Natular® G Exposure Assessment, Summary

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Summary of Environmental Fate & Behavior

Spinosad is relatively rapidly dissipated in water. Photolysis is predominant, with hydrolysis and dissipation to sediment also contributing. The degradation in sediment is slower than from the water column but is still regarded as rapid, with 15-20% of the applied dose being found after 35 days. Degradation is via a fairly complex pathway beginning with an initial rapid loss of parent compound activity and ending in complete breakdown to CO2. Tables 1 and 2 summarize the physicochemical endpoints and environmental degradation of Spinosad, respectively.

TABLE 1. Physicochemical endpoints of Spinosad

Property	Spinosyn A	Spinosyn D	Notation
Dissociation constant (pKa)	8.10	7.87	Amino group protonates in neutral and environmentally relevant acidic pH conditions
Water Solubility mg/L (Distilled Water	89.4	0.495	Slightly to moderately soluble
pH 5	290	28.7	Becomes less soluble as pH increases (consistent with protonation of the amino group)
pH 7	235	0.332	
pH 9	16	0.53	
Henry's law Constant ($Pa.m.^3mol^{-1}$)	2.46×10^{-7}	3.01×10^{-5}	Very slightly volatile from water
Partition Coefficient (log Pow)	3.9	4.4	
pH 5	2.8	3.2	Affinity for the organic phase increases with PH (consistent with protonation of the amino-group)
pH 7	4.0	4.5	
pH 9	5.2	5.2	

TABLE 2. Route and rate of degradation

Property	Findings
Aerobic metabolism	Half-lives of 9.4 to 17 days for spinosyn A and 15 days for spinosyn D in a sandy loam soil.
Field Dissipation	Half-lives of spinosyn A determined to be < 1 d
Residues on leaves	Half-lives of 2-3 days
Hydrolysis	Spinosyn A and spinosyn D are hydrolytically stable at pH 5 and 7.

	At pH 9, the extrapolated half-life calculated by first order kinetics was estimated at 200 and 259 days for spinosyns A and D, respectively
Photolysis	The half-lives of spinosyn A and spinosyn D were determined in a buffer of pH 7 in natural sunlight to be 22.3 and 19.7 *hours*, respectively. In natural pond water, the half-life of the total spinosad component was 4.3 hours. In an aquatic microcosm study, at 2 days spinosyn A accounted for < 15% of that applied (it had more than 85% degraded)

Effects on Aquatic Organisms

A summary of the acute and chronic toxicity endpoints for aquatic organisms is provided in Table 3. Spinosad is slightly or moderately toxic to fish on an acute and chronic basis. All algal species tested showed some sensitivity to spinosad but the difference was marked. Spinosad is slightly to moderately acutely toxic to daphnia and other aquatic invertebrates such as oysters and shrimp. However, on a chronic basis spinosad is highly toxic to daphnia.

TABLE 3. Acute and Chronic Toxicity Endpoints for Aquatic Organisms

Species	Study-Type	Endpoints
Fish	Acute LC50	Carp (*Cyprinus carpio*): 4.99 mg/L Sheepshead minnow (*Cyprinodon variegatus*): 7.87 mg/L Bluegill sunfish (*Lepomis macrochirus*): 5.94 mg/L Trout (*Oncorhynchus mykiss*): 30 mg/L
	Early Life Stage (62 days)	*Oncorhynchus mykiss*: 0.498 mg/L
Daphnia	48 hour static test	EC50 1.48 mg/L
	48 hour semi-static (renewal at 24 hours)	EC50 = 14 mg/L
	21 day chronic flow through	NOEC = 0.62 µg/L
	21 day outdoor microcosm	NOEC < 8 µg /L (recovered populations)
Marine Amphipod	10 day acute test	NOEC > 63 mg/kg dry sediment; > 1.38 mg/L pore water; 0.327 mg/L overlying water
Grass Shrimp	96-hr semi-static (renewal every 24 hours)	NOEC = 9.76 mg/L
Mysid Shrimp	28 day chronic test	NOEC = 84 µg /L
Eastern Oyster	96 hour flow through	EC50 (shell growth) 295 µg /L
Algae	96 hour static	Green algae EC50: > 110 mg/L Freshwater diatom EC50, 0.11 mg/L Marine diatom EC50, 0.23 mg/L Cyanobacteria EC50 8.1 mg/L
Duckweed	14 day acute	EC50 based on growth rate: 12.7 mg/L

Peak Environmental Concentration (PEC)

For single-brood formulations like Natular G granules, spinosad will be applied directly to the aquatic environment and the Peak Environmental Concentration (PEC) may be calculated from the application rate and water depth. The aqueous concentration at the time of introduction (A_0) at water depths of 10 – 60 cm (4 – 24 inches) is expressed in Table 4, for applications at 3.5 and 6.5 lb Natular G per acre.

