Ballard 11-3C (may contain CBI)

Rec/10/2782

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

SUBJECT: Position Paper on Dyfonate[R] DATE: April 9, 1976

FROM: Team Leader of Dyfonate[R]
Substitute Chemical Review

TO: Acting Director,
Criteria and Evaluation Division

I have attached the position paper on Dyfonate[R] for your review. A separate memo answers your questions on the first position paper.

William L. Burnam

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EPA Form 1320-6 (Rev. 6-72)

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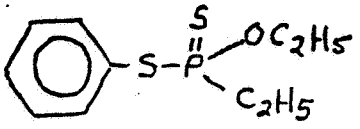
I. Background and History

Dyfonate^{R} is the U.S. tradename for the organophosphate insecticide O-ethyl S-phenyl ethylphosphonodithioate having a structural formula as shown below:



This insecticide was introduced commercially in 1967 by the Stauffer Chemical Company. It is primarily a non-systemic soil insecticide with one registered foliar use.

II. Regulatory Aspects

Dyfonate^{R} is registered for use against soil insects attacking tobacco, corn, turf, peanuts, Irish and sweet potatoes, onions, cole crops, sugarcane, sugar beets and several crops of lesser importance.

Formulations currently available are an emulsifiable liquid containing 4 lb of active ingredient per gallon, and four granular formulations (2,5,10 and 20% active ingredients). In addition, Stauffer offers a combination product in which Dyfonate^{R} is combined with a selective herbicide pebulate (Tillam^{R}) at the ratio of 1 lb of Dyfonate^{R} plus 4 lb of

Tillam^{R} active ingredients per gallon. The 2% and 5% granules are labeled only for very specific uses or experimental uses. The other formulations are labeled and recommended for use on certain agricultural crops by soil application.

Current U.S. tolerances for Dyfonate^{R} are 0.1 ppm (negligible residue) for fruiting vegetables, seed and pod vegetables, leafy vegetables, beans, peanuts, corn and soybeans (including grain portions as well as fodder and forage portions) Asparagus has a tolerance of 0.5 ppm. All tolerances include not only the parent pesticide but also the oxygen analog.

An acceptable daily intake (ADI) has not been established for Dyfonate^{R}.

III. Manufacture and Analytical Methods

Stauffer is the only basic producer of Dyfonate^{R} in the United States.

[redacted]

The technical product is a yellow or amber liquid having a pungent, mercaptan-like odor. Technical Dyfonate^{R} contains a minimum of 93.0% of the active ingredient, O-ethyl-S-phenyl ethylphosphonodithioate.

MANUFACTURING INFORMATION IS NOT INCLUDED

Dyfonate[R] and its oxygen analog can be analyzed by GLC using a flame thermionic detector. Clean-up procedures for residues of both compounds include liquid-liquid partition chromatography to remove oily materials and silicic acid chromatography for final clean-up. (PAM II 1967).

IV. Toxicity Studies

General Toxicity:

Dyfonate[R] is an organophosphate insecticide which is metabolized to the toxic oxygen analog in mammals. Signs of acute Dyfonate[R] poisoning are similar in most animals and include diarrhea, excessive urination, tremors, ataxia, salivation, fasciculation, lacrimation and excessive masticatory movements (Horton, 1966a, 1966c, 1966e, Meyding 1965, Wright and Beliles 1966) which are symptoms common to cholinesterase inhibiting pesticides.

The acute oral LD_{50} of technical Dyfonate[R] ranges from 3.16 mg/kg to 17.5 mg/kg for rats, females being almost twice as sensitive as males (Horton 1966a,b, Ray 1963, Meyding 1960, 1965). The acute oral LD_{50} of technical Dyfonate[R] for dogs is 3 to 4 mg/kg (Woodard, 1966). In acute dermal studies with rabbits the LD_{50} of technical Dyfonate[R] ranged from 35 to 121 mg/kg and the dermal LD_{50} of the 10% granular formulation was 215 mg/kg (Horton 1966a,b,c,d; Johnston 1963).

