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Demetonmethyl

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Demetonmethyl

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DEMETONMETHYL

Demetonmethyl, known in the Soviet Union as methylmercaptophos, belongs to the group of organophosphorus pesticides. This preparation represents a mixture of isomers and consists of 30 percent of 0,0-dimethyl-S-2 (ethylthio)-ethylthiophosphate (P–O isomer) and 70 percent of 0.0 dimethyl-0-2 (ethylthio)-ethylthiophosphate (P–O isomer).

Molecular formula: $C_6H_{15}O_9S_2P$

Structural formula:

$$(CH_3O)_2\overset{\overset{S}{\|}}{P}OCH_2CH_2CH_2SC_2H_5$$

$$(CH_3O)_2\overset{\overset{O}{\|}}{P}SCH_2CH_2SC_2H_5$$

Synonyms: methylsystox, metasystox, Bayer 21/116.

Density: 1.1904 (P–S isomer) and 1.2070 (P–O isomer).

Boiling point: P–S isomer	P–O isomer
106°C (at 133.322 Pa)	134°C (at 333.3 Pa)
74°C (at 19.998 Pa)	118°C (at 133.322 Pa)
68°C (at 13.33 Pa)	92°C (at 26.664 Pa)
58°C (at 6.66 Pa)	

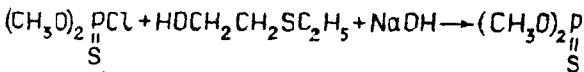
Water solubility: 0.03 g/100 g (P–S isomer) and 0.3 g/100 g (P–S isomer) at 20°C [1].

In the USSR demetonmethyl is manufactured in the form of 50 per cent emulsion concentrate comprising 50 per cent of demetonmethyl, 20 per cent of a surface-active agent, grade OP-7 or OP-10 (GOST 8433-57), and 30 percent of a methylnaphthalene fraction (VTU STU 77-4-61-63)[2].

The commercial material contains a small amount of admixed trimethylthiophosphate, beta-oxydiethylsulphide and other ethers of thiophosphoric acid[3].

PRODUCTION PROCESS

Demetonmethyl is obtained by reaction of beta-oxydiethylsulphide with dimethylchlorthiophosphate in the presence of hydrogen chloride acceptors (part of the product subsequently isomerizing into a thiolic isomer)



USE

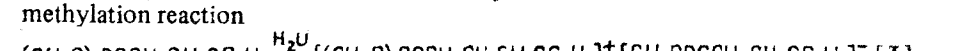
Demetonmethyl is widely used in agriculture as systemic and contact types of insecticide and acaricide. This is one of the main preparations used for the control of sucking cotton pests. Cotton treatment is performed by aerial and ground-rig application at a rate of 1.5-2 kg/ha.

Demetonmethyl is also used to control aphides and phytophagous acaruses on fruit crops (0.8-2 kg/ha), hop (a.5-2 kg/ha) and sugar beet (0.8-1 kg/ha)[5].

PATHWAYS INTO THE ENVIRONMENT

The material is brought into the environment mainly by aircraft and ground spraying of agricultural crops. In aerial treatment of cotton plants, demetonmethyl was found in the atmospheric air during the first 24 hours after application at a distance of 0.5 km from the treated field. [6]. Aerosol and vapours of demetonmethyl are found in the air.

In the presence of water demetonmethyl can enter into an intermolecular methylation reaction



The resulting chemical compound possesses distinct anticholinesterase activity and high toxicity. This reaction may be observed in storing demetonmethyl and its solutions at a temperature of 35°C for one day. For rats, LD_{50} of the substance decreases from 60 to 2 mg/kg, i.e. toxicity increases 30 times [7].

CONCENTRATIONS

Concentration of demetonmethyl in the air in the area treated for cotton pest control is 0.01-4 mg/m^3. In aerial treatment of cotton, concentration of demetonmethyl at a distance of 0.5 km from the treated area is 0.33 mg/m^3, at a distance of 1 km concentration is 0.1 mg/m^3; during the second 24 hours after treatment concentration of demetonmethyl is hundredths of mg/m^3 [6]. In treating orchards and cotton with demetonmethyl, concentration of this chemical in the airplane cabin air is 0.25-1.76 mg/m^3 for An-2 airplanes and 0.1-0.97 mg/m^3 for Yak-12 airplanes. In the helicopter cabin air, concentration of demetonmethyl at various flight speeds and air temperatures is from 0.002 to 0.47 mg/m^3 [8].