TABLE 4. Peak Environmental Concentrations (PEC) of spinosad subsequent to application of Natular G at rates of 3.5 to 6.5 lbs/acre in varying water depths (10 – 60 cm)

Application Rate				Depth	PEC
lb/A	lb ai/A	g ai/A	mg ai/m^2	m	mg ai/L
3.5	0.0175	7.938	1.96	0.10	0.0196
				0.15	0.0131
				0.30	0.0065
				0.45	0.0044
				0.60	0.0033
6.5	0.0325	14.742	3.64	0.10	0.0364
				0.15	0.0243
				0.30	0.0121
				0.45	0.0081
				0.60	0.0061

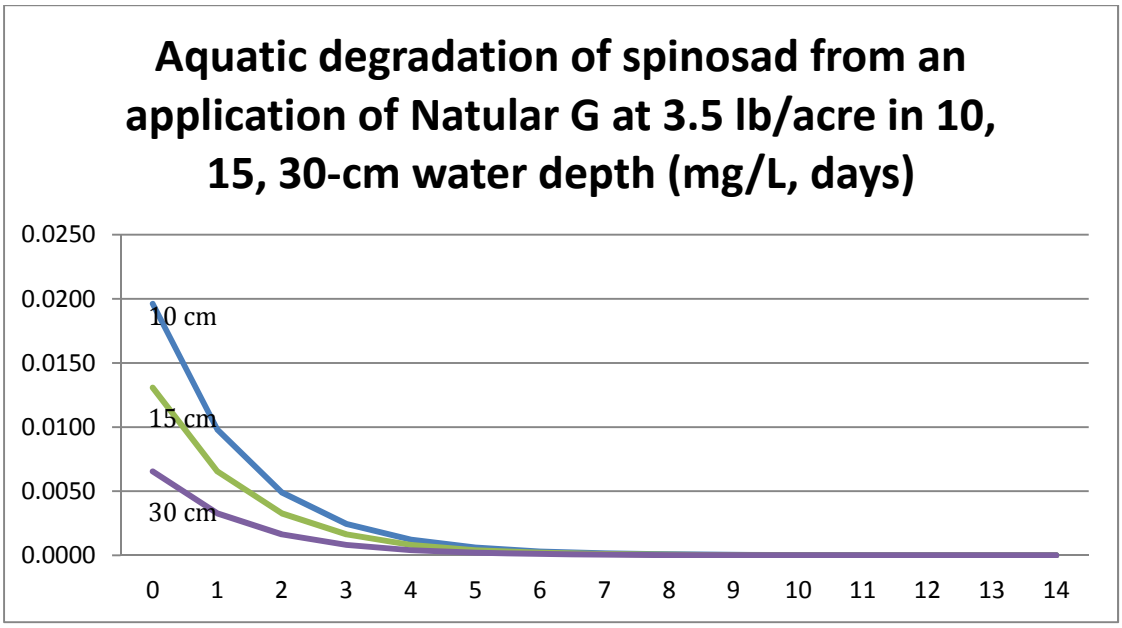
With consideration for the rapid degradation of spinosad by photolysis, estimates of concentration over time may be expressed in terms of first order kinetics. The aqueous concentration may be expressed as $A_{[t]} = A_0e^{-kt}$, where $k = \ln(2)/t_{½}$. Given the low application rate and the dominance of the initial photolytic processes, the use of first order kinetics is not likely to under predict the PEC even though degradation may slow with time. In turbid situations, degradation by photolysis may be slightly slower, but is likely to be balanced by spinosad's proclivity for organic sorbtion. Exceptionally turbid environments are likewise not anticipated to support significant non-target populations.

Consideration is given here (Table 5, Figure 1) to degradation using the reported aquatic photolytic half-life rounded up to the nearest full day (1-day) and the most conservative water depths (10 - 30 cm). Minimum application intervals of 7 to 14 days ensure that degradation is sufficiently complete before re-application and that long term chronic exposure does not occur. PEC for single-brood formulations is achieved upon application (day 0) and concentration is decreases thereafter until degradation is complete.

