Triadimefon in Forestry Nurseries: Operator Exposure and the Effectiveness of Spraying Methods

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Abstract

Concentrations of triadimefon fungicide in breathing zone and on the skin were measured in order to assess the exposure of an operator treating birch seedlings with hand-held equipment in a Finnish forestry nursery. The actual exposure was found to be low, only 10 % of the acceptable operator exposure level (AOEL). When exposure was assessed using the results of potential exposure measurements,when the samplers are attached on the top of the protective clothing, the acceptable level was, however, exceeded by 850 %. Hands were the main route of exposure. Simultaneously, the effectiveness of four different spraying methods was studied by analysing the amount of triadimefon residue on leaf samples for 20 days after spraying. A hand-held sprayer has traditionally been considered to be the most effective method available for spraying fungicides. In this study, some new, safer and more economical methods of spraying were compared to hand-held application. After the test period of 20 days, the highest concentration of residue was measured on birch leaves collected from an area treated with conventional hand-held equipment. Nonetheless, the new methods are safer to the operator and probably friendlier to the environment due to less leaching of the pesticide.

Key words: Triadimefon, forestry nurseries, operator exposure, occupational safety, plant protection

Introduction

New, economical and more effective methods are being developed in Finland for treating seedlings with pesticides in forestry nurseries (*e.g.* Tervo *et al*. 1991, 1994, Tuomainen *et al*. 2003). The intentions of this work are also to save manpower, to reduce the use of pesticides due to tightened environmental regulations and also to reduce the exposure of the workers. In this study, the effectiveness of four methods of application were compared. Operator exposure during manual spraying was assessed with air samples collected from the breathing zone of the worker and with patch and handwash samples.

Triadimefon or 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazole-1-yl)-2-butanone is a systemic fungicide commonly used to control powdery mildews and many other diseases in, for example, cereals, vegetables and some fruit (Tomlin 2000). Triadimefon can also be used in forestry nurseries. In Finland, it has been used to protect pine and birch seedlings against rust diseases. The amount of triadimefon in the wettable powder product used in this study was 250 g/kg. Furthermore, the concentration of the active ingredient recommended by the importer is 0.05 %.

Triadimefon can penetrate the operator via the lungs or the skin. In animal studies, 50-80 % of triadimefon has been observed to be absorbed through the skin (Knaak *et al*. 1984). Triadimefon is a neurotoxic compound, causing, for example, motoric hyperactivity in test animals (Crofton *et al*. 1988, Moser *et al*. 1989). Exposure to triadimefon has also been reported to serve as an environmental risk factor for dopamine-associated, long-term or even permanent, behavioral and psychiatric disorders by affecting both developing and adult neurotransmitter systems (Reeves *et al*. 2003, 2004). Indications of teratogenicity, mainly craniofacial and axial skeletal defects, have also been reported (Groppelli *et al*. 2005, Menegola *et al*. 2005 a, b) In a two-year feeding trial on dogs (and rats) the no-observed-effect level (NOEL) was found to be 2.5 mg/kg body weight/day (U.S. EPA/IRIS 1998).

In humans, exposure to triadimefon has been shown to cause contact dermatitis (Winter *et al*. 1985). However, the effects of chronic exposure are not yet known. Overexposures of humans are said to have resulted in hyperactivity followed by sedation (Reigart and Roberts 1999). Occupational exposure to triadimefon has been studied in three forestry nurseries in the United States, where exposure was found to occur in all work phases, for example, mixing and loading, application with tractor-mounted equipment, packaging and weeding (Lavy *et al*. 1993).

The dose caused by the measured exposure can be compared to the Acceptable Operator Exposure Level (AOEL), which is defined from the NOEL by dividing the value by a safety factor (Krieger *et al*. 1992). In the Nordic countries, the most commonly applied safety factor is 100.

The aim of this study was to compare different methods of spraying for their efficacy (reduction of the residue level), and to assess the exposure of an operator using hand-held equipment. It was assumed that the best coverage and preservability of the fungicide would be reached with the hand held sprayer. However, using *e.g.* knapsack sprayer causes dermal contamination and possibly inhalational exposure. We wanted to see whether that exposure was acceptable, and whether the other, more automatised methods would be effective enough.

