Derivation of "No Application Periods" for Interim Use Pesticides

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I. INTRODUCTION

The South Florida Water Management District (SFWMD) is actively acquiring agricultural lands in South Florida in connection with the Everglades Restoration Project. These lands are slated for various water management projects including conversion to water attenuation reservoirs, creation of stormwater treatment areas (STAs) for removal of phosphorus and other nutrients, and restoration of wetlands in areas formerly drained for agriculture. All of these projects will likely attract large numbers of birds and other wildlife. Since all of these areas were, or still are, agricultural areas, they have probably been exposed to heavy pesticide applications for decades and residues of some of those pesticides very likely still remain in the soil. Some of the pesticides used were organochlorine compounds such as toxaphene and DDT, which are now banned due to their extreme persistence in soil and their tendency to bioaccumulate in the food web. Residues of these chemicals in soils at a recent wetland restoration project in Florida (Lake Apopka) have resulted in bird die-offs following flooding of the site.

Following land acquisition for a water management project, there may be a delay of up to five years before completion of the project and actual flooding of the wetland or reservoir occurs. During this "interim use period," the former landowner is usually allowed to lease the property and continue with existing agricultural uses. Because of the risks to fish and wildlife that will be attracted to the site following flooding, questions arise as to what types of pesticides, and in what quantities, should be allowed to be applied to these lands during the interim use period. This document was developed in response to these questions.

Because the U.S. Fish and Wildlife Service (Service) must approve these interim uses of grant lands, it has sought to discover what chemicals are being used in conjunction with the uses. The Service has sought the assistance of the SFWMD in this effort; however, the Service and the SFWMD do not agree as to the necessity for, and the feasibility of, obtaining this information from the former landowner. This issue has delayed the finalization, acceptance and implementation of a mutually agreeable protocol by which the SFWMD can seek, and the Service grant, approval of the interim uses. Until the protocol can be developed, the Service cannot provide formal approval of the uses.

In order to resolve this issue, the Service has developed an alternative to requiring the SFWMD to submit chemical use information. Instead, the protocol itself will contain the following chemical use schedule, which the SFWMD will incorporate the pertinent portions into any leases, reservations, or any other methods of allowing an interim use on lands acquired with grant funds. The schedule identifies chemicals which may be used on grant lands, and the amount of time the use of each chemical must cease prior to the incorporation of the parcel into an Everglades restoration project. The time period for each chemical is based upon that chemical's $T_{1/2}$ value (half-life). Accordingly, regardless of which chemicals had been applied to a specific parcel before it was acquired by the SFWMD with grant funds, the SFWMD will be authorized only to allow the use of certain chemicals for certain amounts of time.

II. METHODS

Information on persistence and degradation, toxicity, and use of pesticides in Florida was obtained from various internet databases and published references. The publication *Summary of Agricultural Pesticide Usage in Florida: 1995 - 98* (Shahane, 1999) was reviewed to develop a list of pesticides commonly used in South Florida. Data on half-life, degradation rate, and toxicity of these substances were obtained primarily from the Hazardous Substances Data Bank (HSDB), the Environmental Fate Database (EFDB), and the Extension Toxicology Network (EXTOXNET). For many of the chemicals used in Florida, environmental fate has been researched extensively and numerous literature values for half-life and/or degradation rate were available. For some chemicals, only a few values could be located.

Degradation rates of pesticides in soil can vary tremendously depending on soil type, climate, soil pH, moisture content, depth beneath the surface, and other variables. Therefore, the $T_{1/2}$s and degradation rates reported in the literature for the same chemical may vary over a wide range, depending on the conditions in the different studies. No attempt was made to select only those studies most appropriate to conditions in Florida soils. All relevant values for a chemical, including both field and laboratory experiments, were included in the database for that chemical; however, obviously irrelevant studies (such as those using sterile soils) were not included.

Many studies presented calculated soil $T_{1/2}$ values for the chemical being studied, and these values were entered directly into the database for that chemical. Other studies did not calculate $T_{1/2}$ values, but instead presented raw degradation rates. For example, an entry might state that the chemical was 67% degraded in 10 days. For these situations, the $T_{1/2}$ was calculated using the following formula (assuming 1st order kinetics) (Casarett et al., 1996):

$$T_{1/2} = \frac{.693 * t}{2.303(2 - \log(100 - d))}$$

where t = time since application and d = percent degraded.

