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PP# 9F2163 and FAP# 9H5204 Glyphosate on irrigated crops, fish, shellfish and water. Evaluation of analytical methods and residue data.

R. B. Perfetti, Chemist, Residue Chemistry Branch, HED (TS-769)

Product Manager No. 25 (R. Mountfort), Registration Division (TS-767) and Toxicology Branch, Hazard Evaluation Division (TS-769)

THRU: Acting Chief, Residue Chemistry Branch (TS-769)

Monsanto requests the establishment of tolerances for residues of the herbicide glyphosate (N-phosphonomethylglycine) and its metabolite aminomethylphosphonic acid, resulting from the use of irrigation water following applications on or around aquatic sites in or on the crop groupings cucurbits, fruiting vegetables, small fruits, stone fruits and the individual commodity hops at 0.1 ppm. Where tolerances exist for these or other commodities at higher levels (40 CFR 180.364), the higher tolerance applies also to residues from the uses cited. Other proposed tolerances are for fish at 0.2 ppm and for shellfish at 2.0 ppm. A food additive tolerance for potable water at 0.1 ppm is also proposed.

Tolerances have been established for glyphosate on a variety of commodities. These tolerances range from 0.1 to 15 ppm.

Two other glyphosate petitions are currently pending PP#'s 6F2122 and 9F2223.

Conclusions

1) Appropriate tolerances for irrigated crops should be proposed for all the crop groupings listed in 40 CFR 180.34(f) along with cottonseed, hops and avocados. The proposed regulation should be expressed in the form found in 40CFR 180.142(c) for 2,4-D. This should be submitted in a revised Section F.

2a) The nature of the residue in plants and animals (except fish and shellfish) is adequately understood. The terminal residue will consist of parent and aminomethylphosphonic acid.

2b) Specific details for the 1976 studies on catfish and carp at a 10 ppm exposure level are needed.

2c) No clear residue plateau was observed for edible tissue of bass and carp indicating that longer exposure periods are needed before a final conclusion with respect to bioaccumulation in these species can be made.

2d) There are no concerns over N-nitrosoglyphosate residues in fish at this time.

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2e) Studies on fish and shellfish employing "aged" residues of glyphosate do not fulfill RCB requirements with respect to residue levels in these species. Studies using "aged" residues would be an EFB concern. Therefore, since we do not normally require metabolism studies for shellfish, we will need only residue studies on this r.a.c. using "non-aged" residues of glyphosate and aminomethylphosphonic acid.

2f) The catfish study using radiolabeled glyphosate was very vague with respect to which of the samples were used for characterization of the residue. Also the bioaccumulation data was in direct conflict with results of an earlier study on bluegills. Finally, less than 50% of the radioactivity in the fish was characterized. We will need therefore clarification to which samples were used to characterize the radioactivity in fish as well as further identification of this residue. The conflict over the difference in bioaccumulation in the catfish vs bluegill studies should also be addressed.

2g) "Cold" residue experiments will be more informative at such time as the metabolism picture in fish is more clearly delineated.

2h) The nature of the residue and bioaccumulation factors in fish are not adequately understood at this time.

3) Adequate analytical methods are available for enforcement purposes.

4a) Combined residues of glyphosate and its metabolite in water after ditchbank treatments would not be expected to exceed 0.2 ppm provided the follow modifications in the label are made:

1) A specified interval before retreatment of a bank should be prescribed.

2) The treatment length should be limited to 1 mile in any 24 hour period.

3) The word "average" should be deleted from the water overlap statement.

4) The treatment of banks within 0.5 miles of potable water intakes should be prohibited.

5) A maximum application rate of 4 lb acid equivalent/acre per treatment of a bank should be prescribed.

4b) Extensive studies on the dissipation of residue in moving bodies of water are needed before any general uses involving direct application to flowing water could be approved and tolerances granted. This data should reflect adequate geographical representation and representative water situations. Also, any such uses would need to be so circumscribed that residues would not exceed the desired level when the water was diverted for either domestic or irrigation purposes.

4c) Combined residues of glyphosate and its metabolite would not be expected to exceed 0.5 ppm in water for the following uses: Shoreline treatments to impounded waters, levee applications (rice or sugarcane plots), total surface treatments to impounded waters and "dry-ditch" or "draw-down" applications (de-watered systems including irrigation ditches, canals and impounded waters) provided the label modifications described below for each use are submitted in a revised Section B.

1) Shoreline treatments to impounded waters: The statement that treated water may be used immediately for irrigation and fishing should be deleted as should the statement that treated water should not be used for domestic purposes as for watering livestock within 24 hours of treatment. Additional label restrictions which are required include: 1) Prescribing a specified interval before retreatment; 2) limiting overlap of water to 1 foot; 3) prohibiting treatment of shoreline within 0.5 miles of potable water intakes; and 4) prescribing a maximum application rate of 4.0 lb. acid equivalent/acre..