The exposure of an operator was measured and the concentrations of the residues in leaf samples were analysed (20 days after spraying). The internal dose of the operator was calculated from the results of actual and potential exposure measurements.

Materials and methods

Spraying methods. The four spraying methods of interest were tested in a research nursery in Suonenjoki, eastern Finland. Birches were cultivated as ball seedlings (25 seedlings in one plastic case on open ground). The fungicide studied was sprayed by the following methods:

1. powered knapsack spraying;
2. spraying with a mobile irrigation boom;
3. mobile irrigation boom equipped with an airflow system;
4. new precision-sprayer model called M. Pitkäniitty.

The commercial product containing triadimefon (100 g) was mixed with water in the tank (200 l) of a tractor-mounted sprayer, from which the dilute was led to the equipment used or pumped into the tank of the knapsack sprayer.

The mobile irrigation boom (Methods 2 and 3) covered the whole area of seedlings. The speed of the boom was 0.15 m/s and the height was 115 cm (measured from the surface of the turf of the seedling box). The boom contained 21 swirl nozzles (type TeeJet 11003), but the spray from some of the nozzles hit the walkway between the boxes. For this reason the total yield of the method was calculated from only nine nozzles. When this system was equipped with air flow (Method 3), all the other parameters remained the same, except for the number of nozzles reaching the actual plants. In this case there was one nozzle less than in Method 2. Therefore, 59 l of the spray was comsumed.

The new precision sprayer has a tractor-mounted boom equipped with 67 nozzles (Method 4). For the study, a conveyor version of the sprayer was constructed. The boxes of seedlings were put onto the conveyor manually (speed 0.27 m/s). The number of boxes treated was 48. The distance between the nozzles and the turf surface of the cases was 8 cm. Three nozzles were used. Detailed information about the test areas and the seedlings is presented in Table 1 and the amounts of active ingredient and spray liquid used with different methods in Table 2.

Table 1. Properties of the test areas and seedlings treated with different spraying methods

	Knapsack sprayer	Irrigation boom	Irrigation boom + air	Precision sprayer
# of seedling boxes	2285	868	1001	48
Seedlings / test area	54625	21700	25025	1200
Test area (m^2)	788	392	376	8
Seedlings / m^2	70	55	67	156
Height of seedlings (range), cm*	55 (26-74)	72 (60-85)	53 (36-66)	68 (47-83)

* = average height of 50 seedlings

Table 2. The amount of pesticide consumed by different spraying methods

	Knapsack sprayer	Irrigation boom	Irrigation boom + air	Precision sprayer
Amount of active ingredient consumed (g)	15	32	29	0.8
Amount of spray liquid consumed (ml/seedling)	1.1	3.0	2.3	1.4
Amount of spray liquid consumed (l/m^2)	0.076	0.168	0.156	0.214
Amount sprayed (l/min)	2.3	1.4	1.4	0.46

The operator. Occupational hygiene samples were collected only from the operator using a knapsack sprayer, because the other methods tested, if used correctly, were assumed to cause negligible exposure. During both mixing and loading phase and during application of the fungicide the operator was wearing a motorized breathing apparatus equipped with filters for both particulate and gaseous matter, thick nitrile rubber gloves, PVC-trousers, cotton-nylon coat and rubber boots. He was also well trained and very experienced.

Sampling; Occupational hygienic measurements. Respiratory exposure of the operator was assessed with air samples collected from the breathing zone. Due to low vapour pressure, it was assumed that all airborne triadimefon would be in solid phase. Therefore, the samples were collected onto glass fibre filters (Gelman Sciences, USA) with personal sampling pumps (SKC 224, SKC Inc. USA). The first sample was taken during mixing and loading and the second one during application. The samples were extracted with ethyl acetate and analysed the same day.

Exposure through the hands and the effectiveness of the protective gloves were evaluated with handwash samples (Fenske 1993). The hands (left and right separately) were washed after the working period by rinsing the palms and fingers thoroughly for one minute with 100 ml of ethanol (Aa). The samples were stored in glass bottles in a freezer (-18°C) until analysed within a week.