All $T_{1/2}$ values obtained directly from the online databases and those calculated from raw degradation data were entered into a spreadsheet (see Appendix A). Using all of these data, median and maximum $T_{1/2}$ values were determined for each chemical. In addition, some studies presented persistence times for pesticides, i.e., the length of time required for all of the chemical to be degraded. Although $T_{1/2}$ values could not be calculated from these data, the range of reported persistence was also recorded. Table 1 summarizes all half-life, persistence, and toxicological information considered for each chemical.

The "no application period" is defined as the period of time prior to conversion of the agricultural land to conservation purposes (e.g., flooding to create wetlands) during which a particular pesticide hazardous to fish and/or wildlife should *not* be applied, in order to allow adequate time for breakdown of pesticide residues before use of the land by Service trust resources. This period of time was defined as 5 times the median half-life, representing 97 percent degradation. Based on this 5 X $T_{1/2}$ value, the pesticide was placed into one of the following no application periods: 3 months, 6 months, 1 year, or 2 years (Table 1). Due to uncertainties of the planning and scheduling process, it was decided that those rare pesticides requiring more than 2 years to break down should not be applied at all.

In those cases where $T_{1/2}$ data were scanty or differed substantially from persistence data, professional judgement was used. Preference was sometimes given to persistence data, particularly in the case of highly toxic compounds. For example, the pesticide disulfoton, which is highly toxic to fish and wildlife, was placed in a 1 year no application category based on the longer persistence of toxic metabolites compared to the parent compound. In this case, use of five times the median half-life of the parent compound would have underestimated the breakdown time to nontoxic products (Table 1).

III. RECOMMENDATIONS

A. The following pesticides are approved for application during the interim use period with **no restrictions** other than those required by the label:

2,4-D	glyphosate
Bacillus thuringiensis (Bt)	metolachlor
copper compounds	metribuzin
dicamba	norflurazon
diquat	potassium salts
diuron	sethoxydim
EPTC	sulfur
fluazifop-p-butyl	simazine

B. The following lists include some of the most commonly used pesticides in South Florida that are thought to be hazardous to fish and wildlife. These chemicals are approved for application during the interim use period with the following restriction: Use of these chemicals should be discontinued for the indicated time period prior to flooding agricultural lands for wetland restoration, creating water retention reservoirs, or any other activity likely to attract fish and wildlife to the site.

Use of the following should be **discontinued at least 3 months** prior to flooding:

acephate	malathion
alachlor	methidathion
diazinon	methyl parathion
dimethoate	oxamyl
	trichlorfon

Use of the following should be **discontinued at least 6 months** prior to flooding:

aldicarb	ethoprop
azinphos-methyl	ethyl parathion
carbaryl	permethrin
carbofuran	phorate
chlorpyrifos	terbufos

Use of the following should be **discontinued at least 1 year** prior to flooding:

atrazine	esfenvalerate
cyfluthrin	fenamiphos
disulfoton	fonofos
endosulfan	

Use of the following should be **discontinued at least 2 years** prior to flooding:

dicofol	trifluralin

C. Due to their high toxicity and/or extreme persistence in the environment, the following chemicals **should not be applied** during the interim use period to lands being acquired for wetland restoration, water retention, or similar purposes. Interim uses which require these chemicals will not be permitted.

benomyl	paraquat

D. Other pesticides which do not appear on the above lists may come up from time to time. These will be evaluated on a chemical-by-chemical basis and added to the appropriate category above.

E. *Any* pesticide, regardless of the above categories, shown to already be present in soil at or above the appropriate sediment guideline, may require additional restrictions. For example, copper is a metal which does not degrade in the environment and may already be present in some soils (e.g., orchards) at levels above the Florida Department of Environmental Protection's Sediment Quality Assessment Guideline (MacDonald, 1994). In this case, further use of copper compounds during the interim use period would have to be reduced or eliminated altogether. These situations will be evaluated on a case-by-case basis. Add: can't push over SQAGs.

IV. SOURCES OF INFORMATION

A. Publications

Casarett, L.J., M.O. Amdur and C.D. Klaasen (eds.). 1996. Casarett and Doull's Toxicology: The Basic Science of Poisons, 5th Edition. McGraw Hill.

1997 Farm Chemicals Handbook (Vol. 83). Meister Publishing Co., Willoughby, Ohio.

MacDonald, D.D. 1994. Approach to the Assessment of Sediment Quality in Florida Coastal Waters. Florida Department of Environmental Protection, Office of Water Policy, Tallahassee, Florida.