Concentration of demetonmethyl in the air after treating cotton fields is 2 mg/m^3, in 24 hours it is 0.4 mg/m^3, in 48 hours no chemical is found in the air. Demetonmethyl is found in a concentration of 0.15-0.5 mg/m^3 at a distance of 25-250 m from the treated field. On cotton fields, concentration of demetonmethyl in the air decreases from 0.5-1 mg/m^3 on the first day after treatment to 0.3 mg/m^3 on the sixth day after treatment [9].

In low-volume demetonmethyl spraying of cotton, average concentration of the chemical is 0.24-0.29 mg/m^3 in the cabin of an An-2 airplane, 0.62-0.9 mg/m^3 on the airfield, and 0.45-0.62 mg/m^3 in the signalmen breathing area [10].

The demetonmethyl concentration in the air at a distance of 500 m from the edge of the sprayed plantation on the day of the treatment was 0.55 mg/m^3 (the maximum single measurement) and 0.33 mg/m^3 (mean daily); at a distance of 1.000 m from the edge of the treated plantation it was 0.11 and 0.06 mg/m^3 correspondingly. The demetonmethyl concentration gradually decreased to hundredth fractions of mg/m^3 on the 2nd, 3rd and 4th days after the treatment, and to thousandth fractions of mg/m^3 on the fifth day [11].

The concentration of demetonmethyl in soil was 0.15-0.45 mg/m^3 [9].

Demetonmethyl concentration in sugar beet, cabbage, tomato, black currants and apples was from 0.001 to 5 mg/kg [6].

A total of 1414 samples of food were analyzed and demetonmethyl was not found in either of them.

ENVIRONMENTAL FATE TESTS

As is known, microorganisms accelerate the decomposition of demetonmethyl in the environment [13].

An increase in temperature and pH results in a 50% reduction of time during which the P–S isomer of demetonmethyl is hydrolyzed. Thus, at 1-5 pH and 20°C it takes 88 days, 7.5 days at 40°C and 2.03 day at 50°C. A corresponding increase in temperature and pH to 70°C and 7 slashed the time of hydrolysis by 50% to 3.5 hours and at pH 9 this process took only 1.25 hour [13].

Demetonmethyl is decomposed in soil, plants, and living bodies. The main pathways by which the chemical is destroyed are hydrolysis and oxidation. The P–O isomer of demetonmethyl is rearranged into the P–S isomer. The time of rearrangement of 10 percent of the P–O isomer into the P–S isomer at a temperature of 20°C is 104 days; at 30°C 26 days, and at 40°C 8 days [14].

BIOCONCENTRATIONS/CLEARANCE TIME/MAMMALIAN METABOLISM

Demetonmethyl is quickly absorbed in the body from the alimentary tract and also through the skin to enter all organs and tissues. 97-98 percent of the preparation are eliminated from the body in 15 hours [14].

Demetonmethyl is oxidized to sulphoxide and sulphon in warm-blooded animals [14].

MAMMALIAN TOXICITY ARRAY

LD_{50} of demetonmethyl given intragastrically to albino rats is from 55 to 133 mg/kg, to albino mice, from 46 to 70 mg/kg and to cats, 30-50 mg/kg. Lethal doses with skin application was 75-100 mg/kg for rabbits.

A single four-hour exposure of cats to demetonmethyl aerosol in the concentration of 20-33.0 mg/m^3 killed some animals. Vapour of the same concentration had no lethal effect on the animals, but resulted in intoxication symptoms. The threshold concentration for cats during repeated exposures was lower for aerosol (1.0 mg/m^3) than for vapour (5.0 mg/m^3) as measured by the decreasing activity of cholinesterase.

Lethal doses of demetonmethyl given to laboratory animals caused their inhibition, lowered mobility, induced dyspnea, hypersalivation, lacrimation, tremour of the head, fibrillar convulsions of the muscles of the back and extremities, which were especially marked in rats. Before death, mice and rats had attacks of clonico-tonic convulsions. Symptoms of poisoning in cats were accompanied by disorders in the coordination of movements, retarded and shallow breathing. The animals die in the state of adynamia with progressive respiratory insufficiency. The clinical picture of poisoning in man is similar to that of mercaptophos poisoning, but with prevalence of the inhibition of the central nervous system.