Acute LD_{50}'s for technical Dyfonate^{R} administered in-

chickens (Wright and Beliles 1966). In an acute inhalation study with rats a one hour LC_{50} of 1.3 mg/l was recorded for the dust (fines) for a 10% granular formulation (Beliles 1966).

In a comparative acute oral toxicity study of Dyfonate^{R} and its metabolites in the rat, all metabolites except the oxygen analog were much less toxic than the parent compound (McBain et al., 1970).

Atropine plus pralidoxine chloride has been shown to be an effective antidote in rats (Wright & Beliles, 1966), and this treatment is recommended on the label.

In subacute oral toxicity tests, cholinesterase levels were reduced in rats fed 100 ppm technical Dyfonate^{R} and in beagle dogs fed 240 ppm technical Dyfonate^{R}. In subacute dermal studies with rabbits treated with 10% granular Dyfonate^{R}, Horn et al., (1969), classified the product as mildly irritating. Death was observed in 3 of 10 rabbits at 70 mg/kg and 1 of 10 at the low dose, 35 mg/kg.

In 2 year feeding studies with rats and dogs, a "no effect" level was established at the lowest dosage levels tested, 10 ppm & 8 ppm respectively (Banerje et al., 1968; Woodard et al., 1966a). No increase in the incidence of tumors was reported in either study.

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A 10 mg dose of the 10% granular formulation instilled into the eyes of albino rabbits was considered a negligible irritant (Horton, 1966a). Death of all test animals resulted after instillation of 0.1 ml dose of undiluted material into the eyes of albino rabbits (Johnston 1963).

Toxicity to Fish and Wildlife:

Laboratory studies indicate that Dyfonate^{R} is highly toxic to fish. Beliles et al., (1966) reported that rainbow trout had an LC_{50} (96 hr) of 0.050 ppm for technical Dyfonate^{R} and 2.8 ppm for 10% granular Dyfonate^{R} within a temperature range of 16.7-18.3°C. Bluegill tested at 24.4-25.6°C, had an LC_{50} (96 hr) of 0.029 ppm for technical Dyfonate^{R} and 0.32 ppm for 10% granular Dyfonate^{R}. Bluegill exposed to Dyfonate^{R} yielded a maximum concentration of accumulated ^{14}C-residue from 21 to 35 days after exposure (Sleight, 1972b) which was approximately 150 times the concentration in the water. After transfer to clean water, approximately 65% of the residue was eliminated within 24 hours.

In laboratory studies, Schafer et al (1972) found LD_{50} values of 10 mg/kg when Dyfonate^{R} was administered orally to redwinged blackbirds. Dietary administration of Dyfonate^{R} for 5 days produced LD_{50} values of 133 ppm for bobwhite quail and 1,222 ppm for mallard duck (Health et al, 1972). The granular formulation appeared to be less toxic to bobwhite quail than

technical Dyfonate^{R}. Japanese quail receiving up to 26 ppm technncial Dyfonate^{R} experienced no differences in gross appearance, behavior, body weight, egg production or body residues when compared to controls (Kamiensk 1973).

Midwest Research Farms (1974) concluded that Dyfonate^{R} had no effect on ring-necked pheasant under field conditions.

Data are not available regarding the effects of Dyfonate^{R} on honey bees and other beneficial insects, parasites and predators.

Metabolism:

The metabolism of Dyfonate^{R} is similar in plants and animals. Dyfonate^{R} can be converted to its oxygen analog and then enzymatically cleaved to EOP (See Figure I), or P-S hydrolysis can occur to form thiophenol (PSH) and EOP; the former is in turn methylated to form methyl phenyl sulfide (MSP). Additional oxidation of MPS then occurs to form methyl phenyl sulfone ($MPSO_2$) which in turn can be hydroxylated in the 3 or 4 position to form 3-OH-$MPSO_2$ or 4-OH-$MPSO_2$. Conjugation of the hydroxylated products as sulfates or glycosides can then occur (Menn, 1971).

O-Demethylation appears to be of little significance in mammalian metabolism (Menn, 1971).

The major excretion products of Dyfonate^{R} were composed of ETP, EOP, 3-OH-$MPSO_2$. Analysis of rat feces showed major products of excretion to be undegraded Dyfonate^{R}, $MPSO_2$ and an unidentified polar metabolite. Smaller amounts of ETP and EOP were also excreted (McBain et al., 1971).