Milne, G.W.A. 1995. CRC Handbook of Pesticides. CRC Press, Boca Raton, Florida. 402 pp.

Shahane, A.H. 1999. Summary of Agricultural Pesticide Usage in Florida: 1995-98. Florida Department of Agriculture and Consumer Services, Tallahassee, Florida. 111 pp.

B. Online Databases

Environmental Fate Database, Syracuse Research Corporation, Syracuse, New York. http://esc.syrres.com/efdb.htm

Hazardous Substances Data Bank (HSDB), TOXNET, National Library of Medicine, Washington, D.C. http://toxnet.nlm.nih.gov/

Extension Toxicology Network (EXTOXNET), Oregon State University, Corvallis, Oregon. http://ace.orst.edu/info/extoxnet/ -

Table 1. Environmental and Toxicological Characteristics of Pecticides Considered in Establishing the No Application Period.

Pesticide	No Application Period	$T_{1/2}$ soil (days) median	$T_{1/2}$ soil (days) max	Persistence	5 X $T_{1/2}$ (months)	Class	Bird Kills?[1]	LD50 (rat, oral) mg/kg	LC50 (fish) mg/l
acephate	3 mo.	3	14		0.5	OP	YES	866 - 945	>1000
alachlor	3 mo.	14	133	6 wk - >1 yr	2.3	acetanilide		930 - 1350	(3.7)
aldicarb	6 mo.	19	990	1 - 15 d	3.2	carbamate	YES	1	1.5
atrazine	1 yr.	63.8	1898	73 d - 2 yr	10.6	triazine		1780	slightly toxic
azinphos-methyl	6 mo.	37.0	484		6.2	OP	YES	4.4 - 16	0.003
benomyl	Do Not Apply	270	360	15 d - 4 wk	45.0	carbamate		>10,000	.006 - 14
carbaryl	6 mo.	25.5	379.4	40 d	4.3	carbamate		246 - 283	28
carbofuran	6 mo.	29	334.2	56 d - 14.5 mo	4.8	carbamate	YES	8	0.24
chlorpyrifos	6 mo.	22.6	84		3.8	OP	YES	96 - 270	0.18
cyfluthrin	1 yr.	56.0	63.0		9.3	pyrethroid			.00068 - .022
diazinon	3 mo.	11.5	35	3 - 14 wk	1.9	OP	YES	1250	toxic
dicofol	2 yr.	60		>1 yr	10.0	OC		570 - 595	0.12 - 0.37
dimethoate	3 mo.	11	122		1.8	OP	YES	235	30.2
disulfoton	1 yr.	5.6	70.0	56 d - 2 yr	0.9	OP	YES	1.9 - 12.5	0.038
endosulfan	1 yr.	40.5	150	10 - 160 d	6.7	OC	YES	18 - 160	0.001
esfenvalerate	1 yr.	52.5	90		8.8	pyrethroid		458	.0002 - .001
ethoprop	6 mo.	19.5	84		3.3	OP	YES	61.5	
ethyl parathion	6 mo.	22	2957.2	20 d - >16 yr	3.7	OP	YES	2	1.5
fenamiphos	1 yr.	43.5	470.2	92 d	7.3	OP	YES	2 - 19	0.11 - 9.6
fonofos	1 yr.	42.5	93.3		7.1	OP	YES	8 - 17.5	0.05
malathion	3 mo.	1.7	6.0		0.3	OP		5500	200
methamidophos	3 mo.	4.8	12.0		0.8	OP	YES	16 - 21	25 - 100
methidathion	3 mo.	7.0	23.0		1.2	OP		25 - 54	.002 - .014
methyl parathion	3 mo.	15.0	915.6	3 - 5 mo.	2.5	OP	YES	6 - 50	1.9 - 8.9
oxamyl	3 mo.	12.5	50		2.1	carbamate	YES	5.4	4.2 - 17.5
paraquat	Do Not Apply	1000	2409		166.7	bipyridyl		150	13 - 32
permethrin	6 mo.	34	38		5.7	pyrethroid		430 - 4000	.0018 - .0054
phorate	6 mo.	23.3	167.6	2 wk - 4.5 mo	3.9	OP	YES	2 - 4	0.002
propargite (omite)	no data					??		1480 - 2200	.031 - .100
terbufos	6 mo.	19.5	151.8		3.2	OP	YES	1.3 - 1.6	.001 - .39
trichlorfon	3 mo.	0.97	140	8 d - 1.5 mo.	0.2	OP		450 - 650	.26 - 2.5
trifluralin	2 yr.	88.2	405	157 d - >40 wk	14.7	dinitroaniline		>10,000	.02 - 3.4

[1]YES in this column indicates pesticides that have caused documented die-offs of migratory birds.

