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AGENCY
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ENVIRONMENTAL FATE AND EFFECTS DIVISION

OFFICE OF PESTICIDE PROGRAMS

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Chemical: Sodium Acifluorfen

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THRU: Kevin Costello, Acting Branch Chief
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RE: Response to BASF's "60-day" comments posted to the Public Docket OPP-34241 on the draft RED on Sodium Acifluorfen.

EFED has reviewed BASF's 60-day comments on Environmental Risk Assessment prepared by the Environmental and Effects Division (EFED) of OPP for the reregistration of the herbicide sodium acifluorfen. This document is the Agency's response to BASF's comments concerning the Environmental Fate, Transport and Water Assessment.

FATE, TRANSPORT, AND WATER ASSESSMENT ISSUES

The following EFED responses correspond to Fate and Transport and Drinking Water issues as presented in the BASF response letter dated September 18, 2001 and Appendices 3 and 4 of the BASF submittal. The major issues appear to be over the Agency's recommendation for additional fate studies for sodium acifluorfen and the potential for ground-water contamination, specifically the SCI-GROW input values and the estimated drinking water concentrations estimated by SCI-GROW. The Agency's main fate data concern with sodium acifluorfen is the sorption/desorption (163-1) of acifluorfen under different soils. The Agency will require additional sorption/desorption (163-1) studies on acifluorfen and amino acifluorfen. Depending on the outcome of the sorption/desorption studies additional terrestrial field dissipation studies (164-1) may be required. The other fate studies (aerobic and anaerobic soil metabolism, aerobic and anaerobic aquatic metabolism, and aquatic dissipation studies) were intended to be implemented as needed to support the sorption/desorption data and will not be required. The Agency has requested the additional data to allow for more specific and focused mitigation actions.

The Agency considered all the fate and transport information submitted by the registrant and presented in public literature. The surface, ground-water, and drinking water assessment considered both monitoring data and estimates generated by linked PRZM and EXAMS and SCI-GROW. The modeling generally followed the "then" current EFED modeling practices. Monitoring data were obtained from registrant sponsored studies, USGS (NAQWA), and others (STORET). Based upon the review of the materials submitted by BASF, the Agency determined that the water assessment will not change or will not change appreciably.

The BASF comments in Appendix 3 appear to deal with the environmental fate studies submitted and reviewed by the Agency. With the exception of a photolysis study, most of the fate Data Evaluation Records were completed by EFED in 1996, then forwarded to the Registrant. Thus, there has been ample time for the registrant to bring to Agency's attention any specific issues associated with these studies.

The BASF comments dealing with Appendix 4 are addressed throughout this memo as no specific question was made. Efforts were made to capture the intent of the comments.

BASF Comment:

1. p.1. In its overview summary document, EPA states that its ability to predict the fate or concentrations of acifluorfen in soil or water has considerable uncertainty and that additional studies are needed to better define the persistence of the compound in the environment. The Agency states:

EPA recommends: that additional fate studies be conducted for sodium acifluorfen to better understand the fate processes that control its movement in soil under different environmental conditions. Desirable studies include OPP Guidelines 163-1 (Soil Partition Coefficient), 162-1 (Aerobic Soil Metabolism), 162-2 (Anaerobic Soil Metabolism), 162-3 (Anaerobic Aquatic Metabolism),

162-4 (Aerobic Aquatic Metabolism), 164-1 (Terrestrial Field Dissipation), and 164-2 (Aquatic Dissipation).

BASF would like to point out that the Agency has stated elsewhere in its review that all environmental fate guideline data requirements for sodium acifluorfen have been adequately fulfilled. More detailed discussions of the data submitted to fulfill each of these guideline requirements are presented in Appendix 3 and in Appendix 4.

EFED Response:

EFED did indicate that the environmental fate guideline data requirements for sodium acifluorfen have been adequately fulfilled. The fate of sodium acifluorfen, or acifluorfen in the environment, is dependent on a number of soil chemical and physical properties, in addition to different climatological conditions. The Agency had requested the additional data to allow for more specific and focused mitigation actions.

The Agency's main fate concern with sodium acifluorfen is the sorption/desorption (163-1) of acifluorfen under different soils. Therefore the Agency will continue to require additional sorption/desorption data. The (164-1) terrestrial field dissipation study may be required depending upon the results of the sorption/desorption studies. The other fate studies ((162-1) aerobic and (162-2) anaerobic soil metabolism, (162-4) aerobic and (162-3) anaerobic aquatic metabolism and (164-2) aquatic dissipation) were intended to be implemented as needed to support the sorption/desorption data and will not be required.

The Agency is not implying that all use sites will result in levels of contamination as observed in the Wisconsin small-scale Prospective Ground-Water Monitoring Study, but does not believe that the data are sufficient to allow for the development of mitigation actions.

BASF Comments:

In addition, BASF is submitting with this document literature references concerning the environmental fate of acifluorfen. These literature references address some of the specific concerns cited by the Agency and are consistent with the environmental fate data submitted by BASF. BASF believes that laboratory and field data do present a consistent picture of the fate of the compound in the environment and BASF does not believe that conducting additional studies will add more to this understanding.

In the overview EFED document, under Data Requirements, EPA outlines a set of additional data that it states are "necessary to be able to understand the importance of the different processes under different environmental conditions." BASF is hereby responding to those comments from the Agency.

EFED Response:

EFED appreciates the literature citations presented by BASF, but these papers were considered in the environmental fate assessment.

EFED's main fate concern with sodium acifluorfen is the sorption/desorption of acifluorfen under different soils. The dissociated sodium acifluorfen (anionic form acifluorfen) should be repelled by negatively charge soil surface. However, the fate properties suggest that acifluorfen is mobile in mineral soils, but does have a capacity to sorb as Freundlich K_{ads} of 5.22 mL/g or less were measured in mineral soils. The degradate amino acifluorfen is at least as mobile as acifluorfen in sand ($K_{ads} = 1.25$ mL/g), in other soils (3) it was much less mobile.

The Agency thinks that the environmental fate data, public literature, and ground-water monitoring data suggest that the acifluorfen detections (frequent and high concentrations) that occurred in the Wisconsin small-scale Prospective GW monitoring study are possible and the no detections or low (low concentrations and/or infrequent) seen at the sodium acifluorfen retrospective sites and the lactofen small-scale prospective GW monitoring studies are also possible. The Agency is interested in better understanding differences in sorption of acifluorfen in the Plainfield sand from other vulnerable (but apparently less vulnerable) soils such as those found at the retrospective ground-water study sites. EFED recognizes that the Wisconsin site (Plainfield sand) is extremely vulnerable, the other ground-water monitoring sites (retrospective study sites), while vulnerable, may have had subtle (but significant) differences (some can be identified others cannot) making the sites less vulnerable to acifluorfen leaching and therefore few if any detections. The Plainfield sand is a Benchmark Soil Series as defined in the National Soil Survey Handbook (NSSH) (USDA-NRCS, 2001), and thus is important in Wisconsin. The Plainfield soil is of large extent and is found in Wisconsin, Illinois, Indiana, Michigan, Minnesota, New York, and Ohio. Of these, the states with highest acifluorfen use included Illinois, Indiana, Minnesota, Ohio, and Wisconsin (<http://water.wr.usgs.gov/pnsp/use92/acflrfn.html>, USGS, 1999). Other similarly vulnerable soils may also exist in the acifluorfen use areas.