The patch sampling method was used to assess the exposure of the body (actual exposure) and the effectiveness of the protective garment (potential exposure) (Ness 1994). The samples were collected with 10 cm x 10 cm alpha cellulose patches, attached with tape on and underneath the protective garment. The patches were located on the chest, upper back, thighs and forearms (on the garment on right arm and under the garment on left arm). After sampling, the patches were removed carefully using disposable gloves and put into glass tubes containing ethanol. The patches were stored at -18°C for a week before they were analysed.

Collection and handling of leaf samples. The residues on the leaves of the seedlings were studied for 20 days after the sprayings to ascertain how long triadimefon stays on the plants when sprayed with different methods. The leaves from the four test areas were picked randomly into plastic bags using disposable gloves and then stored at -18°C until the dislodgeable foliar residues were analysed with a modification of the method first introduced by Iwata *et al*. 1977. After the leaves were defrosted, they were cut into round 5 cm^2 pieces with a leaf sampler (Birkenstrand Co.,USA). All samples (one sample consisting of 40 pieces, 400 cm^2) were analysed within two months. Blank samples were collected just before spraying and the first actual samples right after the spray had dried on the leaves. Other samples were collected 2, 6, 12 and 20 days after spraying. The climatic conditions on those days are presented in Table 3. The precipitation for the 20-day period was 14.4 mm.

Analytical methods. All samples, and triadimefon and triadimenol (metabolic product of triadimefon) standards were analysed with a gas chromatograph (HP 5890, Hewlett Packard Inc., USA) equipped with an EC detector and a HP-1 column.

Table 3. Climatic conditions at 12.00 on the days the analysed leaf samples were collected.

	Temperature (°C)	Relative humidity (%)
Spraying day (1st samples)	+ 13	42
2 days after spraying	+ 14	47
6 days after spraying	+ 17	46
12 days after spraying	+ 11	57
20 days after spraying	+ 10	92

Results

Occupational exposure of the operator. The concentrations of triadimefon in the air samples collected from the breathing zone during mixing and loading and during application were both under the limit of detection. On the other hand, it can also be assumed that the motorised respiratory device provides full protection for the operator and that the exposure through respiratory organs can be considered negligible. The exposure rate measured on the protective garment was 1850 μg/h. Accordingly exposure rate under the protective garment was 12 μg/h. Exposure rate of the hands was 10 μg/h (both hands combined). In this case, the actual total exposure rate of the operator was 22 μg/h.

Residues in the seedlings. The reduction of the triadimefon concentrations measured from the leaf samples collected on different days are presented in Figure 1. The concentration on the last day of the test period (day 20) was highest in samples collected from an area sprayed with a knapsack sprayer.

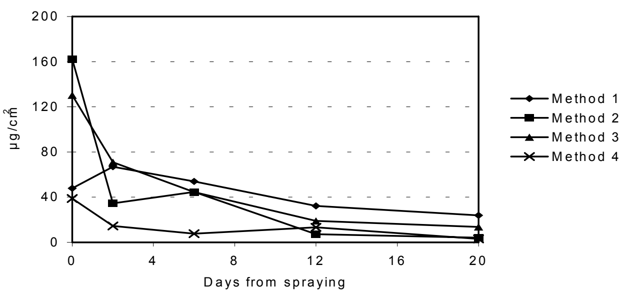

Figure 1. Residues of triadimefon found in the seedlings for 20 days

Discussion

Exposure to triadimefon through the respiratory system evidently was low. The operator was experienced and skilled. In addition, he continually walked away from the pesticide when he was spraying. Moreover, the weather was calm.

The personal protective clothing used by the operator proved effective. The amount of triadimefon measured under the protective garments (actual exposure) was only 0.6 % of the amount found on top of them. In these circumstances, the personal protection was adequate. The amount of triadimefon measured in handwash samples accounted for half of the total dermal exposure. This was presumably due more to unhygienic use of the protective gloves or some earlier contamination of them than to penetration through the glove material.