Rats were shown to excrete an average of 88% of either an oral or an intraperitoneal dose within 48 hours. Excretion occurred predominantly through the urine and feces 96 hours after dosing with ^{35}S-Dyfonate^{R}. Nearly 53% of the dose was accounted for in the urine, 32% in the feces, 2% in expired air and less than 1% in the tissues. During the interval from 2 to 16 days, an average of 99+% of the radiolabeled residues of ^{35}S-Dyfonate^{R} were eliminated from all tissues and organs.

Detectable levels of ^{14}C residues were not found from rats treated with ^{14}C-ethoxy-labeled Dyfonate^{R} 15 days after treatment with a single oral or intraperitoneal dose. (Hoffman et al., 1971).

Reproductive Effects:

No evidence of reproductive effects was found in rats in one 3 generation study of Dyfonate^{R} at levels up to 31.6 ppm.

Neurotoxicity:

Doses of 0-20 mg/kg/day of Dyfonate^{R} were fed to adult hens for 46 days. A slight focal demyelination of the peripheral nerve

was seen in 1 of 10 birds at the 20 mg/kg/day feeding level. No adverse effects were noted at 0, 2 or 5.32 mg/kg/day (Woodard, 1966). Another neurotoxicity study showed no changes which were visible at necropsy 14 days after a single intramuscular dose up to 50 mg/kg. (Wright & Beliles, 1966).

Accident Reports"

Accidental exposures to Dyfonate[R] are recorded by the EPA Pesticide Episode Review System (PERS). Eight Dyfonate[R] episodes are included in the computerized data through January 1974, and 6 additional episodes have subsequently been reported. Approximately two-thirds of these episodes involve human exposure.

The death of one raccoon and several fish (no species available) occurred following a spill of 2 gallons of 46.8% AI Dyfonate[R] into a pond (EPA, 1974). In a second incident, several gallons of 4EC Dyfonate[R] spilled into a pond, killing an estimated 648 red sided shiners, squawfish, bluegills and brown bullheads (EPA, 1973). In addition, one frog and an estimated 1,500 angleworms were found dead. Accidents of this nature should not occur if label specifications, which warn about keeping Dyfonate[R] out of bodies of water, are followed.

V. Use

For 1974 it was estimated that about 80% or approximately 2.6 million pounds of active ingredient was used on corn. The remaining 20% was used on potatoes, sugar beets, tobacco, vegetables, other crops and lawn turf (RvR estimates).

Regional distribution of Dyfonate^{R} in 1974 was estimated to be heavily concentrated in the North Central states, which include Ohio, Indiana, Illinois, Minnesota, Wisconsin, Michigan, Iowa, Missouri, North Dakota, South Dakota, Nebraska and Kansas (RvR estimates). This region accounted for 80 to 85% of the 1974 Dyfonate^{R} consumption and over 87% of U.S. corn production in 1973 (USDA, 1974).

In 1974, the Western states accounted for about 10% of the Dyfonate^{R} used, with the remaining small proportion distributed among other regions (RvR estimates).