Chronic action of demetonmethyl on cats (daily intragastric administration) is toxic in doses of 0.1 LD_{100}. Rats showed significantly lower sensitivity to the preparation.

Vapour of demetonmethyl, in the concentration of 0.7-4.0 mg/m^3 (mean of 1.7 mg/m^3 in daily 4-hour exposure) killed some rats in 20-21 days. Demetonmethyl in the concentration of 0.3-1.5 mg/m^3 (mean 0.9 mg/m^3) did not produce toxic action in a chronic two-month experiment. Inhaled demetonmethyl in the concentration of 0.3-2.3 mg/m^3 (mean, 0.9 mg/m^3) did not produce marked signs of intoxication in the animals in the course of two months, but conditioned reflexes and the activity of erythrocyte cholinesterase decreased by 37-52 percent. An aerosol of demetonmethyl in the concentration of 0.22-1.3 mg/m^3 (mean of 0.7 mg/m^3) did not cause any changes in the behaviour of cats, but the activity of their blood cholinesterase lowered by 11-63 percent. It follows that the concentration of 0.7 mg/m^3 of demetonmethyl is a threshold one when the exposure is repeated [15].

Skin application of 25 and 50 mg/kg to albino rats increased the erythrocyte, hemoglobin and reticulocyte counts in the animals during the first hours of the experiment. The white blood was affected as well: leucocytosis due to neutrophiles lymphocytopenia and eosinopenia developed [16]. Similar results were obtained in other experiments [17] and [18].

Rabbit experiments (1/2 LD_{50} of demetonmethyl given intragastrically) showed changes in ECG which were manifested in marked alternation of the

ventricular complexes, and also changes in the heart response to pituitrin [19].

Acute poisoning in men is characterized by disorders in the protein metabolism: accelerated peramination of glutamic acid in the liver, kidneys, muscles and the heart; increased content of gamma-globulin and decreased albumin level in the serum [20]. People occupationally exposed to demeton-methyl and other organophosphorus and organochlorine pesticides (pilots and technicians) had vegetative-vascular disorders and asthenovegetative syndrome which in most cases was associated with hypertension. Diencephalic syndrome developed in more serious cases [22].

For humans the olfactory threshold was established at the level of 0.0009 mg/m^3. In the concentration of 0.0004 mg/m^3, demetonmethyl affected the bioelectrical activity of the brain [22].

SPECIFIC TOXICITY STUDIES

Mutagenicity. The mutagenic effect of demetonmethyl was revealed in experiments of microorganisms. A negative effect was obtained in experiments on cells of warm-blooded animals [23].

Neurotoxicity/Behaviour. Daily exposure to demetonmethyl vapour in the concentration of 0.3-2.3 mg/m^3 for two months affected the conditioned reflexes in cats. People poisoned with demetonmethyl had inhibited the central nervous system [17].

The pathomorphological studies on laboratory animals poisoned with demetonmethyl revealed plethoric and edematous soft cerebral membranes and also subarachnoidal hemorrhage, chromatolysis, cariolysis, shrunk cells and affected Nissl's bodies. The most marked changes were in the cerebral and cerebellar cortexes [24].

Potentiation. Combined action of demetonmethyl with sinerphos (4-nitrophenoxydiethylsulphide) results in synergism in their action on insects. Synergism is absent when the preparations act on warm-blooded animals [25].

Antagonism is observed with the combined action of demetonmethyl, atropine and other cholinolytic compounds and cholinesterase reactivators [26].

Reproduction. Demetonmethyl acts embryotoxically on rats to decrease their fertility by more than 30 percent at the expenses of intrauterine destruction of eggs and embryos [27].

When given the concentration of 0.5 mg/m^3, 53 percent of embryos had hydrocephalia, and 5.3 percent had profuse hemorrhage into the peritonium. The process of ossification of minor bones of the extremities was inhibited and defective ossification of the skeleton and scoliosis were reported [27].

Primary Irritation. Demetonmethyl has no irritative action [15].

EFFECTS ON ORGANISMS IN THE ENVIRONMENT

Fresh–water fishes and other aqueous biota are less sensitive to demeton-methyl than to most other insecticides. Lethal concentration of the prepara-

tion to daphnia is 440 mg/l to young trouts it is 7.5 mg/litre, to pike yearlings it is 4 mg/litre and to carps over 100 mg/litre [13].