2) Levee applications: The label statements that treated water may be used immediately for fishing a irrigation purposes and that treated water should not be used for domestic purposes or for watering livestock within 24 hours of treatment should be deleted. Also, additional label restriction which are needed include proposing a specified interval before retreatment, limiting the overlap of water to 1 foot, and prescribing a maximum treatment rate of 4.0 lb acid equivalent/acre.

Finally, tolerances for crayfish (shellfish) must be established simultaneously with any water tolerance for this use since crayfish farming in rice paddies is practiced extensively in the South. The petitioner should be so informed.

3) Total surface treatments to impounded waters:

Raw data for the Florida study should be submitted.

The label restriction prohibiting use of treated water for livestock or domestic purposes is not practical and should be deleted in light of the recommended higher tolerance level. Also the statement that water may be used immediately for irrigation and fishing should also be deleted. Additional label restrictions which must be proposed include: 1) Prescribing a specified interval before retreatment of the water surface; 2) prohibiting treatment within 0.5 miles of potable water intakes; and 3) prescribing a maximum application rate of 4.0 lb acid equivalent/acre.

4) Dry-ditch or draw-down applications:

1) A specified interval before retreatment must be prescribed; 2) The statements, "Do not use for livestock or domestic purposes for 24 hours

following introduction of water" and "water may be used immediately for fishing or irrigation purposes," should be removed; 3) the treatment length should be limited to 1 mile for any 24 hour period; 4) treatment should be prohibited within 0.5 miles of potable water intakes; and 5) a maximum application rate of 4.0 lb acid equivalent/acre should be prescribed.

4d) In our conclusions above, all but one use (direct application to moving water) allowed us to recommend a suitable level in raw water. These levels ranged from 0.2 ppm for ditchbank applications to 0.5 ppm for all other uses. For the sake of consistency we conclude that for all of the uses proposed, with the exception of direct application to moving water, the proposed tolerance level in potable water should be 0.5 ppm. Should the additional residue data required above for direct application to moving water indicate that a higher level is needed for this use, this level should be proposed for residue in potable water for all uses.

4e) Residue data for irrigated crops reflected alfalfa, field beans, sorghum, squash, sugar beets, and tomatoes. In light however, of the 0.5 ppm (and possibly higher) level needed for this permanent tolerance, it is our judgement that additional data for irrigated crops reflecting at least 2 crops from each of the crop groupings listed in 40 CFR 180.34(f) as well as the individual crops sugarcane, cottonseed and hops, (Data for avocados is not needed) and different irrigation systems with exaggerated application rates is needed.

4f) No estimation of an appropriate tolerance level in fish can be made until such time as the metabolism and residue questions discussed in the conclusions above are resolved.

4g) Since we don not find residue studies using "aged" residues appropriate for determining a tolerance level in shellfish we can make no favorable recommendation for a tolerance in this r.a.c. until residue studies in various species of shellfish using "non aged" residues of glyphosate are submitted. No tolerances for potable water can be granted for the uses proposed until tolerances for fish and shellfish are also established.

5a) Until such time as a final conclusion with respect to tolerance levels needed in potable water and irrigated crops can be made, we cannot make any judgement with respect to the need for higher tolerances in liver and kidney and/or tolerances in meat, milk, poultry and eggs. This determination will be made when the deficiencies described above are satisfactorily resolved.

5b)
Should a 0.5 ppm tolerance for potable water be deemed adequate this would contribute ca. 4.5 ppm/day to the diet of cattle and ca. 0.82 ppm /day to the diet of poultry.

5c) Feeding studies submitted to date should be adequate for determination of appropriate tolerance levels in meat, milk, poultry and eggs unless exorbitant levels are needed for the potable water and irrigated crop tolerances.

Recommendation

We recommend that the proposed tolerances not be established for the reasons given in conclusions 1, 2b, 2c, 2e, 2f, 2g, 2h, 4a, 4b, 4c, 4d, 4e, 4f, 4g and 5a above. The petitioner should be informed of the additional information needed for resolution of these deficiencies. These are also given in the appropriate conclusions above.

Detailed Considerations

Formulation

The formulation to be used on aquatic sites is Monstanto's Roundup Herbicide. This formulation contains 41% of the isopropylamine salt of glyphosate and is marketed as an aqueous concentrate (EPA Reg. No. 524-308). The concentrate contains 3 lb of the acid/gallon (4 lb of the isopropylamine salt/gallon).

All inerts in the formulation are cleared under Section 180.1001.

The manufacturing process for technical glyphosate was submitted in conjunction with PP# 6E1809. The process was discussed in detail in our reviews of PP# 6G1826/FAP# 6H5140. Technical glyphosate contains 10% (maximum) impurities which were most recently listed in our review of PP# 9G2150. We expect no residue problems with these impurities in the formulation.

Nnitrosoglyphosate has also been found in the Roundup formulation and in the techncial material. This material has been undergoing an evaluation of hazard, with the result that OPP is, at present, not stopping the establishment of glyphosate tolerances because of the presence of N-nitrosoglyphosate (see memos of 8/24/78 R. Taylor to, E. L. Johnson and 9/5/78 memo for records R. Taylor).