If 100 % dermal absorption is assumed, the actual total exposure was 22 μg/h. As a worst-case scenario, 8-hour exposure is presumed. The dose would then be 176 μg per work day, which corresponds to 2.5 μg/kg bw/day for an operator weighing 70 kg. The AOEL of triadimefon is 0.025 mg/kg bw/day (25 μg/kg bw/day). NOEL obtained from a 2-year feeding trial on dogs is 2.5 mg/kg bw/day, and the safety factor used for non-carcinogenic pesticide is 100. Thus, the exposure accounts for 10 % of the acceptable value for triadimefon. When the comparison for AOEL is made by using the potential exposure of the body (1850 μg/h), the exposure would almost be nine times higher (850 %) than the acceptable level. This emphasises the importance of proper protection of the skin.

The highest concentrations of residue 20 days after spraying of triadimefon were found in leaf samples treated with a knapsack sprayer (Method 1). At that time the amount of triadimefon was about half that measured immediately after spraying. From this point of view, the manual spraying method was indeed the most efficient. When the methods based on an irrigation boom (Methods 2 and 3) were used, the concentration of triadimefon measured from the leaves immediately after spraying was considerably higher than with the other two methods. For treatment of seedlings, the new precision sprayer is probably the optimal method of those tested in this study. When mounted on tractor, it is safe for the operator. Furthermore, because of its low and accurate use of spray, it is also friendly to the environment, including the ground water.

Conclusions

The difference between actual and potential dermal exposure of the body was quite marked in this study. Half of the actual dermal exposure, however, was due to the exposure of the hands. This finding is representative of Finnish conditions, because in most cases the use of personal protective equipment is comfortable due to the temperate weather conditions in Finland during the growing season. The training and education of operators are also generally well organized. In all kinds of pesticide work, however, wearing the protective gloves correctly has always been a problem (Nigg *et al*. 1986, Fenske 1988).

Leaching of pesticides to the soil and further to the ground water is a possible problem in nurseries (*e.g.* Juntunen 2002). Development of new, safer spraying techniques is, therefore, an important task.

References

Crofton, K.M., Boncek, V.M. and Reiter, L.W. 1988. Hyperactivity induced by triadimefon, a triazole fungicide. *Fundamental and Applied Toxicology,* 10: 459-465.

Fenske, R.A. 1988. Comparative assessment of protective clothing performance by measurement of dermal exposure during pesticide applications. *Applied Industrial Hygiene,* 3: 207-213.

Groppelli, S., Pennati, R., De Bernardi, F., Menegola, E, Giavini, E. and Sotgia, C. 2005. Teratogenic effects of two antifungal triazoles, triadimefon and triadimenol, on *Xenopus laevis* development: Craniofacial defects. *Aquatic Toxicology,* 73: 370-381.

Iwata, Y., Knaak, J.B., Spear, R.C. and Foster, R.J. 1977. Worker reentry into pesticide-treated crops. 1. Procedure for the determination of dislodgeable pesticide residues on foliage. *Bulletin of Environmental Contamination and Toxicology,* 18: 649-655.

Juntunen, M.-L. 2002. Environmental impact of fertilizers and pesticides used in Finnish forest nurseries. Academic Dissertation, University of Kuopio. The Finnish Forest Reseach Institute, Research Papers 849, 58 p + app.

Knaak, J.B., Yee ,K., Ackerman, C.R., Zweig, G. and Wilson, B.W. 1984. Percutaneous absorption of triadimefon in the adult and young male and female rats. *Toxicology and Applied Pharmacology,* 72: 406-416.

Krieger, R, Ross, JH, and Thongsinthusak, T. 1992. Assessing human exposures to pesticides. *Reviews of Environmental Contamination and Toxicology,* 128: 1-15.

Lavy, T.L., Mattice, J.D., Massey, J.H. and Skulman, B.W. 1993. Measurement of year-long exposure to tree nursery workers using multiple pesticides. *Archieves of Environmental Contamination and Toxicology*, 24: 123-144.

Menegola, E., Broccia, M.L., Di Renzo, F., Massa, V. and Giavini, E. 2005. Craniofacial and axial skeletal defects induced by the fungicide triadimefon in the mouse. *Birth Defects Research Part B: Developmental and Reproductive Toxicology,* 74:185-195.

Menegola, E., Broccia, M.L., Di Renzo, F., Massa, V. and Giavini, E. 2005. Study on the common teratogenic pathway elicited by the fungicides triazole-derivatives. *Toxicology in Vitro*, 19: 737-748.