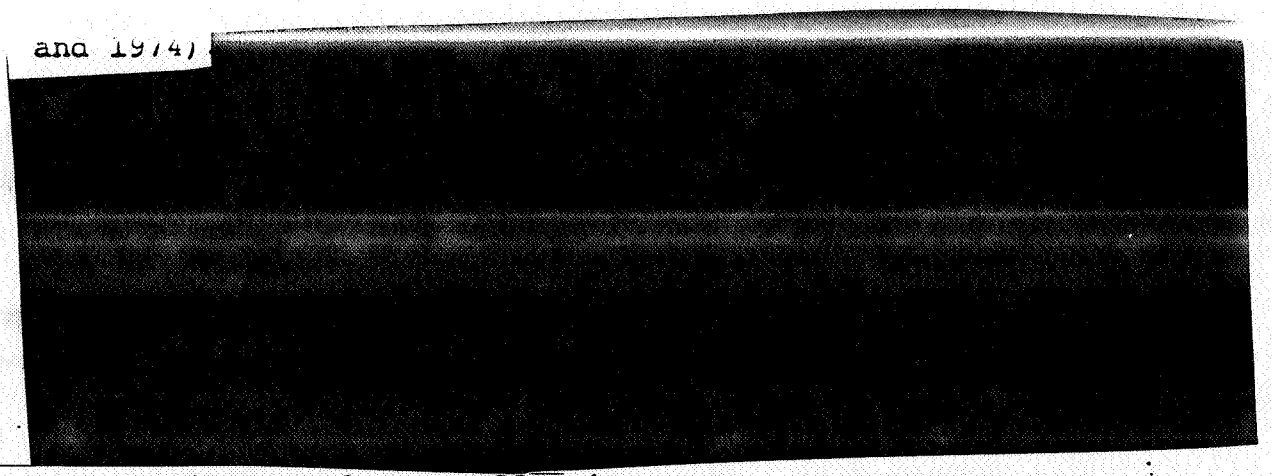
VI. Economics

Supply:

Dyfonate^{R} is produced domestically by a single manufacuturer: the Stauffer Chemcal Company. The chemical was market introduced in 1967 and the 1974 estimate of production was more that [redacted] active ingredient (RvR estimates).

According to the Tariff Commission Publications 601 and 688, there were no imports of Dyfonate^{R} into the United

States during 1972 and 1973 (U.S. Tariff Commission, 1973 and 1974).



Efficacy and Cost Effectiveness:

Corn - Dyfonate[R] control of the western corn rootworm, measured by average root damage ratings, ranged from 1.0 to 3.25, where a rating of 2.5 was considered acceptable control (Hills and Peters, 1972; Hills et al., 1972). The best control was achieved with granular Dyfoante[R] applied as a preplant treatment. In a 1967 Missouri test, this chemical had the lowest root damage ratings for western corn rootworm control when several insecticides were tested (Musick and Fairchild, 1968).

The control of the northern corn rootworm with Dyfonate[R] ranged from 58.6 to 70.2% (Apple et al., 1969). A summary of several Illinois tests conducted from 1968 to 1972 averaged 59.3% larval control, a root damage rating of 2.3 relative to 3.6 for the check, and a yield increase of 9.3% (Petty and Kuhlman, 1972; Kuhlman and Petty, 1973).

In a 1971 Illinois experiment, 40% control of the European corn borer was achieved with Dyfonate^{R}. (Rohlman and Petty, 1972) In another experiment 82% and 81% control was achieved respectively on the first and second generation borers (Harding et al., 1966).

Other Crops - Dyfonate^{R} was found to be an effective control against the onion maggot and against wireworms in peanuts, sugar beets, sugar cane, tobacco and potatoes. Dyfonate^{R} was also an effective control against the sugar beet root maggot, the cabbage maggott and the symphylan in pole beans, strawberries and peppermint.

Dyfonate^{R} is a useful substitute for chlordane-heptachlor against the corn rootworm, seed corn maggot and beetle, and against corn, potato and tobacco wireworms.

VII. Environmental Impact

Dyfonate^{R} is only slightly soluble in water (13 ppm at 22^{o}C) but is miscible with most organic solvents including acetone, ethanol, kerosene and xylene.

Dyfonate^{R} has a vapor pressure of 2.1 x 10^{-4}mm Hg at 35^{o}C which classifies it as a highly volatile pesticide.

Hydrolysis of Dyfonate^{R} at environmentally encountered pH's procedes very slowly. A 30 ppm solution in buffer (pH=7) at 40^{o}C gave a half-life value of 127 days. (Stauffer, 1971)

Chemical oxidation of Dyfonate^{R} results in both Dyfonate^{R} oxygen analog and Dyfonate^{R} -oxon disulfide (See Figure I). Dyfonate^{R} -oxon in turn would be subject to hydrolysis to 0-ethyl ethylphosphonic acid (EOP) and Dyfonate^{R} -oxon disulfide would hydrolyze to 0-ethyl ethylphosphonic acid (EOP) and 0-ethylphosphonothionic acid (ETP). (McBain et al., 1971)