Proposed Use

The use on water calls for application of up to 4.5 lb active ingredient/acre applied to shorelines or banks of moving bodies of water or impoundments or other non-flowing waters or to dewatered ditches or waterbeds. The contemplated use therefore will involve all types of water systems and will reflect terrestrial application and treatment of open bodies of water.

Specific directions for application to moving bodies of water are as follows: When applying this product along shorelines or banks of moving waters always do so while traveling upstream to prevent concentration. Spray only one bank at a time. Do not spray across open moving bodies of water. Do not overlap the water more than one foot average. Treated water may be used immediately for irrigation, livestock, fishing and for domestic purposes.

When treating the entire surface area of moving bodies of water apply while traveling upstream. Do not use for livestock or domestic purposes within 24 hours of application. Water may be fished or used for irrigation purposes immediately.

Specific directions for treatment of impounded or non-flowing bodies of water are as follows:

When treating weeds along shorelines of impounded water or in open water, avoid spraying where emerged weeds do not exist. Treated water may be used immediately for irrigation and fishing. Do not use for domestic purposes or for watering livestock within 24 hours of treatment.

When treating the entire surface of a body of water do not use treated water for livestock or domestic purposes for 30 days after the last treatment. Water may be used immediately for irrigation and fishing.

Specific instructions for dewatered systems are as follows:

When treating weeds in dry ditches or water beds following draw-down, allow 7 or more days before the introduction of water. Do not use for livestock or domestic purposes for 24 hours following introduction of water. Water may be used immediately for fishing or irrigation purposes.

We will discuss the practicality and ramifications of these label directions and various uses in the appropriate parts of the Residue Data and Meat, Milk, Poultry and Eggs Sections below.

Nature of the Residue

Metabolism studies submitted previously on a number of crops demonstrated that glyphosate is not readily absorbed from the soil via the root system of plants. Translocation does occur when the compound is applied to aerial plant parts. Metabolism occurs slowly in plants, for example, after 4-7 weeks 90% of the total material applied to apples was parent compound while metabolites aminomethylphosphonic acid and methylaminomethylphosphonic acid comprised <5% of the total residue. Degradation occurs by C-N bond cleavage to form aminomethylphosphonic acid and glyoxylate which are further catabolized with subsequent incorporation into natural plant contituents.

Metabolism studies in rats, rabbits and cows indicated that parent compound makes up the major portion of the residue in mammals with only trace amounts of aminomethylphosphonic acid being observed.

The nature of the residue in plants and animls (except fish and shellfish) is adequately understood. The terminal residue will consist of parent and aminomethylphosphonic acid.

With respect to the metabolism of glyphosate in fish, only one study, involving bluegills exposed to ^{14}C labeled glyphosate has been submitted previously. This study reflected glyphosate levels of about 1 and 0.01 ppm in the water. After 28 days exposure the fish were transferred to uncontaminate water for 14 days. Concentration of radioactive residues in the edible portions of fish plateaued at ca. 2X the concentration in the water. Radioactivity in fish in contaminated water were 10 times greater in the non-edible vs the edible portions. Little or no elimination of radioactive residues were observed after the 14 day recovery period. A redistribution of radioactivity from non-edible to edible portions of the fish was observed. Total radioactive residues at the higher exposure level were 3 ppm (calculated as glyphosate). This level is roughly the maximum recommended treatment rate. No identification of the radioactivity was performed.

The petitioner has now submitted additional studies on fish and shell-fish. These are discussed below.

The first study reflected exposing channal catfish and crayfish to model aquatic systems contining residues of radiolabeled glyphosate (equivalent originally to 4 lb acid equivalent/acre) which had been aerobically "aged" for 3 days followed by anaerobic "aging" for 27 days. After the 30 days of "aging" weld water was added to the system and equilibrated for 2 days at which time the catfish and crayfish were introduced into the system. After 28 days of exposure samples of both species were transferred to glass aquaria for 28 days (catfish) and 14 days (crayfish) depuration. Water, soil, catfish and crayfish were sampled periodically. Radioactive residues in water ranged from 0.043 to 0.089 ppm during the exposure period. Radioactivity in the soil was quite variable ranging from 4.5 to 15 ppm during the exposure period. With respect to catfish, radioactive residues in the muscle tissue plateaued at ca. 7 days and reached a maximum of 0.19 ppm at day 1 of depuration. The range after plateau was 0.09 to 0.19 ppm based on a mean residue in the water of 0.073 ppm. This would give a concentration factor of 2.6X in catfish tissue. Radioactive residues in the tissue decreased slowly to 0.1 ppm after a 28 day depuration period. Radioactivity in catfish viscera did not plateau until ca. day 14 of the exposure period. Residues of radioactivity ranged from 0.1 to 0.88 ppm during this period. Radio-activity decreased rather rapidly to 0.12 ppm in the viscera after 28 days of depuration. Based on the 0.073 mean residue in water, the concentration factor for glyphosate in catfish viscera is 12.05X. Detection limits in catfish tissue and viscera were given as <0.043 and <0.077 ppm respectively.