Demetonmethyl is less dangerous to useful insects and ticks-of-prey than other insecticides [13].

SAMPLING/PREPARATION/ANALYSIS

The phosphorus content array in demetonmethyl is based on the oxidation of the organophosphorus compound with ammonia persulfate to orthophosphoric acid. The latter is determined in the form of phosphomolybdic heteropoly acid after extraction with isobutyl alcohol. The sensitivity of analysis is 1 mcg of preparation in the sample [28].

TREATMENT OF POISONING

The specific remedy against poisoning with demetonmethyl is atropine and other cholinolytic preparations and also cholinesterase reactivators.

Treatment of demetonmethyl poisoning is described in detail by several researchers [6, 7, 29].

REMOVAL

Inactivation of demetonmethyl is effected by alkaline compounds. The DIAS preparation (a mixture of synthetic surfactants with organic solvents and alkalis) and 3-5 percent solutions of potassium hydroxide, soda ash or chloride of lime (1 kg in 4 litres of water) are recommended for the purpose. The decontamination is more effective with heating [30].

Overalls contaminated with demetonmethyl should be shaken to remove dust, and then soaked in a solution containing soap and soda for 6 to 8 hours. The overalls should finally be washed 2 or 3 times in a hot solution of soap and soda and rinsed thoroughly.

Containers are decontaminated with a 5 percent solution of sodium hydroxide or soda ash (30-50 g/l). The overalls are first soaked in the solution for 6-12 hours and then rinsed with ample water. If soda is not available, wood ash can be used instead.

Demetonmethyl unfit for use, or containers freed from the preparation should be disposed of in accordance with the existing sanitary regulations [30].

RECOMMENDATIONS/LEGAL MECHANISMS

Underaged persons, pregnant and lactating women, and also men aged over 55 or women aged over 50 are not allowed to work with demetonmethyl.

Workers exposed occupationally to this compound should be given a preliminary medical examination.

The activity of blood cholinesterase of workers exposed to demetonmethyl should be checked before admission to work and later once a week. Persons in whom the cholinesterase activity decreased by 25 percent and over, should be dismissed from direct contact with the organophosphorus compounds until the activity of the enzyme is not restored. Persons in whom first signs of illness are revealed, should not be admitted to the work either.

The daily exposure to the pesticide should not exceed four hours. The rest of the working time should be devoted to operations out of contact with the chemical.

All persons engaged in work with demetonmethyl should be given all necessary safety instructions. They should be supplied with means of individual protection: RU-60 or RPG-67-type respirators equipped with A-type cartridges, PO-2 and PO-3-type protective goggles, overalls of dense cloth or water-repelling fabric, rubberized or PVC aprons, high rubber boots and rubber gloves.

If said respirators are not available, industrial gas masks provided with filters (marked by a white vertical strip) should be used.

Signalmen should in addition be supplied with an oil cloth or PVC overalls provided with hoods.

Demetonmethyl should be sprayed from airplanes equipped with special containers fastened on the outside of the fuselage. Special care should be taken in aerial spraying as not to inflict any damage to the nearby settlements, water reservoirs and channels and other objects (in accordance with sanitary regulations). Only trailer blowers pulled by tractors equipped with closed cabins should be used for ground spraying.

Non-mechanic methods of spraying (with hand-operated sprayers, hoses, etc.) are not allowed. Concentrated pesticides are especially dangerous since they can cause poisoning when even tiny amounts are uptaken by various routes, through the skin included.

Chemical treatment of plants should be carried out early in the morning or in the evening, under supervision of agricultural experts and medical personnel (doctor or junior medics) who should supervise strict adherance to the safety regulations.

The maximum allowable concentration of demetonmethyl in the air is 0.1 mg/m^3 (vapour and aerosol) [7].

The maximum allowable concentrations in the air over settlements are as follows (theoretical): maximum single concentrations, 0.005 mg/m^3, mean daily, 0.001 mg/m^3 [7].

The maximum allowable concentration in water intended for domestic and welfare purposes, 0.01 mg/litre (organoleptic criterion) [7, 32].

The allowable residual quantity of demetonmethyl in apples, sugar beet and hop, 0.7 mg/kg [7].

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