BASF Comments:

163-1 Soil Partition Coefficient for acifluorfen, amino acifluorfen, and desnitro acifluorfen

The Agency states: 163-1 Soil Partition Coefficient for acifluorfen, amino acifluorfen, and desnitro acifluorfen. This study is necessary to support the registration of the herbicide because the sorption of acifluorfen depends upon a number of soil properties. Acifluorfen sorption is also a non-equilibrium, time-dependent process. The mobility of acifluorfen in soil is affected by the rate as well as the maximum extent of sorption. Amino acifluorfen is highly variable, depending upon soil texture. By better understanding the conditions that influence sorption, management options to prevent water contamination would be easier. This information is also needed for subsoils.

BASF responds:

Two studies were submitted for fulfilling requirements of soil adsorption studies with sodium acifluorfen. One was carried out with acifluorfen acid and one on the acifluorfen amine since this was the only metabolite found at >10% TAR in the environmental fate studies. For the acifluorfen, Koc values for sand, sandy loam, loam, low organic clay and high organic clay soils were 50.22, 73.52, 56.96 198.7 and 168.89, respectively. Adsorption and desorption were strongly correlated with soil clay content. For the acifluorfen amine, Koc values were 431 for sand, 652 for clay, 741 for loam and 7368 for loamy sand, indicating that amino acifluorfen is immobile in loamy sand, of low mobility in loam and clay soil, and of medium mobility in sand soil.

In addition to this worked performed by BASF, the sorptive properties of acifluorfen have been thoroughly examined in recent papers by Gennari et al., (1994) and Locke et al., (1997). Scientific papers cited in this section and following sections are found in Appendix 4. In summary, Gennari et al., show that acifluorfen binding in soil is dependent on organic carbon content and soil pH. Destruction of the organic carbon portion of the soils results in lost sorption by the soils. The pH effect was attributed to the net increase in positive charge on the surfaces of iron oxides in soil (not pKa). Since a change in binding was due to the increased charge on the clay portion of the soil, as pH decreased acifluorfen adsorption increased. Locke et al., (1997) attributed sorption of acifluorfen to organic carbon content, cation exchange capacity (CEC) and soil acidity. Detailed examination of the data indicates that the overwhelming contributor to sorption was made by the soil organic carbon content.

With regard to the primary transformation product of acifluorfen, amino acifluorfen, Andreoni et al., (1994) found that acifluorfen degraded to amino acifluorfen under both oxygen limited and oxygen unlimited conditions. Locke et al., (1997) observed transformation of acifluorfen to amino acifluorfen within 96 hours at 9.9% and 17.8% on Dundee and Sharkey soils respectively. They also looked at the effect of soil temperature on the degradation of acifluorfen indirectly through binding experiments. In their report, they stated that decreased binding was observed in the 4°C treatment compared to the 25C ° treatment. They also observed that the decrease in binding indicated that the transformation of acifluorfen to amino acifluorfen was microbially mediated. It was also noted that amino acifluorfen had a high affinity for soil, which explained the high sorption irreversibility they observed (K_{df} 41.3 and 47.2 for Dundee and Sharkey soils respectively). In an additional paper by Gaston et al., (2000), it was determined that intermediate products of acifluorfen were apparently highly sorbed as well.

From the literature it is clear that once degradation of acifluorfen occurs, transformation products adsorb strongly to soil.

EFED Response:

The Agency considered all the data presented by Suter (1993), Locke et al. (1997), and others as noted concerning sorption (Freundlich K_{ads}) and the relationship to ancillary soil properties (e.g., CEC, AEC, pH, OC, %-clay) as shown in Table 1. Ancillary data (CEC, pH, OC, %-clay) for the Plainfield sand (Appendix 1, Table D) is similar to several of the soils used by Suter (1993) and Locke et al. (1997) for which sorption and desorption values were measured. The literature cited by both the registrant and the Agency (here and in the RED) indicates that soils with potential for pH dependent charge can sorb acifluorfen even though it is negatively charged. The majority of the soils used by Suter (1993) and Locke et al. (1997) to evaluate acifluorfen sorption tended to be soils with a capacity for pH dependent charge. The prospective ground-water study monitoring suggested that sorption was much less than suggested by Suter (1993) and Locke et al. (1997) as considerable acifluorfen leaching occurred. The Plainfield sand and other similar soils may have a lower

capacity to sorb acifluorfen, or other negatively charged species, than suggest by the data of Suter and Locke et al. Other ancillary factors (e.g., clay mineral type and amount, iron and aluminum oxides and hydroxides) not measured can also influence sorption of negatively charged ions. Differences in organic matter, due to geographic location, may also be a factor. The Agency is therefore interested in better understanding differences in the sorption or binding potential of other vulnerable, relative to acifluorfen, soils in the acifluorfen use area (e.g., can additional significant correlation factors be found).

BASF is incorrect in their assertion that EFED incorrectly interpreted pKa. The following paragraphs were taken from the EFED RED chapter.

“Acifluorfen contains a carboxylic acid group with an acid dissociation constant (pKa) of 3.8. Thus, acifluorfen exists as an anion in most agricultural soils since the pH of these soils usually exceeds the pKa of the acid (Celi et al., 1997).”

“The sodium (Na⁺) on sodium-acifluorfen will dissociate resulting in negatively charged acifluorfen. Negatively charged sorption sites, such as clays, are therefore expected to have little contribution to the adsorption process. The adsorption/desorption of acifluorfen is dependent upon pH, organic carbon (OC) content, and ammonium oxalate extractable iron content of the soil (positively charged), but not clay content (Celi et al., 1996).”

EFED was clearly referring to variably charge soil surfaces (i.e., pH dependent charge). The factors that influence this phenomenon is discussed in detail in Appendix A.

Acifluorfen: The unaged batch equilibrium study gives a strong indication of the high mobility of acifluorfen. In four soils (sand, sandy loam, loam, and clay soils), acifluorfen appears to be highly mobile to mobile with Freundlich K_{ads} values of 0.148 to 3.10 $\mu\text{g/g}$ soil (Suter, 1993, MRID 427935-01) (Table 1). Although, Suter (1993) found that sorption and desorption were strongly correlated with soil clay content, sorption (K_{ads}) was not significantly correlated with OC and pH (as H⁺) (Table 2). Corresponding non-linear Koc values were 50.22, 73.52 56.96, 198.7 and 168.9 $\mu\text{g/g}$ soil organic carbon. Using the classification system in Dragan (1988), K_{oc} values between 50 and 150 are “mobile.”

Because sorption is measured by the Freundlich K_{ads} includes that which is “sorbed” by organic carbon and AEC and is influence by pH, soil mineralogy, clay types and percent, extent of weathering, etc., the Koc model may not be a good representation of the acifluorfen mobility.

Additional information (Locke et al., 1997) (Table 1) was also considered in the assessment. Locke et al., (1997) calculated Koc from the linearized Freundlich K_{ads} , thus, becoming K_d . Locke et al., (1997) reported Freundlich K_{ads} that were similar to those of Suter (1993); ranging from 0.47 to 5.22 ML/g with Kocs ($K_{oc1} = K_d/foc$) ranging from 51.4 to 140.5. Suter (1993) also linearized Freundlich K_{ads} , or K_d , which were used to calculate

K_{oc} . The K_d s in Suter's data ranged from 0.087 to 1.70 mL/g, and K_{oc} values for 29.6 to 109.9 mL/g_{oc}. The K_{oc} s also fall with the very mobile to mobile classification of Dragan (1988).

Table 1. Soil series, mineralogy, CEAC, foc, CEC, pH and sorption coefficients (Freundlich K_{ads} , and linearized K_d) and Koc ($K_{oc_f} = K_{ads}/foc$; $K_{oc_l} = K_d/foc$) for soils analyzed by Suter (1993) and Locke et al. (1997).