Radioactivity in crayfish appeared to plateau at day 7 in tissue and viscera. Radioactive residues ranged from 0.1 to 0.44 ppm in tissue and from 1 to 5 ppm in viscera. Maximum residues were observed on day 1 of depuration for both types of samples. The maximum values represent a 6.03X and a 68.49X concentration factor of crayfish tissue and viscera respectively based on an average concentration of 0.073 ppm in the water. As was observed in catfish radioactivity decreased slowly in tissue to a value of 0.34 ppm after 14 days of depuration and more rapidly to 1.91 ppm in viscera after the same 14 day depuration period. Detection limits in crayfish tissue and viscera were given as < 0.04 and <0.063 respectively.

A second study involving exposing marsh clams to model aquatic ecosystem containing "aged" residues of radioactive glyphosate. (The inital application rate was 4 lb acid equivalent/acre) for 35 days followed by a 21 day depuration period. The glyphosate residues were "aged" by spraying the material on a soil surface followed by aerobic "aging" for 5 days and 25 days of anaerobic "aging."

Sea water was then added and the system was allowed to equilibrate for 2 days after which time the clams were introduced. The clams were suspended in wire baskets in the tanks. Samples of soil, water and clams were taken periodically. Radioactivity in water ranged from non-detectable ($<$ 0.014 ppm) to 0.054 ppm during the exposure period. Radioactive residues in the soil were again quite variable and ranged from 6 to 12 ppm. Residues of radioactivity in clams did not appear to plateau until 21 days of exposure and ranged from 0.15 to 0.59 ppm during exposure and the maximum residue was observed on the 1st day of depuration. This maximum value represented a concentration factor of 20.6X for clams based on an average concentration of 0.029 ppm of radioactivity in the water during the exposure period. Residues decreased only slightly during 21 days of depuration to 0.43 ppm. The detection limit for clams was given as $<$0.025 ppm.

The third metabolism study reflected exposing channel catfish to radiolabeled glyphosate at a level of 0.58 ppm for 10 days followed by a 14 day depuration period. Fish were sampled at the end of the exposure period and at the end of the depuration period and separated into tissue and viscera. Water was sampled at 1,3,7 and 10 days after initiation of the experiment. Radioactive residues in the water ranged from 0.58 to 0.77 ppm during the 10 day period with low values appearing randomly throughout the period. Radioactivity in the catfish tissue was 0.057 ppm after exposure and 0.02 ppm after depuration. Catfish viscera showad 0.25 and 0.075 ppm of radioactivity respectively after exposure and depuration. This amounts to a whole fish residue of 0.14 ppm after 10 days exposure and 0.047 ppm after 14 days of recovery. Again, residues decreased more rapidly from the viscera than from the tissue during recovery as was seen in previous studies on catfish and crayfish.

Identification of the radioactivity in catfish fillet and viscera before and after depuration was attempted. Samples were separated into extracted tissue, aqueous extract and a precipitated protein fraction of the aqueous extract. A sample of the precipitated protein was hydrolzed with HCl and the resulting solution was also cleaned-up and taken for analysis. The report is very vague with respect to which aqueous and hydrolysed protein samples were finally analyzed via hplc. The following tentative results were observed. In the exposed catfish fillet apparently as little as 48% of the total radioactivity was identified. This minimum value in catfish fillet after depuration was ca. 32%. In the viscera the apparent minimum percentages of identified radioactivity were 62% and 35% for exposed and depuration viscera respectively. In all samples the only identified compounds were parent and aminomethylphosphonic acid. The percentage of aminomethylphosphonic acid in the samples analyzed ranged from 3.7 to 20.25% of the identified radioactivity.

The final study involved exposure of various species of fish to unlabeled glyphosate. The species were rainbow trout, largemouth bass, channel catfish and carp. The experiments reflected exposing trout, bass and catfish to glyphosate at levels of 0.1, 1.0, 3.0 and 10 ppm for 14 days. After the 14 day exposure period groups of the fish were exposed to untreated water for 35 additional days. Samples of water were taken for all experiments at 2 day intervals prior to and during the exposure period. Water was also sampled on days 3, 7, 14, 21, 28 and 35 of the withdrawal period. Fish samples were taken for all experiments at days 1, 3, 7, 10, and 14 of the exposure period and at days 3, 7, 14, 21, 28 and 35 of the withdrawal period. No specifics for the 1976 studies carried out on catfish and carp at an exposure level of 10 ppm were submitted, other than a statement that these experiments were conducted in a similar manner to those discussed above.

