdf/sedqg_summary_table.pdf. Accessed 6 Nov 2007.

Castillo L.E., Ruepert, C., and Solis, E. 2000. Pesticide residues in the aquatic environment of banana plantation areas in the North Atlantic Zone of Costa Rica. *Environ Toxicol Chem*, 19, 1942-1950. Abstract only.

Cioce, D. 2008. GIS maps complied by data from PA Geological Survey, Susquehanna River Basin Commission, Department of Environmental Resources, and United States Geological Survey and Wilderman, 2004., and accessed through the Alliance for Aquatic Resource Monitoring database, Dickinson College, Carlisle, PA.

Commission for Environmental Cooperation (CEC). 2001. History of DDT in North America to 1997. Commission for Environmental Cooperation. Available at: http://www.cec.org/files/PDF/POLLUTANTS/HistoryDDTe_EN.PDF. Accessed 21 April 2008.

Commonwealth of Pennsylvania. 2005. Chapter 93: Water Quality Standards. In Pennsylvania Code. Available at: http://www.pacode.com/secure/data/025/chapter93/chap93toc.html. Accessed 15 April 2008.

Cumberland Valley Trout Unlimited. 2008. "Lower Letort Designated Class A". Cumberland Valley Trout Unlimited. Available online at: http://cvtu.homestead.com/. Accessed 15 April 2008.

Edwards, C.A. 'Pesticide Residues in Soil and Water'. In Edwards, C.A., Ed. 1973. Environmental Pollution by Pesticides. Plenum Press, London.

Extension Toxicology Network (Extoxnet). 1996. DDT. Pesticide Information Profiles. Extension Toxicology Network. Available online at: http://extoxnet.orst.edu/pips/ddt.htm. Accessed 21 April 2008.

Florida Department of Environmental Protection (FL DEP). 1994. Florida Sediment Quality Assessment Guidelines (SQAGs): Chapter 6. Numerical Sediment Quality Assessment Guidelines for Florida Coastal Waters. Florida Department of Environmental Protection. Available online at:

http://www.dep.state.fl.us/waste/quick_topics/publications/pages/default.htm. Accessed 6 Nov 2007.

Fukuto, T.R., and Sims, J.J. 'Metabolism of Insecticides and Fungicides'. In White-Stevens, R., Ed. 1971. Pesticides in the Environment, Volume 1, Part I. Marcel Dekker, Inc., New York.

Gonzalez-Lopez, N., Rail-Otero, R., Cancho-Grande, B., Simal-Gandara, J. and Soto-Gonzalez, B. 2005. Occurrence of Organochlorine pesticides in stream sediments from an industrial area. *Archives of Environmental Contamination and Toxicology*, 48, 296-302.

Hill, D.W. and McCarty, P.L. 1966. The Anaerobic Degradation of Selected Chlorinated Hydrocarbon Pesticides. EPA 904-R-97-003. US EPA, Region 4, Water Division, Wetlands Section. Atlanta, GA.

Hoffman, R.S., Capel, P.D., and Larson, S.J. 2000. Comparison of Pesticides in Eight U.S. Urban Streams. *Environmental Toxicology and Chemistry*, 19 (9), 2249-2258.

Ingersoll, C.G., MacDonald, D.D., Wang N., Crane, J.L., Field, L.J., Haverland, P.S., Kemble, N.E., Lindskoog, R.A., Severn, C., and Smorong, D.E. 2000. Prediction of sediment toxicity using consensus-based freshwater sediment quality guidelines. United States Geological Survey (USGS) final report for the U.S. Environmental Protection Agency (USEPA) Great Lakes National Program Office (GLNPO). EPA 905/R-00/007. Available online at: http://www.cerc.usgs.gov/pubs/center/pdfdocs/91126.pdf. Accessed 6 Nov 2007.

Klasic, M. 2006. The Use of Submerged Aquatic Vegetation (SAV) as a Bioindicator for Letort Spring Run, Cumberland County, PA. Senior Independent Research. Dickinson College, Environmental Studies Department.