Suter, 1993 (MRID 427935-01)										
Soil		Mineralogy/ % clay	CEAC ¹	foc ²	CEC meq/100 g soil	pH	K_{ads} μg/g	K_d μg/g (linear)	K_{oc_f}	K_{oc_l}
Series	#									
Wagram	1	kaolinitic /2.0		0.0029	1.9	6.9	0.1477	0.0870	50.22	29.58
Greenfield	2	mixed /13.0		0.0047	12.5	7.5	0.3460	0.2116	73.52	44.96
Savoy	3	-/23.0		0.0262	22.4	6.3	1.5078	0.9381	56.96	35.44
Dowling	4	smectitic /41.5		0.0093	2.14	6.9	1.8701	1.0340	198.7	109.86
Fargo	5	smectitic /49.0		0.0186	41.0	6.8	3.1038	1.6970	164.9	90.15
Locke, M. A., L.A. Gaston, and R.M. Zablotowicz. 1997. Acifluorfen sorption and kinetics in soil. J. Agr. Food Chem. 45:286-293.										
Dundee loam (0-10 cm)	1	mixed /13.1	active	0.0075	12.1	5.59	0.84	0.48	NC	64.3
Dundee silty clay loam (0-10 cm)	2	mixed /35.2	active	0.0075	19.5	5.08	0.89	0.56	NC	74.9
Dundee silt loam (0-5 cm)	3	mixed /22.0	active	0.0119	14.3	5.29	2.04	1.30	NC	109.5
Dundee silt loam (0-5 cm)	4	mixed /22.0	active	0.0224	16.7	5.13	5.22	3.15	NC	140.5
Mahan loamy fine sand (0-13 cm)	5	kaolinitic / 4.7		0.0120	3.8	4.20	2.64	1.66	NC	138.0

Mahan fine sandy loam (26-36 cm)	6	kaolinitic /14.8		0.0001	4.1	4.40	1.22	0.86	NC	8600
Miami silt loam (0-10 cm)	7	mixed /40.0	active	0.0190	14.1	6.16	1.64	1.10	NC	57.9
Miami silt loam (0-10 cm)	8	mixed /40.0	active	0.0350	15.6	6.36	2.34	1.80	NC	51.4
Sharkey clay (0-10 cm)	9	smectitic /60.0		0.0169	43.7	6.00	3.24	2.16	NC	128.2
Ships clay (0-10 cm)	10	mixed /50.0	active	0.0083	40.1	7.50	0.98	0.61	NC	73.1
Weswood silt loam (0-10 cm)	11	mixed /21.0	super-active	0.0031	16.4	7.70	0.47	0.30	NC	95.2
Lafitte muck (0-10 cm)	12	20.0		0.1913	78.0	4.10	92.1	89.6	NC	468.4

¹ CEAC - Cation-Exchange Activity Class

² Fraction soil organic carbon (foc = % organic mater/(1.7 *100))

In addition to the registrant's submittals to meet Guideline Data Requirements (Suter, 1993 (MRID 427935-01) a number of researchers (e.g., Locke et al., 1997; Gaston and Locke, 2000; Gennari et al., 1994) have studied the adsorption and desorption of acifluorfen. The papers by Locke et al. (1997) and Gaston and Locke (2000) demonstrated the complex nature of the fate and transport properties associated with acifluorfen. However, as noted in the above paragraph, sorption has been measured for acifluorfen (Freundlich K_{ads}) in a number of soils. The sorption K_{ads} has been correlated to soil organic matter (measured as organic carbon (OC), cation exchange capacity (CEC), hydrogen ion concentration (H^+), clay content in all or some of the studies (Table 2). In Locke et al. (1997) data, the correlation between K_{ads} vs. OC decreased from 0.99 to 0.60 with the removal of the organic soil (muck) and K_{ads} vs. CEC was no longer correlated when the organic soil was omitted. Suter (1993) found significant correlations between K_{ads} vs. CEC and K_{ads} vs. %clay, Locke et al. (1997 did not (Table 2).

The data of Suter (1993), Locke et al. (1997) and others both show that sorption (Freundlich K_{ads}) can be significantly correlated to some (Table 2) ancillary soil properties. The results are however not entirely consistent and are somewhat dependent upon specific samples (e.g., Lafitte muck). Most of the soils presented by these authors represent soils that would be more likely to have the capability to sorb acifluorfen (e.g., high organic

carbon content, kaolinitic clay, significant levels of oxides and hydrous oxides). Specifically, the Agency is interested in soils that would be expected to have a low potential to sorb a negatively charge ion. These soils would be low in organic carbon content, low in clay content, dominated by smectitic clay minerals (e.g., 2:1 lattice, low iron and aluminum oxides), and is where sorption would be thought to be near zero.

Table 2. Summary of Pearson Correlation (r, p-value) of Freundlich K_{ads} and linearized K_d versus soil organic carbon (OC) content, cation exchange capacity (CEC), hydrogen ion concentration (H^+), and percent clay.

Study ID	K_{ads} vs. OC	K_d vs. OC	K_{ads} vs. CEC	K_{ads} vs. H^+	K_{ads} vs. %clay
Suter, 1993	0.65, 0.24	0.69, 0.19	0.97, 0.007	0.22, 0.72	0.96, 0.01 ¹
Locke et al., 1997 ²	0.99, 0.000	0.98, 0.000	0.82, 0.001	0.71, 0.01	-0.16, 0.62
Locke et al., 1997 ³	0.60, 0.049	0.68, 0.022	0.086, 0.802	0.098, 0.77	0.062, 0.86
Locke et al., 1997 ⁴	0.59, 0.070	0.68, 0.029	0.022, 0.951	0.20, 0.57	0.013, 0.97

¹ Bold values identified significant correlations.

² All soils considered, n = 12

³ Lafitte muck omitted, n = 11, remaining soils are mineral soils

⁴ Mahan fine sandy loam omitted because it is a non-surface soil (26-36 cm), n = 10, remaining soils are surface soils (0-5 or 0-10 cm).

Note: the K_{ads} and Koc_f for the Lafitte muck (92.1 mL/g and 468.4 mL/g_{oc}, respectively) and the Mahan fine sandy loam [22-36 cm] (1.22 mL/g and 8600 mL/g_{oc}), respectively, were not considered in the water assessment (Tables 1 and 2). The Lafitte muck is a non-mineral soil and should be considered separately from the other soils. The measured K_{ads} for the Mahan subsoil [22-36 cm] and the Mahan surface soil [0-13 cm] were 1.22 and 2.64 mL/g, respectively. The subsoil Koc was not considered, because sorption is related to other factors in addition to organic carbon. With the low organic carbon content 0.01 percent, the importance of organic carbon as the Koc is overestimated. BASF appears to have also done this in their Appendix 4.

The Agency is requesting additional mobility data, because the sorption data has shown that acifluorfen is very mobile to mobile. Currently, with the exception of the Mahon soil (26-36 cm)(in Locke et al., 1997) all the Freundlich K_{ads} were measure on surface soils (0-10 cm). The Mahon soil is characterized as having kaolinitic type clay, and is a mineral type conducive to pH dependant charges and low organic carbon (matter) content. The soil texture of the Plainfield sand is similar to the Mahan soil, but the Plainfield CEC (0.2 to 2.7 meq/100g) is lower than the Mahan soil (4.1 cmol(+)/kg)). The organic carbon content for the Mahan, (0-5 cm) soil is 1.2 percent, appears to be higher than for the Plainfield sand (0 - 30 cm) is 0.29 to 0.41 percent (there is uncertainty because the depth increments are

different). Thus, there is an indication that less sorption potential for the Plainfield sand than the Mahan loamy fine sand. The mobility of the acifluorfen is demonstrated in the Plainfield sand by the small-scale prospective ground-water monitoring study (Norris, 1989, MRID 411728-01).