Dyfonate^{R} in the presence of sunlight was degraded (both in the presence and absence of photosensitizer) on bean plant surfaces and on silica gel chromatoplates. The rate of degradation was increased in the presence of photosensitizers. No identification of photoproducts was made, but the products resulting from photosensitized degradation on silica gel plates were not the same as found without sensitizer. (Hoffman, 1973)

A study conducted by Stauffer (Hoffman et al., 1973) involving exposure of dilute aqueous Dyfonate^{R} solutions to sunlight resulted in no findings of photolysis products. Under the conditions of the test, Dyfonate^{R} was readily lost by volatilization. Therefore, volatile photoproducts would not have been determined.

Lichtenstein and Schulz (1970) found that Dyfonate^{R} is rapidly volatilized from both water and soil-water interfaces. For example, at 30^{o}C an initial soil-water concentration of 12.5 ppm Dyfonate^{R} was reduced to 1/2 in only 4.8 days.

Residues of Dyfonate^{R} or its oxygen analog were not found in milk, or in tissue samples (adipose, muscle, liver and kidney) from lactating cows, which had been fed up to 1.0 ppm Dyfonate^{R} for 28 days. The levels of detection were 0.01 ppm in milk and 0.03 ppm in tissue (Stauffer, 1972)

Residues in Soil

Field studies in a number of states (Kiigemagi & Terriere, 1971b; Stauffer Chemical Company, 1971a; Schulz and Lichtenstein, 1971) indicated an initial half-life of Dyfonate^{R} ranging from 30 co 40 days. However, degradation after this initial period was found to proceed more slowly with about 25% still remaining 120 days post-treatment in each of two studies (Kiigemagi & Terriere, 1971a, Schulz and Lichtenstein, 1971). The rapid initial loss (first 30 days) as compared to slower loss thereafter is possibly related to rapid volatilization of Dyfonate^{R} from the upper surface layers (Lichtenstein and Schulz, 1970), followed by a slower dissipation, mediated by other factors, including hydrolysis and microbial action (Kiigemagi & Terriere, 1971a).

Schulz and Lichtenstein (1971) and Read (1971) have noted that Dyfonate^{R} residues persist at a relatively constant level throughout the winter months. During this period, mean soil temperatures are sufficiently low that volatilization

losses can be considered minimal. An analysis of soil following treatment with either ^{14}C-ethoxy or ^{14}C-ring labeled Dyfonate^{R} resulted in the same series of major metabolites as those in plants and mammals, namely: EOP, ETP, EOP-CH_3, diphenyl disulfide, MPSO, $MPSO_2$. (See Figure 1)

VIII. Specific Areas For Future Research

1. Oncogenic studies in a second species of rodent as required by the guidelines.

2. Teratology as required by guidelines.

3. In light of the expected increases in usage of Dyfonate^{R} as a result of the cancellation of Chlordane-Heptachlor, Dyfonate^{R} is being studied in the terrestrial-aquatic model ecosystem developed by Metcalf, et al., (1971). The results of the study have not been published to date, but preliminary data indicate that Dyfonate^{R} did not biomagnify in a short food chain consisting of algae, snails, mosquitoes, and mosquitofish (Metcalf, 1975). Depending on the outcome of this experiment, future research on the bioaccumulation of Dyfonate^{R} in the environment may be undertaken.

IX. Conclusions

Although Dyfonate^{R} is highly toxic to mammals and to fish, the compound can be safely used when label directions are followed.

This review indicates that an increased volume of currently registered uses would not pose an unreasonable adverse effect on man or the environment.

However, as with other highly toxic organophosphates and carbamates, it is the opinion of this reviewer that the use or granular formulations of Dyfonate^{R} should be encouraged while the use of emulsifiable concentrates should be carefully controlled and constantly reviewed by OPP because of the high toxicities of the latter formulations.