We will need the specific details of these two studies. The petitioner should be so informed. Maximum residues in the edible tissue of trout were 0.15 ppm for either the 3.0 or 10 ppm exposure levels. This level decreased to 0.1 and 0.14 ppm respectively after 21 days of withdrawal. All values in edible tissue at the 0.1 and 1.0 ppm exposure levels were $<$ 0.05 ppm. This was also the case ($<$ 0.05 ppm) for all values of aminomethylphosphonic acid in edible tissue of rainbow trout at all feeding levels. Detectable levels of glyphosate up to 0.07 ppm were found in the trout after 21 days of depuration. In the case of largemouth bass, maximum residues in edible tissues were $<$0.05 at the 0.1 and 1.0 ppm exposure levels, 0.07 ppm at the 3.0 ppm exposure level and 0.15 ppm at the 10 ppm level. After 21 days of withdrawal these levels increased to maximum levels of 0.09, 0.14 and 0.25 ppm for the 1.0, 3.0, and 10 ppm exposure levels respectively, but then decreased at longer times of up to 35 days. Residues in catfish reached maximums of $<$0.05, 0.10, 0.42 and 0.57 ppm at the 0.1, 1.0, 3.0 and 10 ppm exposure levels respectively. After 21 to 28 day depuration periods the maximum levels observed were 0.10(28), 0.05(21), 0.20(28) and 0.13(21) ppm respectively for the 4 levels. Maximum residues in the heads and viscera were observed at the 10 ppm exposure level and were 0.85 , 0.14 and 0.58 ppm for the trout, bass and catfish respectively. In most cases residues decreased significantly during withdrawal. Residues of inedible tissue during exposure increased and plateaued at ca. day 7 for trout and peaked at about day 10 and then decreased for catfish. With the bass however no clear peak or plateau was reached in edible tissue even after 14 days of exposure. Decreased in residues in edible tissue of all three species during withdrawal were acceptable.

With respect to the 1976 studies on catfish and carp exposed to a 10 ppm level of glyposate and mentioned above, maximum residues of 0.22 ppm in edible tissue were observed in catfish and this level decreased to 0.09 ppm after 14 days of withdrawal. Edible carp tissue(?) contained a maximum residue of 0.44 ppm which decreased to 0.12 ppm after a 3 day depuration period. Maximum residues in heads and viscera were 2.33 and 3.96 ppm for catfish and ca respectiviely. These levels decreases to 1.96 ppm in catfish after 7 days and to 1.38 ppm in carp after 3 days of withdrawal. Residues of aminomethylphosphonic acid were observed in the heads and viscera of both species. The maximum level in catfish was 0.11 ppm which increased to 0.19 ppm after 7 days of withdrawal. For carp, the maximum residue of metabolite was 0.19

ppm which decreased to <0.05 ppm after a 35 day depuration period. In the case of catfish, residues in edible tissue peaked then decreased during exposure as was observed in the previous study. No peak or plateau was observed during the exposure period for the edible tissue of carp however. A peak of residues in the viscera of carp may be tied to a constant increase in residues in carp edible tissue. This is observed in all species probably as a transport of glyphosate from viscera to edible tissue even during depuration.

In both of the above studies no significant bioaccumulation was observed during the exposure period in any species. In bass and carp however, since no plateau was observed, a longer exposure period is indicated before a final conclusion on bioaccumulation in these species can be made.

Various samples catfish and carp tissue and heads and viscera exposed to 10 ppm of glyphosate were analysed for N-nitrosoglyphosate, all values were < 0.02 ppm. We have no questions with respect to this material since this deficiency has been satisfactorily resolved (see R. Taylor, Memo for Records 9/5/78) for glyphosate and its formulated products.

Some of the fish samples were stored for up to seven months and therefore the petitioner has submitted a abbreviated storage stability study. Three samples of fish containing 0.51 and 0.15 and 0.15 ppm of glyphosate were stored frozen for 6.5, 6.0, and 6.0 months respectively. Residues after storage showed percent changes of 12.3,0 and 0 for the three samples, respectively. This alleviates our concern over the long time between sampling and analysis for these studies.

Our general comments on the new studies discussed above are as follows. With respect to the studies on crayfish and channel catfish and marsh clams, we do not consider this type of experiments appropriate for metablism studies in these species. The use of "aged" residues and their effect on organisms is more of a environmental chemistry concern. We observe only that rather significant bioaccumulation factors for all three species were observed in these studies.

We do not normally require shellfish metabolism studies for aquatic uses and we therefore have no questions with respect to the nature of the residue in shellfish at this time. We will need however residue data for shellfish using "non-aged" residues of glyphosate. This deficiency will be discussed further in the Residue Data Section below.

The radio tracer study on catfish showed no bioaccumulation which is in direct conflict with the observations in bluegill and the previous catfish /crayfish experiments. In addition, the report was very vague with respect to which of the samples were used for characterization of the residue. Apparently, in edible partions of the catfish, less than 50% of the total radioactivity was identified as parent and aminomethylphosphonic acid. We will need clarification of this report and, most probably, further characterization of the radioactivity in edible portions of the fish.

With respect to the "cold" study on trout, bass, catfish and carp, these types of experiments will be more informative at such time as acceptable radio-label experiments on metabolism are available. Our only comments refer to: (1) The need for the details of the 1976 catfish and carp experiments at the 10 ppm exposure level which were omitted from the submitted reports; (2) The observation that plateau levels for bass and carp species were not attained in these studies indicating the need for longer exposure periods in these fish.