Amino acifluorfen: Data submitted by BASF showed the percentage of acifluorfen amine sorbed was 92.7, 85.5, 79.2 and 28.7% TAR to loamy sand, loam, clay, and sand soil, respectively. The R^2 values were 0.988, 0.999, 0.869, 0.999 and 0.951, respectively (1/n values were 0.936, 0.893, 0.869 and 0.802). The measured K_{ads} values were 47.01, 19.34, 12.11, and 1.25 for loamy sand, loam, clay, and sand soil, respectively. The Koc values calculated were 7368, 741, 652, and 431 for loamy sand, loam, clay, and sand soil textural classes, respectively. Since the K_{ads} were not linearized to K_d , the Kocs may be over estimated. These data show a considerable range in value. The K_{ads} for amino acifluorfen measured in sand (1.25 mL/g) is less than the lowest K_{ads} measured for acifluorfen (3.10 mL/g). Thus, in some soils the amino acifluorfen degradate may be more mobile than acifluorfen. EFED used a relative mobility classification system to give the Kocs into meaningful perspective. Using McCall's relative mobility classification, an acifluorfen amine is classified as "immobile" in loamy sand, "low mobility" in loam and clay, and "medium mobility" in sand. In the RED Chapter, EFED noted that the mobility varied depending upon soil texture and organic carbon. Table 3 shows that the amino acifluorfen K_{ads} does not increase systematically with increasing organic carbon or decreasing sand content (sand → loamy sand → loam → clay) for the four soils shown. Pearson Correlation (Table 4) shows that K_{ads} was not significantly correlated with organic carbon and "clay content" (Proxied by lowest sand in textural class). EFED stated that the amino acifluorfen is less mobile than acifluorfen. The highest calculated Koc 7368 mL/g_{oc} was obtained from a sample that had the second lowest organic carbon content and second highest sand content.

The concern that EFED is that the K_{ads} for amino acifluorfen is quite mobile in a sand ($K_{ads} = 1.25$ mL/g) and the metabolism studies show that it is fairly persistent (65% TAR at 375 days) in the anaerobic soil metabolism study and (43% TAR at six months) in the aerobic soil metabolism study. Therefore under these conditions amino acifluorfen could contribute to the "toxic acifluorfen residues" in water.

Table 3. Leaching and adsorption/desorption of degradates (amino acifluorfen) MRID 44129-02.

Soil Texture	Kads	Percent Organic C	Koc
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sand	1.25	0.29	431
clay	12.11	1.86	652
loam	19.34	2.61	741
loamy sand	47.0	0.64	7368

Table 4. Pearson Correlation Matrix for amino acifluorfen, K_{ads} , %OC and Low Sand.

	K_{ads}	%-OC
%-OC	-0.067	
p-value	0.934	
LOW SAND ¹	0.127	-0.858
p-value	0.873	0.143

¹ The particle size distribution for the four soils was not available so the lowest sand fraction (%) in the appropriate textural class (e.g., sand has $\geq 70\%$ sand).

BASF Comment:

The Agency states:
162-1 Aerobic Soil Metabolism

The line between metabolic and chemical degradation of acifluorfen is quite blurry. Acifluorfen also degrades to amino acifluorfen and a number of identified polar substances. The fate of these needs to be better characterized.

BASF responds:

The aerobic soil metabolism of sodium acifluorfen was studied in four soils. The parent slowly declined in all of the soils and the half-lives were estimated to be 100 to 200 days. In the aerobic soil metabolism study parent was the only major metabolite accounting for >10% TAR. The residue declined from 90% TAR at 0 DAT to 43% after six months. The amino and the desnitro analogs were minor metabolites, each accounting for 2.4 to 3.1% TAR at six months. Volatiles accounted for less than 1% TAR.

In addition to this work performed by BASF, a study of the aerobic soil metabolism of sodium acifluorfen has recently been reported in the literature (Gaston et. al.,2000). In this study, the half-life of acifluorfen obtained in the laboratory, using soil columns instead of the standard bioflasks, ranged from 7.2 to 63 days. The results of this study are discussed in detail in Appendix 4.

EFED Response (including response to Appendix 4):

The Agency agrees that the work of Gaston and Locke (2000) shows aerobic soil metabolism half-lives, of 100 to 200 days, that are in good agreement with those submitted by the registrant (Argo, 1982, MRID 001227-60; Gemma, 1984, MRID 00143572; and Looper, 1990, MRID 00143572). Thus aerobic soil metabolism (degradation or mineralization) is quite slow, and generally follows first-order kinetics. The half-life values are in agreement with those submitted by the registrant and cited in the RED. The Agency does not anticipate the need for any more aerobic soil metabolism data, the data requirement is satisfied.

Gaston and Locke (2000) also found, in a 49-day study that degradation was faster in the surface soil samples than the subsoil samples. At the end of study, 61.0 to 80.9 percent of the radioactivity was identified as acifluorfen. Mineralization accounted for between four and 6 percent of the applied radioactivity and 3.4 to 12.1 percent was “unextractable” at the end of the study. In leaching columns, effluent contained 35 to 57 percent of applied ¹⁴C acifluorfen. A portion 10.1 to 23.7 percent of applied ¹⁴C acifluorfen was identified as “unextractable.” The Gaston and Locke (2000) suggest that the “unextractable” material is amino acifluorfen which generally appears to have a greater propensity than acifluorfen to bind to soil material (not true for all soils).

The work of Gaston and Locke (2000) suggests that the more rapid degradation in the soil columns may have been the result of poor aeration, as acifluorfen degradation is faster under anaerobic conditions than aerobic conditions. Thus, they conclude that the degradation rates obtained from the mobility studies may tend toward the high end of the possible range of values. EFED notes that the registrant does not necessarily agree with this (per their comment Appendix 4). However, due variability in the laboratory is not unexpected because of small sample size (number and mass) and since microbial populations in soils are highly variable and would influence degradation rates.

Additionally, EFED does not agree with the BASF statement, “The degradation data for acifluorfen is consistent. The half-life of acifluorfen under field conditions is relatively short.” The decline of acifluorfen in field studies is a “dissipation half-life” not a degradation half-life (Wagenet and Rao, 1985). **Dissipation includes leaching.** EFED doesn't know what the “Gustafson-Holden” is.

BASF Comment

The Agency states:
162-2 Anaerobic soil metabolism

Acifluorfen is rapidly transformed to amino acifluorfen. The fate of acifluorfen beyond this point is not clear. Its mobility is quite variable, high to low, with apparent persistence.

BASF responds:

To satisfy the anaerobic soil metabolism data requirements, an anaerobic soil metabolism study was carried out on a clay soil from Mississippi. In this study, acifluorfen rapidly declined from 95.5% TAR at 0 DAT to 6.3% TAR at 10 DAT with a half-life of 2.75 days. The amino analog of acifluorfen was the

major metabolite, formed by rapid reduction of the nitro group. It increased from 1.6% TAR at 0 DAT to 76.9% TAR at 10 DAT and then declined to 64.6% TAR at 375 DAT. Acetamide was a minor metabolite found at a maximum concentration of 3.12% TAR at 375 DAT.