Larson, S.J., Gilliom, R.J., and Capel, P.D. 1999. Pesticides in Streams of the United States- Initial Results from the National Water-Quality Assessment Program. United States Geological Survey, Water-Resources Investigations Report 98-4222. Sacramento, CA.

Letort Regional Authority (LRA). 2007. "The Role of Government in the Letort Watershed". Available online at: http://www.letort.org/. Accessed 18 Feb 2008.

MacDonald, D.D., Ingersoll, C.G., and Berger, T.A. 2000. Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. *Archives of Environmental Contamination and Toxicology*, 39, 20-31.

Majewski, M.S., and Capel, P.D. 1995. Pesticides in the Atmosphere: Distribution, Trends, and Governing Factors. Pesticides in the Hydrologic System. Volume 1. National Water Quality Assessment Program, United States Geological Survey. Ann Arbor Press, Inc., Chelsea, MI.

Matsumura, F. Degradation of Pesticide Residues in the Environment. In Edwards, C.A., Ed. 1973. Environmental Pollution by Pesticides. Plenum Press, London.

Matsumura, F. 1985. Toxicology of Insecticides, 2nd Edition. Plenum Press, New York.

Mayer, F.L. Jr., Marking L.L., Bills, T.D., and Howe, G.E. 'Physiochemical Factors Affecting Toxicity in Freshwater: Hardness, pH, and Temperature'. In Hamelink, J.L., Landrum, P.F., Bergman, H.L., and Benson, W.H., eds. 1994. Bioavailability: Physical, Chemical and Biological Interactions. Lewis Publishers, Boca Raton.

National Oceanic and Atmospheric Administration (NOAA). 1999. Screening Quick Reference Tables (SQuiRTs) for Organics. Coastal Protection and Restoration Division, NOAA. Available online at http://response.restoration.noaa.gov/book_shelf/122_squirt_cards.pdf. Accessed 6 Nov 2007.

Nowell, Lisa.H. March 18, 2008. Chemist, U.S. Geological Survey. Personal communication via e-mail.

Nowell, L.H., Capel, P.D., and Dileanis, P.D. 1999. Pesticides in Stream Sediment and Aquatic Biota: Distribution, Trends, and Governing Factors. Pesticides in the Hydrologic System. Volume 4. National Water Quality Assessment Program, United States Geological Survey. Lewis Publishers, Boca Raton, FL.

Nyangababo, J.T., Henry, L. and Omutange, E. 2005. Organochlorine pesticide contamination in surface water, sediment, and air precipitation of Lake Victoria Basin, East Africa. *Bulletin of Environmental Contamination and Toxicology*, 75, 960-967.

Paul, M.J., and Meyer, J.L. 2001. Streams in the Urban Landscape. *Annual Review of Ecology and Systematics*, 32, 333-365.

Pesticide Management Education Program (PMEP). 1993. Extension Toxicology Network: Pesticide Information Profile for Endosulfan. Cooperative Extension Offices of Cornell University, Michigan State University, Oregon State University, and the University of California at Davis. Available online at: http://pmep.cce.cornell.edu/profiles/extoxnet/dienochlor-glyphosate/endosulfan-ext.html. Accessed 9 Feb 2008.

Power, E.A., and Chapman, P.M. 'Assessing Sediment Quality.' In: Burton, G.A. Jr., Ed. 1992. Sediment Toxicity Assessment. Lewis Publishers, Boca Raton, FL.

Racke, K.D., Skidmore, M., Hamilton, D.J., Unsworth, J.B., Miyamoto, J., and Cohen, S.Z. 1997. Pesticide fate in tropical soils (technical report). *Pure Appl Chem*, 69, 1349-1371. In Nyangababo, J.T. et al. 2005. Organochlorine pesticide contamination in surface water, sediment, and air precipitation of Lake Victoria Basin, East Africa. *Bulletin of Environmental Contamination and Toxicology*, 75, 960-967.