TABLE 5. Concentration of spinosad (mg/L) subsequent to application at 3.5 lb/acre in water depths of 10 to 30 cm.

	Day									
Depth	0	1	2	3	4	5	6	7	8	9
0.1 m	0.0196	0.0098	0.0049	0.0025	0.0012	0.0006	0.0003	0.0002	0.0001	< 0.0001
0.15 m	0.0131	0.0065	0.0033	0.0016	0.0008	0.0004	0.0002	0.0001	0.0001	< 0.0001
0.18 m	0.0109	0.0054	0.0027	0.0014	0.0007	0.0003	0.0002	0.0001	< 0.0001	< 0.0001
0.30 m	0.0065	0.0033	0.0016	0.0008	0.0004	0.0002	0.0001	0.0001	< 0.0001	< 0.0001

FIGURE 1.



Risk Assessment.

Once obtained, PEC is compared to the toxicity thresholds for sensitive indicator organisms to assess risk to these organisms from acute or chronic exposure to the concentrations. Risk to freshwater organisms from acute exposure to peak concentrations is assessed.

Normally, environmental risk from acute exposure is assessed by calculating the Environmental Risk Quotient [RQ = PEC/LC50 or EC50] for the most sensitive organism(s) representative of the treatment environment. The following guidelines are generally considered appropriate for the assessment of acute risk:

RQ > 0.5 ;	risk is unacceptable (significant impact to non-target populations may occur in the treatment area)
0.1 ≤ RQ ≤ 0.5	risk may be able to be mitigated by some form of operational risk management (mortality in exposed sensitive non-target organisms may occur but may not significantly impact populations)
RQ < 0.1 ;	risk is considered acceptable (minimal impact or not likely to impact individuals or populations)

The acute toxicity end-point (LC_{50} or EC_{50}) for non-target freshwater organisms (Table 3) is compared to the PEC for the varying water depths (Table 5). For fish, freshwater invertebrates, and aquatic plants, exposures are not of concern at any depth. Acute exposure RQ values are acceptable (< 0.1) for all freshwater organisms at water depths > 0.15 m (6 inches). RQs are marginally > 0.1 for the freshwater diatom in water depths < 0.15 m on the day of application but fall below exposure concern threshold within one day. This toxicity to algae, however, has not been observed in the practical operation with Natular products at equivalent application rates, or with the Natular

G at higher labeled rates. Other algal species are not as sensitive to spinosad exposure as the freshwater diatom (96-hour EC_{50} for green algae, marine diatom and cyanobacteria were > 110 mg/L, 0.23 and 8.1 mg/L, respectively).

			ACUTE TOXICITY EC_{50} or LC_{50} (mg/L)				
			Fish	Daphnia	Eastern Oyster	Freshwater Diatom	Plant
			Cyprinus carpio	*D. magna*			Duckweed
			4.99	1.48	0.295	0.11	12.7
depth	**day**	**mg ai/L**	**Acute Risk (RQ = At /EC_{50} or LC_{50})**				
0.1 m	0	0.0196	0.00	0.01	0.07	**0.18**	0.00
	1	0.0098	0.00	0.01	0.03	0.09	0.00
	2	0.0049	0.00	0.00	0.02	0.04	0.00
0.15 m	0	0.013	0.00	0.01	0.04	**0.12**	0.00
	1	0.007	0.00	0.00	0.02	0.06	0.00
	2	0.003	0.00	0.00	0.01	0.03	0.00
0.18 m	0	0.0109	0.00	0.01	0.04	0.10	0.00
	1	0.0054	0.00	0.00	0.02	0.05	0.00
	2	0.0027	0.00	0.00	0.01	0.02	0.00
0.30 m	0	0.007	0.00	0.00	0.02	0.06	0.00
	1	0.003	0.00	0.00	0.01	0.03	0.00
	2	0.002	0.00	0.00	0.01	0.01	0.00

For chronic exposures, risk is considered to be acceptable in environmental risk assessment if the (PEC) estimated for prolonged exposure is less than the chronic no-observed effect concentration (NOEC) for the species most sensitive to chronic exposure (PEC < NOEC). The daphnid is the freshwater organism most sensitive to chronic exposure (NOEC < 0.008 mg/L, Table 3). As described above, the peak environmental concentration from the proposed application of Natular G will exceed the NOEC for the daphnid only in shallow waters, and only immediately upon application. Rapid photolytic processes degrade the insecticide to below chronic exposure threshold within hours of application. Chronic exposures at levels greater than the NOEC will not occur in the proposed application scenario.