In addition, as reported above, recent citations from the literature shed light on the fate of amino acifluorfen under both aerobic and anaerobic conditions. Andreoni, *et al.*, (1994) found that acifluorfen degraded to amino acifluorfen under both oxygen unlimited and oxygen limited conditions. Locke, *et al.*, (1997) observed transformation of acifluorfen to amino acifluorfen within 96 hours at 9.9% and 17.8% on Dundee and Sharkey soils respectively. They also looked at the effect of soil temperature on the degradation of acifluorfen indirectly through a binding experiment. In their report, they stated that decreased binding was observed in the 4°C treatment compared to the 25°C treatment. They also observed that the decrease in binding indicated that the transformation of acifluorfen to amino acifluorfen was microbially mediated. It was also noted that amino acifluorfen had a high affinity for soil, which explained the high sorption irreversibility they observed (K_{df} 41.3 and 47.2 for Dundee and Sharkey soils respectively). Gaston, *et al.*, (2000) determined that intermediate products of acifluorfen were apparently highly sorbed as well.

From the literature it is clear that once degradation of acifluorfen occurs, whether under oxygen limited conditions or oxygen unlimited conditions, transformation products adsorb strongly to soil.

EFED Response:

The Agency has concerns with amino acifluorfen as it is included in HED's toxicity assessment. The data cited by BASF shows under anaerobic conditions the decline of acifluorfen and the formation of amino acifluorfen (as 65% TAR) remain after 1 year. The K_{ads} for amino acifluorfen, in sand (1.25 mL/g) is lower than highest K_{ads} (3.13 mL/g) for parent acifluorfen, thus, once in water, the potential exists for this degradate to remain in solution phase for considerable time. The Agency is not requiring additional anaerobic soil metabolism studies.

BASF Comment:

The Agency states:

162-3 Anaerobic Aquatic Metabolism

Need to tie into the aerobic conditions better.

BASF responds:

BASF does not understand the question the Agency is asking. The work of Andreoni, *et al.*, demonstrates that the amino compound is formed under both aerobic and anaerobic conditions. The rate of formation may be different depending on the aerobicity of a given system, but that is going to be true for all compounds. BASF can not envision a study that could definitively determine a rate of formation for all states of aerobicity.

The Agency states:

162-4 Aerobic Aquatic Metabolism

The aerobic aquatic half-life suggest that acifluorfen is persistent in an aquatic environment. Aqueous photolysis is quite rapid.

BASF responds:

An aerobic aquatic metabolism study which was carried out in a clay soil showed acifluorfen to be stable under aerobic aquatic conditions. No other metabolites were detected in this study. The major route of dissipation in water appeared to be by photolysis as shown by the guideline photolysis study where acifluorfen underwent rapid degradation to multiple components, none of which were present at significant concentrations.

EFED Response:

EFED will not require additional (162-4) aerobic or (162-3) anaerobic aquatic metabolism studies. EFED will therefore consider to acifluorfen to be quite stable in the aquatic environment (half-life estimated from 2 data points is about 117 days, times 3 for modeling when only one value the half-live would be 351 days). These are values used in this assessment and will also be utilized in any future water assessments. The anaerobic aquatic was estimated to be 168 days (28 days x 3 x2).

The Agency was making a point that photolysis is only significant where there is light penetration (e.g., shallow, clear water bodies). When light does penetrate, the stability noted by BASF, suggests that acifluorfen residues would be quite persistent in water. Additionally, since light does not penetrate into ground water, this may explain the persistence of the high levels of acifluorfen remaining in the ground water at the Wisconsin study site.

EFED has determined that the most recent photolysis data submitted by the registrant was not included in the assessment. In the assessment a half-life of 3.8 days (92 hrs from the EFED one-liner) was used. Including the most recent data (Venkatesh, 1996, MRID 441950-02) the mean aqueous half-life is 7.08 days (169.9 hrs). The 90 percent upper bound on the mean is 11.2 days (269.8 hrs). Thus, the input rate for EXAMS should have been 0.00256 hr^{-1} rather than the 0.0075 hr^{-1} . This would suggest that the EECs for surface water were under estimated. But EFED does not believe that this would have a major influence on the results.

BASF Comments

The Agency states:

164-I Terrestrial Field Dissipation

This study may be necessary to relate laboratory results to actual field conditions.

BASF responds:

BASF has carried out a number of studies that examine the behavior of sodium acifluorfen under field conditions. A small scale retrospective study was carried out with the compound (421522-01) in an attempt to answer questions concerning the ability of the compound to leach. Five sites were included in the study. Each site was selected for its representation of a specific growing region (based on

soybean, peanut or rice use patterns). Additionally, prior sodium acifluorfen use history (1 to 4 years of prior use) as well as soil vulnerability characteristics were also considered when selecting sites. DRASTIC scores were used to maximize the probability of selecting vulnerable sites. Final site selection was made from an examination of soil type, hydrogeology and annual precipitation information.

Since soil texture, organic matter content, depth to ground water and annual precipitation were used as selection criterion, the sites chosen were extremely vulnerable. By study completion, all sites had received at least three years of sequential sodium acifluorfen applications. Measured rainfall quantities during the conduct of the studies were close to or exceeded historical rainfall amounts. Well water samples were collected monthly for 12 months following the last test substance application. The analytical method used for measuring samples had a LOQ of 1 ug/L. By study completion not a single sample collected during the duration of the study had quantifiable residues of sodium acifluorfen. Results from this study indicates that acifluorfen is not a groundwater concern under conditions of use even on highly vulnerable soils. Additional data collected in this study were field half-lives for the compound at 5 different locations. These were found to be 14 days at the VA site; 22 days at the TN site; 15 days at the NC site; 8 days at the IN site; and 55 days at the ND site.

As noted above, field studies have resulted in half-lives of sodium acifluorfen which range from 8 days (IN) to 55 days (ND). Aerobic soil metabolism studies have given values that range from 108 days (NJ) to 200 days (KS). The Agency has questioned the relationship of field results to laboratory studies, and has stated that a new field study may be required to sort out this discrepancy. Recent results from the literature provide important clarity to this issue. In a study carried out by Gaston, *et al.*, (see Appendix 4), the half-life of acifluorfen obtained in the laboratory using soil columns instead of the standard bioflasks was in excellent agreement with results obtained in field studies. The laboratory degradation data for acifluorfen obtained by Gaston, using the soil column technique, ranged from 7.2 to 63 days.

These results are consistent with the data obtained under field conditions, where the measured half-lives ranged from 8 to 55 days.

EFED Response

The Agency is reserving the need for additional terrestrial field dissipation studies on the outcome of the sorption/desorption studies. Thus, the terrestrial field dissipation studies (164-1) would be anticipated to address specific issues.

The Agency states:

164-2 Aquatic Dissipation

The rice studies showed rapid degradation of acifluorfen with low concentrations of degradates formed. The importance of aqueous photolysis (*e.g.*, the rice pond was only 4 inches deep) and reducing (anaerobic processes) conditions is unclear in other water bodies.

BASF responds:

BASF does not understand the Agency's question. Photolysis will play a role in all aquatic systems where there is exposure to light. Since the rate of photolysis is directly related to light intensity and light intensity is directly related to depth, one presumes that a rate constant for photolysis could be calculated at a given depth. The work of Andreoni, *et al.*, demonstrates that amino acifluorfen is formed under both aerobic and anaerobic conditions. The rate of formation may be different depending on the aerobicity of a given system, but that is going to be true over a continuum of

environmental conditions and for nearly all compounds which are degraded under both aerobic and anaerobic conditions. BASF can not envision a study that could definitively determine a rate of formation for all states of aerobicity.

Based on the discussion above, BASF believes that the data required to understand the behavior of sodium Acifluorfen in soil and water under different environmental conditions exist. The Agency has stated in its review that all environmental fate guideline requirements for sodium acifluorfen have been fulfilled and BASF does not believe that repeating any of these studies will allow a better definition of the variability of the persistence or mobility of the compound in the environment.