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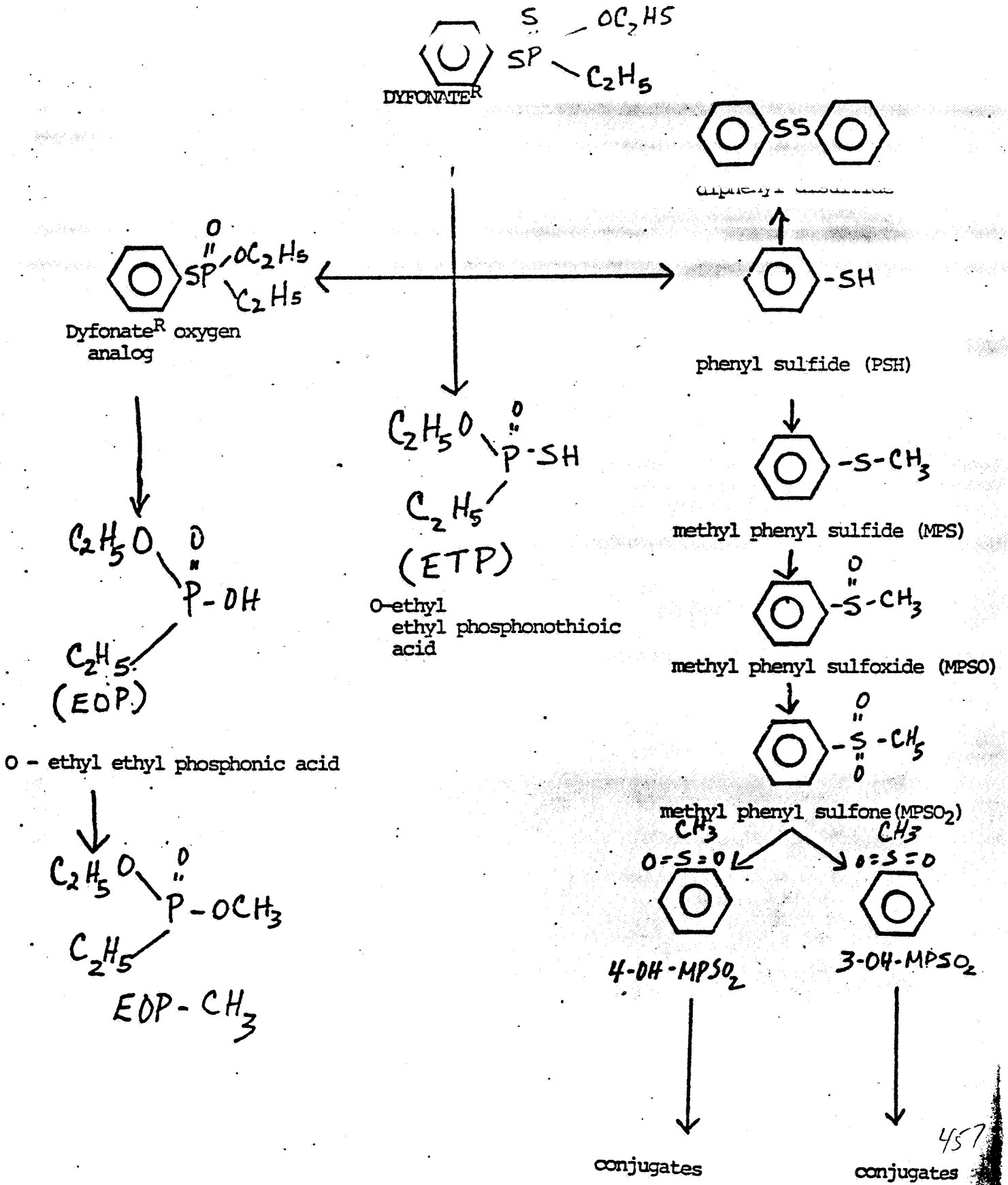
Figure 1


DYFONATE R
Dyfonate R oxygen analog
O - ethyl ethyl phosphonic acid
(EOP)
EOP - CH3
(ETP)
O-ethyl ethyl phosphonothioic acid
phenyl sulfide (PSH)
methyl phenyl sulfide (MPS)
methyl phenyl sulfoxide (MPSO)
methyl phenyl sulfone (MPSO2)
4-OH-MPSO2
3-OH-MPSO2
conjugates
conjugates