Appendix A. Reported Soil Half-Lives (in days) for South Florida Pesticides.*

alachlor	aldicarb	atrazine	azinphos-methyl	benomyl	carbaryl	carbofuran	chlorpyrifos	cyfluthrin	diazinon	dicofol	dimethoate	disulfoton	endosulfan
Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)
15	9.9	15	5	180	22	26	81	56	7	60	2.5	1	32
7	23	300	484	360	12	110	28	63	14		4	4	150
14	990	1898	21		25.5	14	84	Calc. $T_{1/2}$	35		122	7	39
4	7	53	68		8	28	7	42.1	11.5		7	56	42
49	12	113	10		12	60	18		6.3		11	70	Calc. $T_{1/2}$
7.8	23	28	30		Calc. $T_{1/2}$	75	11.5				29	Calc. $T_{1/2}$	42.0
Calc. $T_{1/2}$	2	181	Calc. $T_{1/2}$		379.4	30	25.1				36	4.3	24.2
133.3	15	115	44.0		195.2	60	8.7				Calc. $T_{1/2}$	3.1	
	54	48	51.3		51.7	28	Calc. $T_{1/2}$				6.6	10.5	
	20	357			43.8	43	20.1				53.1		
	46	78				53	30.0						
	18	20				8							
	154	58				10							
	60	67				14							
	9	Calc. $T_{1/2}$				73							
	12	84.0				Calc. $T_{1/2}$							
	20	48.3				9.7							
	361	20.0				2.8							
	Calc. $T_{1/2}$	10.0				334.2							
	8.9	48.3				113.4							
	2.0	127.5				22.6							
		56.7											
		26.4											
		134.3											
		279.9											
		149.9											
		36.5											
		89.7											
		23.4											
		92.3											
		60.6											

*Values were taken directly from the literature or calculated from degradation rates.

Appendix A. Reported Soil Half-Lives (in days) for South Florida Pesticides.*

esfenvalerate	ethoprop	ethyl parathion	fenamiphos	fonophos	malathion	methamidophos	methidathion	methyl parathion	oxamyl	paraquat	permethrin	phorate
Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)
15	25	7	50	40	1	1.9	5	4	11	1000	30	82
90	3	11	2.1	30	6	4.8	7	45	15	2409	38	2
	56	112	4	45	Calc. $T_{1/2}$	6.1	23	10	6	Calc. $T_{1/2}$		6
	14	182	11	18	4.3	12		15	14	268.7		30
	84	22	Calc. $T_{1/2}$	82	2.3	Calc. $T_{1/2}$		Calc. $T_{1/2}$	4			69
	12	23	13.1	Calc. $T_{1/2}$	1.0	2.7		4.3	33			Calc. $T_{1/2}$
	16	Calc. $T_{1/2}$	138.2	93.3	0.3			915.6	8			167.6
	73	12.1	462.8	75.0				203.1	50			23.3
	Calc. $T_{1/2}$	34.2	470.2	28.5								7.5
	23.0	2.4	43.5									98.2
	12.6	4.9										20.8
		16.2										1.6
		131.5										
		20.0										
		2957.2										
		224.9										

*Values were taken directly from the literature or calculated from degradation rates.

Appendix A. Reported Soil Half-Lives (in days) for South Florida Pesticides.*

terbufos	trichlorfon	trifluralin
Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)	Lit. $T_{1/2}$ (d)
5	1.1	38
22	140	61
16.9	0.6	211
86.6	0.8	405
12.8		Calc. $T_{1/2}$
66.5		66.7
10		109.8
4.5		
Calc. $T_{1/2}$		
22.5		
12.1		
151.8		
97.8		

*Values were taken directly from the literature or calculated from degradation rates.

Appendix B. Half-life Calculation Worksheet.