EFED Response:

The agency is also not asking for an aquatic dissipation study. The Agency was also not requesting another aqueous photolysis study, but only noting that the fate of acifluorfen in deeper water bodies may be different than a 4 inch deep rice pond. Photolysis is only significant where there is light penetration (e.g., shallow, clear water bodies). When light does not penetrate, the stability noted by BASF, suggest that acifluorfen residues could be quite persistent in water.

BASF Comments:

DRINKING WATER EXPOSURE ASSESSMENT

1. p. 20. Water Resources Assessment: The Agency states that it believes that the major risk associated with the use of sodium acifluorfen is the contamination of surface and ground water. EPA has used the SCI-GROW model to estimate potential ground water concentrations for acifluorfen and acifluorfen as a degradate of lactofen under hydrologically vulnerable conditions. BASF does not agree with the Agency's use of certain values in the SCI-GROW calculations and has data that contradict certain of the values that were used in the modeling exercise. BASF presents a detailed response to these evaluations in Appendix 4.

Based on the data presented in Appendix 4, BASF has calculated a revised worst case SCI-GROW Ground Water Screening Concentration of 0.401 ppb. Therefore, the modeled concentrations of sodium acifluorfen in ground water would be recalculated as:

Target Maximum Water Exposure (mg/kg/day): 7.8×10^{-5}

EEC of Sodium Acifluorfen (Ground Water): 0.401 $\mu\text{gm/l}$

EEC of Sodium Acifluorfen (Surface Water): 1.4 $\mu\text{gm/l}$

Total EEC for Surface and Ground Water: 1.801 $\mu\text{gm/l}$

The DWLOC for cancer risk for sodium acifluorfen has been recalculated by BASF (see page 6 of this document) to be 2.8 $\mu\text{gm/l}$. Therefore, modeled water concentrations do not exceed the DWLOC and the modeled water concentration is below the Agency's level of concern.

EFED Response:

The small-scale prospective ground-water monitoring for acifluorfen, conducted in the Wisconsin, confirmed the potential for acifluorfen to contaminate ground water. SCI-GROW is a screening model that estimates the concentration of a pesticide in shallow ground water (average depth 15 feet) beneath sandy, highly permeable soils when monitoring data are not available. The monitoring data and the SCI-GROW estimates were considered when selecting an estimated drinking water concentration (to prevent the estimate from going to high). The monitoring data would likely result in a higher estimated drinking water concentration than that of SCI-GROW.

As stated above, SCI-GROW is a very simple model and does not fully address all the factors which ultimately result in a pesticide leaching to ground water. SCI-GROW was not developed to address anionic pesticides. SCI-GROW requires sorption to be considered as K_{oc} (OC only explained about 60 percent of the sorption measured (Table 2) as K_{ads}), which as supported in literature may not adequately represent a pesticide's mobility under all conditions. Gennari et al., (1994) demonstrated a reduction in the sorption affinity (%OC decreased from 14.8 to 3.8) of soil E. The Freundlich K_{ads} decreased from 43.1 to 21.7. **Further reduction of OC in soil E to 0.55% resulted in negligible adsorption, and no significant relationship between adsorption and herbicide concentration was found.** Thus K_{oc} may not adequately present the mobility of a pesticide when soils have low organic matter and are dominated by permanent charge surfaces.

BASF Comment:

In Appendix 4, BASF questions the K_{oc} value used in the water assessment

EFED Response:

When the initial water assessment was conducted (DP Barcode 239268, 10/99), EFED did not have any of the registrant studies data in house. All that was available was the "K_d" of 1 mL/g that was present in the EFED One-Linear Data Base. No information concerning the soil was available, thus 1 percent organic carbon was assumed, which resulted in a "K_{oc}" estimate of 100 mL/g soil organic carbon.

During the RED process the registrant data was retrieved and public literature was considered and are listed in Table 1. The BASF data (Suter, 1993, MRID 427935-01) measured K_{ads} in five soils, which were linearized to K_d by the registrant (Table 1). Locke et al., (2000) measured K_{ads} in twelve soil samples (Table 1) and also linearized the K_{ads} to K_d. The calculated K_{oc}s, where $K_{oc} = ((K_d/oc)*100)$, are given in Table 1. As noted elsewhere, the Lafitte muck and Mahan subsoil was omitted from the calculations used in this assessment. The mean and standard deviations for K_d and K_{oc} for Suter's (n = 5) data, Locke et al., (n = 10), and the combined data (n = 15) are shown in Table 5. For these data the range of K_d is 0.087 to 3.15 mL/g.

The surface water assessment used K_d equal to 1 mL/g, since PRZM and EXAMS can use either K_d or K_{oc} . The value of 1.0 mL/g is slightly higher than the mean K_d submitted by BASF (0.79) and slightly lower than either the Locke et al., (1997) data (1.31 mL/g) or mean of both data sources (1.14 mL/g) (Table 9). This small difference will have little influence on the surface water concentrations estimated by the linked PRZM/EXAMS models. **Due to other uncertainties (these have been fully documented elsewhere) associated with the surface water assessment, the small difference in K_d will have no impact on the water assessment.**

Table 5. Summary of K_d and K_{oc} for studies of Suter (1993) and Locke et al., (1997).

Source	n	mean K_d (mL/g)(std)	mean K_{oc} (mL/g-soil oc)(std)
Suter, 1993	5	0.79 (0.66)	61.99 (35.81)
Locke et al., 1997	10	1.31 (0.90)	93.30 (33.84)
combined	15	1.14 (0.84)	82.87 (36.55)

BASF Comment:

BASF suggest that rapid degradation of acifluorfen to amino acifluorfen which bind tightly to soil is why there are no detections of acifluorfen in ground water, excluding the PGW study.

In their Appendix 4, the registrant presents arguments about the Small Scale Prospective Ground Water Monitor study.

EFED Response:

In the prospective ground-water monitoring study, sodium acifluorfen was applied to a crop, acifluorfen and the two primary degradates were analyzed for (amino acifluorfen, desnitro acifluorfen), no degradates were detected, acifluorfen concentrations decreased with time in the soil samples, the suction lysimeters were effective in collecting water samples which contained acifluorfen residue, and acifluorfen residue was eventually detected ground-water monitoring well samples. The fact that no degradates were detected suggests no “binding” of acifluorfen residues which leached out of soil to ground water.

The functioning of the suction lysimeters indicates that leaching occurred through the soil matrix. The acifluorfen levels continued to remain through the term of the study. Since acifluorfen levels in soil decreased and no degradates were detected the major route of dissipation appears to be by leaching. This is supported by the persistence of acifluorfen (an aerobic metabolism half-life) and photolysis would not contribute once entering the soil or

aquifer. Additionally since the organic carbon (matter) content of the Plainfield sand is extremely low, the potential to sorb to the organic fraction would be limited.

In their Appendix 4, BASF also states that the Agency focused too much on the PGW monitoring data. They suggest a number of flaws in the Prospective Study. The Agency has considered the Retrospective studies (EPA can identify a number of flaws in these studies including the same ones BASF cited for the prospective study) and the NAWQA data as suggested by BASF. The retrospective and prospective studies are targeted studies (we know that sodium acifluorfen was used in recent history). The NAWQA study is not targeted for acifluorfen. Finally, the Agency believes that the environmental fate profile for acifluorfen suggests that not all “vulnerable sites” are equally vulnerable.

BASF also identifies some “issues” concerning the prospective ground water study. The Agency is well aware of these issues and the registrant’s desire to downplay to results of the prospective ground-water monitoring study and to put more emphasis on the retrospective studies. The registrant has failed to acknowledge that the retrospective ground water study had many of the same limitations as the Prospective Study (e.g., the monitoring wells were also installed by hand augers, were cased with PVC tubing, and not cased at the surface with concrete (Phone-Poulenc Ag. Company Protocol No EC/P-89-0017). In other words, the retrospective study has many of the same or more limitations than the registrant identified in the prospective study. The Agency has previously identified a number of “issues or limitations” associated with the retrospective study as well as the prospective study. The Agency has not discounted the issues that the registrant has made, but considered them together with all the information that is available.