We do not consider the nature of the residue or bioaccumulation in fish adequately understood at this time. The petitioner should be informed of the additional metabolism information needed for resolution of this deficiency. These are discussed above.

Analytical Method

The analytical method used to determine residues in water, fish and various other crop is the PAM II method which has previously undergone a successful method trial on soybeans and beef liver (PP# 5F1536). Although the method is time-consuming RCB, after consultation with the FDA, has concluded that it is adequate for enforcement purposes (memo of 1/6/77, J. G. Cummings). Breifly, the method involves extraction with water or a chloroform: water mixture for fish and other crops (Water samples may require filtration or certrifugation to remove particulates.), followed by separation, if needed, of the aqueous extract by centrifugation. Glyphosate and aminomethylphosphonic acid are isolated via ion exchange chromatography, coverted to their corresponding N-trifluoromethyl derivatives and determined via glc using a phosphorous specific flame photometric detector. Certain samples may require additional column clean-up. A second procedure utilizing TLC and in situ fluorometry is available as a confirmatory procedure in water samples.

Validation data for water and crops was submitted in conjunction with PP# 6G1679 and discussed therein (memo of 1/3/76, D. Duffy). Recoveries in water and crops ranged from 48-98% for parent and from 60-103% for aminomethylphosphonic acid. For fish, recoveries ranged from 45-109% and from 49-116% for parent and metabolite respectively. Controls were <0.003 ppm for water and <0.05 ppm for other crops and fish.

Validation data for water submitted in this petition reflected fortification levels of 10 to 500 ppb for either glyphosate or its metabolite and recoveries ranged from 45 to 148% for parent and from 45 to 130% for aminomethylphosphonic acid with ca 67 and 66% of the analysies for parent and metabolite respectively falling between 65 and 120%. Lower or higher recovery percentages were evenly distributed over all fortification levels. Blank crop values for glyphosate ranged from 0.00 to 10.75 ppb and aminomethylphosphonic acid from 0.00 to 7.5 ppb.

We conclude that adequate analytical methods are available for enforcement purposes.

Residue Data

Ditch bank applications (Application to moving water uses) a total of nine studies were carried out on irrigation canals in the states of Colorado (3), California (2), Florida (1), Georgia (1), Washington (1), and in Alberta, Canada (1). One of the canals was concrete lined the rest were unlined. Application rates were 1.5 to 4.0 lb acid equivalent/acre in 19 to 150 gallons of water with 1 to 1.5 foot overlap of water along the edge of the canal to maximize residues. Spray swaths were 3 to 10 ft wide and from 0.25 to 1.1 mile of bank was treated. The canals had flow rates of 3.6 to 95 cubic feet/second with velocities ranging from 0.3 to 1.5 feet/seconds. Widths of the canals were 5 to 74 feet. Applications were made while traveling upstream and samples were taken at 2 to 3 sites downstream at distances ranging from 20 feet to 5 miles. Distances downstream from treated areas were marked by dye or floating objects. Residues of glyphosate ranged from non-detectable to 0.112 ppm with many values <0.005 ppm. The 0.112 ppm value did however occur 2.5 miles from the treated areas. Residues of metabolite ranged from non-detectable to 0.017 ppm.

This gives a maximum total residue of 0.129 ppm in treated water. It is our judgement that residues of glyphosate and aminomethylphosphonic acid would not be expected to exceed 0.2 ppm under this particular use.

The label restrictions for this use prohibit treating both banks simultaneouly, spraying across open bodies of water, and overlapping more than an average of 1 foot of water while spraying. Treatment only while moving upstream is also prescribed. Additional label restrictions which are required for this use include: 1) prescribing a specified interval before retreatment of a bank; 2) limiting the treatment length to 1 mile in any 24 hour period; 3) deleting the word "average" from the water overlap statement; 4) prohibiting treatment of banks within 0.5 miles of potable water intakes; and5) prescribing a maximum application rate of 4 lb acid equivalent/acre per treatment of a bank. These should be submitted in a revised Section B. The petitioner should be so informed.

Direct Application to Moving Water

No new data was submitted in this petition. Data originally submitted in conjunction with PP# 6G1679/FAP# 6H5106 and reviewed therein is referenced. In our review of that petition RCB concluded that before any general uses involving direct application to flowing water could be approved and tolerances granted, extensive studies would be needed to determine dissipation of residues in moving bodies of water. This data would need to reflect adequate geographical representation and representative water situations. Also, any such uses would needed to be so circumscribed that residues would not exceed the desired level when the water was diverted for either domestic or irrigation purposes (memo of 1/30/76, D. Duffy). We reiterate this conclusion and the conditions for a favorable recommendation at this time. The petitioner should be so informed.