Atrazine	Lit. $T_{1/2}$	units	$T_{1/2}$ (days)	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	0.5	mo	15	50	12	wk	12.0	84.0
	10	mo	300	70	12	wk	6.9	48.3
	5.2	yr	1898	50	20	d	20.0	20.0
	53	d	53	75	20	d	10.0	10.0
	113	d	113	70	12	wk	6.9	48.3
	28	d	28	29	9	wk	18.2	127.5
	181	d	181	60	75	d	56.7	56.7
	115	d	115	86	75	d	26.4	26.4
	48	d	48	71	8	mo	4.5	134.3
	357	d	357	13.8	60	d	279.9	279.9
	78	d	78	75	10	mo	5.0	149.9
	20	d	20	85	100	d	36.5	36.5
	58	d	58	90	298	d	89.7	89.7
	67	d	67	93	3	mo	0.8	23.4
				86	262	d	92.3	92.3
				95	262	d	60.6	60.6

Trichlorfon	Lit. $T_{1/2}$	units	$T_{1/2}$ (days)
	1.1	d	1.1
	140	d	140
	14	hr	0.6
	20	hr	0.8

Aldicarb	K_{el}	units	Calc. $T_{1/2}$
	0.078	d^{-1}	8.9
	0.35	d^{-1}	2.0

Phorate	Lit. $T_{1/2}$	units	% degraded	time	units	Calc. $T_{1/2}$
	82	d	18	48	d	167.6
	2	d	76	48	d	23.3
	6	d	90	25	d	7.5
	30	d	47	90	d	98.2
	69	d	95	90	d	20.8
			95	7	d	1.6

Carbaryl	Lit. $T_{1/2}$	units	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	22	d	12	10	wk	54.2	379.4
	12	d	22	10	wk	27.9	195.2
	25.5	d	80	120	d	51.7	51.7
	8	d	85	120	d	43.8	43.8
	12	d					

Methyl	Lit. $T_{1/2}$	units	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
Parathion	4	d	99.5	33	d	4.3	4.3
	45	d	64	45	mo	30.5	915.6
	10	d	99	45	mo	6.8	203.1
	15	d					

Appendix B. Half-life Calculation Worksheet.

Alachlor	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	85	1	yr	0.4	133.3

Carbofuran	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	95	42	d	9.7	9.7
	97	14	d	2.8	2.8
	7	5	wk	47.7	334.2
	60	5	mo	3.8	113.4
	99	5	mo	0.8	22.6

Chlorpyrifos	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	62	4	wk	2.9	20.1
	50	30	d	30.0	30.0

Cyfluthrin	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	90	140	d	42.1	42.1

Dimethoate	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	77	2	wk	0.9	6.6
	98	10	mo	1.8	53.1

Disulfoton	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	68	1	wk	0.6	4.3
	79	1	wk	0.4	3.1
	90	5	wk	1.5	10.5

Endosulfan	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	50	42	d	42.0	42.0
	70	42	d	24.2	24.2

Ethoprop	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	19	1	wk	3.3	23.0
	32	1	wk	1.8	12.6

Ethyl	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
parathion	96	8	wk	1.7	12.1
	20	11	d	34.2	34.2
	96	11	d	2.4	2.4
	95	3	wk	0.7	4.9
	95	10	wk	2.3	16.2
	10	20	d	131.5	131.5
	50	20	d	20.0	20.0
	3	130	d	2957.2	2957.2
	33	130	d	224.9	224.9

Appendix B. Half-life Calculation Worksheet.

Fonophos	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	59	4	mo	3.1	93.3
	67	4	mo	2.5	75.0
	64	6	wk	4.1	28.5

Malathion	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	80	10	d	4.3	4.3
	95	10	d	2.3	2.3
	50	24	hr	24.0	1.0
	90	24	hr	7.2	0.3

Paraquat	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	13	54	d	268.7	268.7

Terbufos	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	35	14	d	22.5	22.5
	80	28	d	12.1	12.1
	12	4	wk	21.7	151.8
	18	4	wk	14.0	97.8

Trifluralin	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	85	0.5	yr	0.18	66.7
	90	1	yr	0.30	109.8

Fenamiphos	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	94.6	55	d	13.1	13.1
	24.1	55	d	138.2	138.2
	9	63	d	462.8	462.8
	9.8	70	d	470.2	470.2
	67.2	70	d	43.5	43.5

Azinphos-methyl	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	50	44	d	44.0	44.0
	93	197	d	51.3	51.3

Methamidophos	% degraded	time	units	Calc. $T_{1/2}$	$T_{1/2}$ (days)
	92	10	d	2.7	2.7