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APPENDIX A: Additional Discussion on Factors That Influence Acifluorfen Sorption.

Note: Tables with numerical values (1 to 4) are in main document. Table with letters are in Appendix A.

EFED studied the papers that BASF is citing in their September 18, 2001 letter and considered them in the initial assessment. EFED agrees that it is the pH effect is attributed

to variably charge soil surfaces (i.e., pH dependent charge) (Uehara and Gillman, 1981) and stated this in the RED. EFED assumed that the pH of all soils used for agricultural would be greater than the pKa, and thus being an anion .

One would expect that the negatively charged acifluorfen would be repelled by negatively charged soils surfaces (mineral and organic). However, the sorption data shows that some sorption is occurring (Table 1). Soils with a pH dependent charge may be the reason. Two mineral-chemical systems found in the clay mineral fraction of soils form the basis for this distinction: a) the constant surface charge and b) the constant surface potential (Uehara and Gillman, 1981). Montmorillonite (a smectite), is a clay mineral that is an example of a constant surface-charge mineral. The surface charge of this type of mineral is due to isomorphous substitution within the mineral structure, and therefore, is permanent. This type of mineral is typically call a permanent charge mineral. In most cases these charges are negative and are balanced by cations in the soil solution (for net charge balance).

Soils with constant surface potential typically occur under in highly weathered conditions, where the permanent charge has been severely altered or completely weathered out, so that the surface charge arises from adsorption of potential determining ions (Uehara and Gillman, 1981). The most important potential determining ions are the hydrogen and hydroxyl ions, thus, the sorption to mineral surfaces depends upon the soil solution pH. These charges are the result of the protonation or addition of H⁺ ions to hydroxyl groups. These minerals are referred to as pH-dependent or variable charge minerals. Kaolinite, a clay mineral, is an example of a mineral with a variable charge. Organic matter, oxides and hydrous oxides, slightly soluble carbonates, and sulfates can be also be treated as variable-charge soil constituents (Uehara and Gillman, 1981). A comparison of CEC and anion exchange capacity (AEC) for different minerals is listed in Table A (Bohn et al., 1979; Klaus and Zech, 1997; Sposito, 1989).

The point of zero charge (PZC) is the pH value where equal amounts of H⁺ and OH⁻ have been adsorbed onto the hydroxylated surface so that the net surface charge from this source is zero (Uehara and Gillman, 1981). It is an important parameter in a variable charge system, because it determines the sign of the net surface charge. If the actual pH of the system is less than pH₀ (i.e., is more acid than pH₀), then the surface is a net positively charged, and conversely, the surface is net negatively charged when pH > pH₀. It is important to remember that the CEC, AEC, and ZPC values given in Table A are pure mineral systems and not mixed as in soils.

Unfortunately, this can be further complicated because the measurement of soil pH can be highly ambiguous (Bohn et al., 1979; Sposito, 1989). Two factors that influence soil pH measurements are the soil-solution ratio and the equilibrium salt concentration. Increasing either factor will decrease the measured soil pH. The combination of exchange and hydrolysis in salt solutions can lower the measured pH unit as much as 0.5 to 1.5 units, compared to the pH in distilled water suspensions (Bohn et al., 1979).

Table A. Cation exchange capacity (CEC) and anion exchange capacity for different soil minerals or amorphous materials (Klaus and Zech, 1997; Sposito, 1989)

Mineral phase	CEC @ pH 7	AEC @ pH 4	PZC ¹
	(mmol/kg)		
Al(OH) ₃	14	295	9.2
Gibbsite	18	57	8.0 - 9.0
Ferrihydrite	18	146	8.5
Goethite	27	117	7.0 - 8.0
Hematite	18	41	7.9 - 8.5
Kaolinite	55	38	4.0 - 6.9
Illite	161	39	not analyzed

¹ PZC is point of zero charge.

Representative CEC values for other soil colloids (any substance whose particles are less than a few micrometers in size (Tan, 198?)) are given in Table B. As can be seen the CEC varies depending on the soil colloid. Excluding, the organic fraction of the soil, the 2:1 lattice clay minerals tend to have greater CECs than 1:1 lattice clay minerals.

Table B. CEC for different soil colloids (Tan, 198?, Principles of Soil Chemistry, Marcel Dekker, Inc.)

Soil Colloid	CEC (meq/100 g or cmol/kg)
Humus (a portion of soil organic matter)	200
Vermiculite (clay mineral) 2:1	100 to 150
Montmorillonite (clay mineral) 2:1	70 to 95
Illite (clay mineral) 2:1	10 to 40
Kaolinite (clay mineral) 1:1	3 to 15
Sesquioxides (Fe and Al hydrous oxides)	2 to 4

A relative comparison between the adsorption of Cl^- and SO_4^{2-} at different pHs to a kaolinitic soil to a montmorillonitic soil is shown in Table C (Bohn, 1979). This clearly demonstrates that certain clay types have a greater affinity for anion exchange than others.

Table C. Adsorption of Cl^- and SO_4^{2-} by a kaolinite soil and Cl^- by a montmorillonitic soil in relationship to pH (after Bohn et al., 1979).

Kaolinitic Soil			Montmorillonitic Soil	
meq sorbed/100 g soil			meq sorbed/100 g soil	
pH	Cl^-	SO_4^{2-}	pH	Cl^-
7.2	0.0	0.0	6.8	0.0
6.7	0.3	2.0	5.6	0.0
6.1	1.1	5.5	4.0	0.05
5.8	2.4	7.1	3.0	0.1
5.0	4.4	10.5	2.8	0.4
4.0	6.0	-	-	-

Uehara and Gillman (1981) presented a scheme for classifying materials into permanent, mixed, and variable categories (their Figure 5.1, page 129). Most soils in the continental United States will be dominated by permanent charge systems. Therefore, soils would possess a “net negative charge,” thus, the negatively charged acifluorfen would tend to be repelled and not sorbed to soil material. An example given is a sample that is by weight 95 percent quartz sand and 5-percent permanent charge smectite will fall into the permanent charge category because the combined variable-charge surface from the quartz and smectite would constitute less than 10-percent of the samples specific surface. This example is similar to the Plainfield (Table D) sand (93 - 97 % sand, 4% clay, and OC (mean) 0.34 to 0.04 percent and CEC) decreasing with depth range. The soil is probably dominated by the clay fraction (mixed mineralogy), with the permanent-charge being dominant. This is confirmed by data in Table D.

Because K_{ads} is not strictly associated with organic carbon, but may also be correlated to clay content and clay type (Table 2), and iron oxides (both can exhibit variably charged surfaces depending upon pH), Koc may not present accurate indication of the potential mobility. Thus, the negatively charged acifluorfen will be dependant upon the surface charge which is pH dependent. The Plainfield sand (soil as prospective study site) has virtually no clay (4%), low organic matter (expressed as percent organic carbon 0.029 to 0.40; mean = 0.11), pH (5.4 to 8.0; mean = 6.8) (Table D).

Table D. Selected summary statistics (mean/standard deviation) of selected soil data for the Plainfield Sand , n = 4 (Norris, 1989, MRID 411728).