Shoreline Treatment to Ponds (Impounded waters)

Residue data submitted for this use reflected five studies carried out on ponds located in California, Florida, Georgia, Texas, and Colorado. The ponds sizes and depths ranged from 0.5 to 2.8 acres and from 4.5 to 9 ft. Glyphosate was applied at 4.0 to 4.5 lb acid equivalent/acre with overlaps of 1 to 3 ft. Samples were taken at 3 points around each pond at 1 and 10 feet from the edge and at the center at 1 hr and 1, 2, 7, 14, 28 and in one study 60 days. Residues of glyphosate as its metabolite at 1 hour ranged from 0.001 to 1.35 ppm and from non-detectable to 0.075 ppm respectively. At longer times, residues of glyphosate were less than 0.1 ppm for most samples with some values ranging up to 0.49 ppm. Residues of aminomethyl-phosphonic acid ranged from non-detectable to 0.045 ppm at 1 to 60 days after treatment.

Based on this limited data, it is our judgement that combined residues of glyphosate and its metabolite would not be expected to exceed 0.5 ppm under this use.

With respect to the label restrictions proposed in section B, the statement that treated water may be used immediately for irrigation and fishing should be deleted as should the statement that treated water should not be used for domestic purposes or for watering livestock within 24 hours of treatment. Additional label restrictions which are required include: 1) Prescribing a specified interval before retreatment; 2) Limiting overlap of water to 1 foot; 3) Prohibiting treatment of shoreline within 0.5 miles of potable water intakes; and 4) Prescribing a maximum application rate of 4.0 lb acid equivalent/acre. These should be proposed in a revised Section B. The petitioner should be so informed.

Levee Application (rice or sugarcane plots)

No new data for this use was submitted in this petition. Based on data submitted in conjunction with PP# 6G1679/FAP# 6H5106 RCB concluded that residues in water from this type of use would not exceed 0.1 ppm. We have now considered this data along with other data on shoreline treatments and it is our judgement that combined residues of glyphosate and its metabolite would not be expected to exceed 0.5 ppm in water under this use, provided a revised Section B proposing a specified interval before retreatment, limiting the overlap of water to 1 foot, and prescribing a maximum treatment rate of 4.0 lb acid equivalent/acre is submitted. Deletion of the label statements that treated water may be used immediately for fishing or irrigation purposes and that treated water should not be used for domestic purposes or for watering livestock within 24 hours of treatment is needed. In additional tolerances for crayfish (shellfish) must be established simultaneously with any water tolerance for this use since crayfish farming in rice paddies is practiced extensively in the South. The petitioner should be so informed.

Total Surface Pond Treatments (Impounded Water)

New residue data submitted for this use reflected 4 studies carried out in Florida and Canada (3). We note that no raw data was submitted for the Florida study. The petitioner should be informed that this should be submitted. Pond sizes and depths ranged from 0.18 to 0.5 acres and from 3.5 to 5.0 feet. Application rates were 4.0 to 8.0 lb of acid equivalents/acre. Residues after 2 hrs ranged from 0.138 to 1.471 ppm for parent and from 0.004 to 0.036 ppm for aminomethylphosphonic acid. Residues of parent ranged from 0.240 to 0.616 ppm and from 0.01 to 0.024 ppm for the metabolite two days post treatment. Halflives ranged from 3 to 22 days. Considering this data along with studies submitted previously on ponds in New York, Florida, Colorado, Illinois, and Wisconsin, we conclude that combined residues of glyphosate and aminomethylphosphonic acid in water would not be expected to exceed 0.5 ppm under this use one post treatment. Therefore, it is our judgement that the label restriction prohibiting use of treated water for livestock or domestic purposes is not practical and should be deleted in light of the recommended higher tolerance level. Also, the statement that water may be used immediately for irrigation and fishing should be deleted. Additional label restrictions which must be proposed include: 1) Prescribing a specified interval before retreatment of the water surface; 2) Prohibiting treatment within 0.5 miles of potable water intakes; and 3) Prescribing a maximum application rate of 4.0 lb acid equivalent/acre. These revisions should be submitted in a revised Section B. The petitioner should be so informed.

"Dry-ditch" or "Draw-down" Applications (De-watered systems; includes irrigation ditches, canals, and impounded water.)

Residue data submitted in conjunction with PP# 6G1679 and reviewed therein, reflected dry-ditch fall applications, applications around a rice plot (described above) and a field run-off study. Residues in these studies ranged from < 0.003 ppm to 0.08 ppm. Additional studies submitted in this petition involved dry-ditch fall applications to canals in Washington (2) and Colorado (2) and a second field run-off study. In the dry-ditch fall application experiments 460 to 1320 ft of canal were treated with 4.0 lb acid equivalent/acre and ditches were refilled after 5 to 11 days. Residues of glyphosate and its metabolite ranged from non-detectable to 0.225 ppm and from non-detectable to 0.004 ppm respectively. The water run-off samples showed maximum residues of 5.68 ppm parent and 0.119 ppm of aminomethylphosphonic acid the evening after treatment. These levels, however, decreased to < 0.002 to 0.064 ppm for glyphosate and to 0.002 to 0.017 ppm for the metabolite after 15 to 364 days. In this trial the application rate was 8.0 lb active ingredient/acre (2).