Moser, V.C. and MacPhail, R.C. 1989. Neurobehavioral effects of triadimefon, a triazole fungicide, in male and female rats. *Neurotoxicology and Teratology,* 11: 285-293.

Ness, S. 1994. Surface and dermal monitoring for toxic exposures. Van Nostrand Reinhold, New York, U.S.A., 561 p.

Nigg, H.N., Stamper, J.H. and Queen, R.M. 1986. Difocol exposure to Florida citrus applicators: Effects of protective clothing. *Archieves of Environmental Contamination and Toxicology,* 15: 121-134.

Reeves, R., Thiruchelvam, M., Richfield, E.K. and Cory-Slechta, D. 2003. Behavioral sensitization and long-term neurochemical alterations associated with the fungicide triadimefon. *Pharmacology, Biochemistry and Behavior*, 17: 315-326.

Reeves, R., Thiruchelvam, M., Richfield, E.K. and Cory-Slechta, D. 2004. The effect of developmental exposure to the fungicide triadimefon on behavioral sensitization to triadimefon during adulthood. *Toxicology and Applied Pharmacology,* 200:54-63.

Reigart, J.R. and Roberts, J.R. 1999. Recognition and management of pesticide poisonings. 5th ed. 1999. EPA Document No. EPA 735-R-98-003. U.S. Environmental Protection Agency/Office of Prevention, Pesticides, and Toxic Substances, 154 p.

Tervo, L., Kangas, J., Kurttio, P. 1991. A nursery sprayer with the recycling principle. *Scandinavian Journal of Forest Research*, 6: 259-270.

Tervo, L., Kangas, J., Kuikka, M., Sarantila, R. 1994. Treatment of container seedlings in the nursery against large pine weevil. *Tree Planters´ Notes,* 45(1): 5-9.

Tomlin, D.C.S. (Editor). 2000. The Pesticide Manual, 12th ed., British Crop Protection Council, Farnham, U.K., 1250 p.

Tuomainen, A., Tervo, L. and Kangas, J. 2003. Application of permethrin in forestry nurseries: Residues in seedlings and exposure of workers. *Baltic Forestry,* 9:75-79.

U.S.EPA. 1998. Integrated Risk Information System, IRIS, Tomes PlusŅ System 35, Micromedex Inc. USA.

Winter, C.K. and Kurtz, P.H. 1985. Factors influencing grape worker susceptibility to skin rashes. *Bulletin of Environmental Contamination and Toxicology*, 35: 418-426.

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ТРИАДИМЕФОН В ЛЕСНЫХ ПИТОМНИКАХ: ЭКСПОЗИЦИЯ НА ОПЕРАТОРА И ЭФФЕКТИВНОСТЬ МЕТОДОВ ОПРЫСКИВАНИЯ

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Резюме

Концентрации фунгицида триадимефона в зоне респирации и на кожных покровах человека измерялись с целью оценки экспозиции на оператора, обрабатывающего саженцы ручным устройством в лесном питомнике Финляндии. Определенная фактическая экспозиция была низка и достигала лишь 10% допустимого уровня экспозиции на оператора. В случаях, когда экспозиция измерялась по результатам потенциальных измерений экспозиции, накладывая пробы на поверхность защитной одежды, допустимый уровень достигал, однако, 850%. Основным путем экспозиции являются руки. Одновременно изучалась эффективность четырех различных методов опрыскивания путем измерения количества остатков триадимефона на пробах листьев в течении 20 дней после опрыскивания. Ручной опрыскиватель традиционно оказался наиболее эффективным методом, доступным для опрыскивания фунгицыдами. В данном исследовании некоторые новые, безопасные и более экономные методы опрыскивания сравнивались с ручным применением. После опытного 20-дневного периода, наиболее высокие концентрации остатков измерены на листьях березы, собранной с площади, обработанной традиционным ручным устройством. Все же, новые методы являются безопасными оператору и возможно окружающей среде, в связи с меньшим вымыванием пестицида.

Ключевые слова: триадимефон, лесные питомники, экспозиция, профессиональная безопасность, защита растений