Depth (cm)	CEC	% Clay	% OC	PH	% Sand
0 - 30	2.43/0.32	4/0	0.35/0.067	6.05/0.58	93.5/1.0
30 - 60	1.53/0.32	4/0	0.15/0.033	6.40/0.36	95/0
60 - 120	0.53/0.28	4/0	0.087/0.034	6.50/0.18	97/0
120 - 180	0.45/0.24	4/0	0.065/0.037	6.67/0.50	97/0
180 - 240	0.53/0.15	4/0	0.044/0.017	7.8/0.51	97/0
240 - 300	0.63/0.17	4/0	0.051/0.015	7.23/0.48	97/0
300 - 360	0.55/0.24	4/0	0.080/0.065	7.33/0.50	97/0

The data when consider together clearly indicate that a soil (such as the Plainfield sand) with low clay content (which dominated by or montmorillonitic (smectitic mineral) and low organic carbon, will not have much capacity to sorb negatively charged ions, such as acifluorfen.

Additional discussion

Selected data (foc, CEC, pH and sorption coefficients) presented by Suter (1993) and Locke et al. (1997) have been combined with soil taxonomic data (mineralogy, CEAC) by soil series and are summarized in Table 1 (DP Barcode D278710 - cover memo to this appendix).

Locke et al. (1997) reported that the linear correlations indicated that organic carbon content $R^2 = 0.99$), soil H^+ concentration $R^2 = 0.71$), and cation exchange capacity (CEC) $R^2 = 0.78$) were positively related to acifluorfen sorption (linearized K_d). Using multiple regression Locke et al. (1997) obtained equation (5) [eq. 5: $K_d = -1.05 + (0.102*OC) + (12769*(CEC)*(H))$ ($R^2 = 0.99$), which estimated K_d (linearized from measure Freundlich K_f (or K_{ads}) from organic carbon (OC), pH (as hydrogen ion concentration (H^+))), and cation exchange capacity (CEC). Note, EFED could not confirm eq. 5, although a similar relationship could be obtained (BASF apparently had similar finding - Appendix 4). Further evaluation, by EFED, of the Locke et al. (1997) showed that Lafitte muck soil is an outlier. This is true from a soil standpoint as the Lafitte soil is organic soil whereas the rest are mineral soils. The linear correlations of the Locke et al. (1997) (Table 2), with the Lafitte

soil removed, was only significant for organic carbon content (0.68, $p = 0.02$), whereas the H^+ concentration (0.09, $p = 0.80$) and CEC (0.10, $p = 0.78$) were not significantly correlated with K_d . Using Locke et al. (1997) data, excluding the Lafitte muck, resulted in an equation similar to Locke et al. (1997 (equation 5) $K_d = 0.0350 + (68.3638 * foc) + (4410.357 * CEC * H)$ ($R^2 = 0.62$). Locke et al. (1997) suggest that the Freundlich coefficient (K_f) with a 24-hour reaction time may underestimate the equilibrium sorption value.

Gennari et al. (1994) measured adsorption and desorption of acifluorfen in five Italian soils. They found Freundlich K_{ads} similar to those of Suter (1993) and Locke et al. (1997). Three (A, B, C) of the five soils would be directly applicable for inclusions in the environmental exposure assessment for sodium acifluorfen and two would not (D and E). Soils A and B are Entisols and C is an Inceptisol under the USDA NRCS Soil Classification System. Soil D is stated to be an Andosols (soils formed in volcanic material) and Soil E is assumed to be a Histosol (stated in paper as an Istosol). The Freundlich K_{ads} are 0.64, 0.57 and 5.48 mg/L for soils A, B, and C, respectively. The Kocs for these three soils, estimated from nonlinear Freundlich K_{ads} , were 65.3, 68.7 and 233.2 mL/g_{oc}. Sodium acifluorfen is not used in areas of US with volcanic soils (D) and sorption of acifluorfen in organic soils (E) is quite high, as noted in Locke et al. (1997). The Freundlich K_{ads} for soils D and E are 16.2 and 43.1 mL/g, respectively. Sorption was correlated to organic carbon content, H^+ concentration ($H^+ = 10^{-pH}$), and ammonium oxalate extractable iron concentration.

Gennari et al. (1994) further suggest that the significant correlation between the Freundlich K_{ads} and ammonium oxalate extractable iron indicates the importance of amorphous and less crystalline iron oxides in acifluorfen sorption in soils. Further literature citations are given concerning the interactions between oxides and hydrous oxides and anionic organic compounds and adsorption of carboxyl acids on iron-oxide surfaces are also noted. The pH is noted to be an important factor in adsorption of anionic pesticides on iron oxides, with decreasing pH favoring the increased adsorption. The increase in sorption, with decreasing pH, is attributed to the increase in the net positive charge at the surface of the iron oxides.

By removing (or lowering) the organic carbon content in soil E (a Histosol or organic soil) by oxidizing the organic matter with hydrogen peroxide (H_2O_2), Gennari et al. (1994) demonstrated a reduction in the sorption affinity (%OC decreased from 14.8 to 3.8) of soil E. The Freundlich K_{ads} decreased from 43.1 to 21.7. Reduction of OC in soil E to 0.55% resulted in negligible adsorption, and no significant relationship between adsorption and herbicide concentration was found. They indicate that the decrease in adsorption capacity of soil E following oxidation confirms that acifluorfen has a high affinity for the organic adsorption surfaces.

BASF Comment:

BASF makes a statement that "from the literature it is clear that once degradation of acifluorfen occurs, transformation products adsorb strongly to soil."

EFED Response:

EFED agrees that under laboratory conditions, the above statement appears to be true. Gaston and Locke (2000) also noted that acifluorfen degradation may be more rapid in the soil columns due to poorer aeration (more rapid degradation under anaerobic conditions). BASF did not entirely agree with this. However, in the Acifluorfen small-scale Prospective Ground-Water Monitoring Study (Norris, 1989, MRID 411728), two degradates (amino acifluorfen and desnitro acifluorfen) were analyzed for and not detected in soil, soil-pore water, ground water samples, suggesting no degradation but only dissipation (primarily as leaching). Additionally, the K_{ads} for sand is 1.25 mL/g, thus appears not to be strongly sorbed to all soils.

Many of thirteen soils (listed below) with sorption/desorption data (e.g., K_{ads}) as presented by the registrant (Suter, 1993) and literature (Locke et al., 1997; Gaston and Locke, 2000) are soils that tend to favor variably charge soil surfaces (i.e., pH dependent charge, high organic carbon content, and ammonium oxalate extractable iron content of the soil, clay type) (Table 1). CEC and clay content may also be important (kaolinite vs. montmorillonite), but they did not appear to important in all soils (Table 2).

Other Considerations by EFED

The Taxonomy of Soils used by Suter (1993, Locke et al., and Gaston et al., 2000) in their study of sorption and/or desorption data are listed below. Bold words is the **CEAC** (cation-exchange activity class).

Wagram - Loamy, kaolinitic, thermic Arenic Kandiodults
Greenfield - Coarse-loamy, mixed, thermic Typic Haploxeralfs
Savoy - not official soil series
Dowling - Very-fine, smectitic, nonacid, thermic Vertic Endoaquepts
Fargo - Fine, smectitic, frigid Typic Epiaquepts

Dundee - Fine-silty, mixed, **active**, thermic Typic Endoaqualfs (4/1999
(in a papers fine-silty, mixed thermic, Aeric Ochraqualf)
Mahan - Fine, kaolinitic, thermic Typic Hapludults
Miami - Fine-loamy, mixed, **active**, mesic Oxyaquic Hapludalfs
Sharkey - Very-fine, smectitic, thermic Chromic Epiaquepts
Ships - Very-fine, mixed, **active**, thermic Chromic Hapluderts
Weswood - Fine-silty, mixed, **superactive**, thermic Udifluventic Haplustepts
Lafitte - Euic, hyperthermic Typic Haplosaprists

References given in accompanying memo.