It is our judgement that residues of glyphosate and its metabolite would not be expected to exceed the 0.5 ppm level in water under the proposed use conditions provided the following restrictions are added to (or deleted from) the label: 1) A specified interval before retreatment must be prescribed 2) The statements "Do not use for livestock or domestic purposes for 24 hours

following introduction of water" and "water may be used immediately for fishing or irrigation purposes" should be removed; 3) The treatement length should be limited to 1 mile for any 24 hour period; 4) Treatment should be prohibited within 0.5 miles of potable water intakes; and 5) A maximum application rate of 4.0 lb acid equivalent/acre should be prescribed. These modifications should be submitted in a revised Section B. The petitioner should be so informed.

Potable Water Considerations

No new information has been submitted. RCB has determined previously that due to the many variables in actual water purification systems used around the United States it would not be advisable to rely on a reduction in residues during the purification process and therefore the tolerance level should be set high enough to cover residues expected in raw water before it enters the treatment plants (See memo of D. Duffy, PP# 6G1679 and FAP# 6H5106, 1/3/76). We reiterate this conclusion at this time. In our discussions above all but one use (direct application to moving water) allowed us to recommend a suitable level in raw water. These levels ranged from 0.2 ppm for ditchbank applications to 0.5 ppm for all other uses. For the sake of consistency we conclude that for all of the uses proposed, with the exception of direct application to moving water, the proposed tolerance level in potable water should be 0.5 ppm. Should the additional residue data required above for direct application to moving water indicate that a higher level is needed for this use, this level should be proposed for residues in potable water for all uses. The petitioner should be so informed.

Irrigated Crops

No new residue data for irrigated crops was submitted. RCB has concluded previously that residues in irrigated crops would not be expected to exceed 0.1 ppm provided glyphosate residues in irrigation water did not exceed 0.1 ppm. Data was presented for alfalfa, field beans, sorghum, squash, sugarbeets and tomatoes. In light however, of the 0.5 ppm (and possibly higher) level needed for this permanent tolerance it is our judgement that additional data for irrigated crops reflecting at least 2 crops from each of the crop groupings listed in 40 CFR 180.34 (f), as well as the individual crops sugarcane, cottonseed and hops (Data for avocados is not critically needed), and different irrigation systems and exaggerated application rates is needed. The petitioner should be so informed.

Fish and Shellfish

Studies on various species of fish and shellfish were submitted in conjunction with this petition. These studies were discussed in detail in the Nature of the Residue section above. For fish, as discussed, above, clarification of the latest study using radiolabeled glyphosate and catfish, and, most probably, further characterization of the radioactivity in edible portions of fish are needed. Also, since details of the 1976 catfish and carp study using unlabeled glyphosate at the 10 ppm exposure level are needed, and since no plateau were observed for bass and carp in the other "cold" study indicating the need for longer exposure periods, we cannot make any recommendation for a tolerance level in fish until such time as the metabolism and

residue questions above are resolved. The petitioner should be so informed.

For shellfish, since we do not require metabolism studies for these organisms and since we do not find residue studies using "aged" residues appropriate for determining a tolerance level in shellfish, we can make no favorable recommendation for a tolerance in this r.a.c. until residue studies in various species of shellfish using "non aged" residues of glyphosate are submitted. No tolerances for potable water can be granted for the uses proposed until tolerances for fish and shellfish are also established. The petitioner should be so informed.

Meat, Milk, Poultry and Eggs

Feed items involved in this petition are livestock drinking water and irrigated crops (forages, grains, etc.). Until such time as a final conclusion with respect to tolerance levels needed in potable water and irrigated crops can be made we cannot make any judgement with respect to the need for higher tolerances in liver and kidney and/or tolerances in meat, milk, poultry and eggs. The petitioner should be informed this determination will be made at such time as the deficiencies described above are resolved satisfactorily

Should a 0.5 ppm tolerance for potable water be deemed adequate this would contribute ca. 4.5 ppm/day to the diet of cattle. This is assuming that a dairy cow can consume up to 139 kg water/day and has a dry diet of 15 kg/day (136 kg/day x 0.5 mg/kg ÷ 15 kg/day).

Similarly, poultry can consume up to 0.23 kg water/day and assuming a dry diet of 0.14 kg/day, this would add ca. 0.82 ppm to the diet of poultry each day. Feeding studies submitted previously in conjunction with PP# 5F1536 and reviewed therein reflected feeding a 3:1 ratio of glyphosate: aminomethyl-phosphonic acid to cattle, poultry and swine for 30 days at levels of 10,30, and 100 ppm. Unless exorbitant levels are needed for the potable water and irrigated crop tolerances these feeding studies should be acceptable for a determination of appropriate tolerances, if needed, in meat, milk, poultry and eggs.

R. B. Perfetti, Ph. D.

cc: Reading file
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FDA
PP# No.
EEE
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Reviewer
Glasgow

RDI:Section Head: RQ:Date:11/21/79:J.G.Cummings:Date:11/21/79
TS-769:RCB:Reviewer:R.B.Perfetti:LDT:X77324:RM:810:CM#2:Date:12/7/79