Samoiloff, M.R. Toxicity Testing of Sediments: Problems, Trends, and Solutions. In Nriagu, J.O. and Lakshminarayana, J.S. S. 1989. Aquatic Toxicology and Water Quality Management. *Wiley Series in Advances in Environmental Science and Technology 22*. Wiley-Interscience, New York.

Sass, J. February 20, 2008. "For a second time, NRDC petitions US EPA to cancel dangerous pesticide, endosulfan." Natural Resources Defense Council switchboard.

Schott, R.J. April 15, 2008. Aquatic biologist, Pennsylvania Department of Environmental Protection. Personal communication via e-mail.

Selan, Peter. February 12, 2008. Treatment Plants Manager. Personal communication at the Carlisle Waste Water Treatment Plant. Carlisle, PA.

Smith, S.L., MacDonald, D.M., Keenleyside, K.A., Ingersoll, C.G., and Field, L.J. 1996. A Preliminary Evaluation of Sediment Quality Assessment Values for Freshwater Ecosystems. *Journal of Great Lakes Research*, 22 (3), 624-638.

Texas Natural Resource Conservation Commission (TNRCC). 2001. Implementation Plan for Arroyo Colorado and Donna Reservoir and Canal Legacy Pollutant TMDLs, for segments 2202 and 2202A. Prepared by the Strategic Assessment Division, TMDL Team, Field Operations Division, Region 4.

United Nations Environment Programme (UNEP). 2002. Chemical Fact Sheet: Chlordane. Regional Reports of the Regionally Based Assessment of Persistent Toxic Substances Program. Available online at: http://www.oztoxics.org/cmwg/chemicals/rbapts_chem/Chlordane.html. Accessed 9 Feb 2008.

United States Geological Survey (USGS). 2000. Pesticides in Stream Sediment and Aquatic Biota. USGS fact sheet 092-00. Available online at http://ca.water.usgs.gov/pnsp/rep/fs09200/. Accessed 3 Sept 2007.

Walker, C.H., Hopkin, S.P., Sibly R.M., and Peakall, D.B. 1996. Principles of Ecotoxicology. Taylor & Francis Ltd, London.

Water Resources of Oklahoma. 2005. "Reconnaissance Investigation of Pesticides and PCB's in Selected Fish Species from Lake Texoma, Oklahoma." United States Geologic Survey. Available online at: http://ok.water.usgs.gov/presentations/ChickasawFishPres01.11.2005.ppt. Accessed 1 May 2008.

Webster, E., Mackay, D., and Wania, F. 1998. Evaluating Environmental Persistence. *Environmental Toxicology and Chemistry*, 1 (11), 2148-2158.

Wilderman, C.C. 1994. A preliminary assessment of the water quality of urban runoff in Carlisle, PA and its effects on the Letort Spring Run. Dickinson College, Environmental Studies Department.

Wilderman, C.C. 1997. An assessment of stormwater runoff quality in Middlesex Township, Cumberland County, PA, with a comparison of the composition and effects of stormwater runoff from four land uses in the Letort Spring Run Watershed. Dickinson College, Environmental Studies Department.

Wilderman, C.C. 2004. The realization of a pipe dream: effective partnerships in community-based urban stream restoration: A case study of the Mully Grub, Letort Spring Run, Cumberland County, PA. Dickinson College, Environmental Studies Department.

Willett, K.L., Ulrich, E.M., and Hites, R.A. 1998. Different Toxicity and Environmental Fates of Hexachlorocyclohexane Isomers. *Environmental Science and Technology*, 32 (15), 2197-2207.

Woodfine, D. and Mackay, D. 2001. Evaluation of Partitioning and Persistence of Organic Substances on Environment Canada's Domestic Substances List. Report to Environment Canada. CEMC Report No. 200105. Trent University, Peterborough, Ontario.