Application of Permethrin in Forestry Nurseries: Residues in Seedlings and Exposure of Workers

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A synthetic pyrethroid, permethrin, was used against the insect pine weevil *(Hylobius abietis)* at two forestry nurseries in Finland. The goal was to determine the residues of permethrin in the seedlings of pine trees and spruces in connection with the spraying operations and to measure the exposure of the nursery workers to permethrin during spraying and during cleaning the sprayers.

The exposure of the workers to permethrin was very low according to the measurements of permethrin in the breathing zone of the workers, and the biological monitoring studies. However, the contamination of the workers' clothes and skin confirmed that the correct use of personal protective equipment is necessary in this kind of work.

After two weeks, the concentration of permethrin in the stems of the pine trees had fallen to 44-54 % and in the spruce to 77 %. In the spruce needles the concentration of permethrin had fallen to 60 % in 10 days, and in the pine needles to 9 % in 3 days. However, there were differences in the uniformity of the spraying technique used in the nurseries, because sizes of the seedlings differed and the seedling densities in the nurseries were also different. In the future, the development of spraying machines is very important in order to ensure a uniform spraying outcome.

Key words: permethrin, pine weevil, exposure, residues

Introduction

Several methods are used to control the insects (e.g. pine weevil); either mechanical or chemical ones, in which insecticides are applied. Nowadays, Finnish nurseries quite commonly use special tractor sprayers to treat seedlings against the insects (Tervo *et al.* 1991, 1994). The use of insecticides in forests is not very common in Finland.

Permethrin is a synthetic pyrethroid type insecticide used against the pine weevil. Its CAS registry number is 52645-53-1, molecular formula $C_{21}H_{20}Cl_2O_3$ and molecular weight 391.3. The commercial preparations are either in liquid or powder form, and contain both the cis and trans isomers of permethrin (usually 40/60 or 25/75). The water solubility of permethrin is $6x10^{-3}$ mg/l (20 °C, pH 7) and it is also very soluble in several solvents like xylene, hexane and methanol. Permethrin has many trade names, such as Adion, Ambush, Assithrin, Cliper, Coopex, Corsair, Dragnet, Dragon and Eksmin (Tomlin 2002).

Permethrin is absorbed into the human body through the alimentary canal and respiratory tract. Absorption through the skin is of minor importance (Elliot *et al.* 1976). The metabolites of permethrin are secreted into the feces and urine, and they seem to be secreted almost totally in 3 to 8 days (Elliot *et al.* 1976, Gaughan *et al.* 1977). The main metabolites are 3-(2,2,-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid (Cl_2CA), 3-phenoxybenzoic acid (3-PBA) and 4-hydroxy-3-phenoxybenzoic acid (4-OH-3-PBA) (Kaneko and Miyamoto 2001, WHO 1990). In animal studies, pyrethroids have been found to be neurotoxic (Wershoyle and Aldridge 1980). The animal studies have not revealed any significant sensitivity, although some animals did show mild skin irritation to permethrin (Metker *et al.* 1977).

Permethrin has been reported to cause skin, eye, and nose irritation in the exposed workers (Wershoyle and Aldridge 1980, Kolmodin-Hedman *et al.* 1982, 1995, Eidman and von Sydow 1989). According to Le Quesne et al. (1981) 19 out of 23 workers exposed to different synthetic pyrethroids, had experienced one or more episodes of abnormal facial sensation, but there were no abnormal neurological signs; also the electrophysiological studies were normal in the arms and legs. However, in a study of Hagberg (1992), the workers planting seedlings treated with permethrin did not experience more symptoms than the workers planting seedlings that were not treated with this insecticide.

In this study permethrin was used against the pine weevil (*Hylobius abietis*) at two forestry nurseries in Finland. The aim was to determine the residues of permethrin in the needles and stems of the seedlings of pine trees and spruces after tractor spraying oper-

ations at these nurseries. The aim was also to evaluate the exposure of nursery workers via inhalation and skin to permethrin during the spraying of the insecticide, and afterwards during the cleaning and washing of the tractor sprayers. In addition, the workers' exposure to permethrin was assessed with biological monitoring by measuring the metabolite of permethrin (3-PBA) in the urine samples collected soon after the exposure.

Materials and methods

The spraying of the seedlings with permethrin was done in the springtime at two forestry nurseries (A and B) located in central Finland. The mean outside temperature was about 19 °C and relative humidity about 73 % during the day time in the studied nurseries. The precipitation was quite small during the study period; it was rainy on two occasions at nursery B (precipitation 2 and 12 mm) and three times at nursery A (precipitation 2.5, 7.5 and 22 mm). At nursery A the seedlings of pine and spruce, and at nursery B the seedlings of pine, were one-year-old container seedlings. The height of the pine seedlings ranged from 15 to 23 cm (n = 21) at nursery A, and from 9 to 14 cm (n = 28) at nursery B. The height of the spruce seedlings at nursery A was 20-30 cm (n = 12). A tractor sprayer was used for the permethrin sprayings at both nurseries (Figure 1). The spraying bar of the tractor had altogether 67 nozzles, which were situated at regular intervals of 15 cm from each other. The diameter of one spraying nozzle was 1 mm. At nursery A the spraying pressure was 5-10 bar and at nursery B 4-5 bar. The tractors used in the spraying operations were equipped with air-conditioned cabins with an air filter.

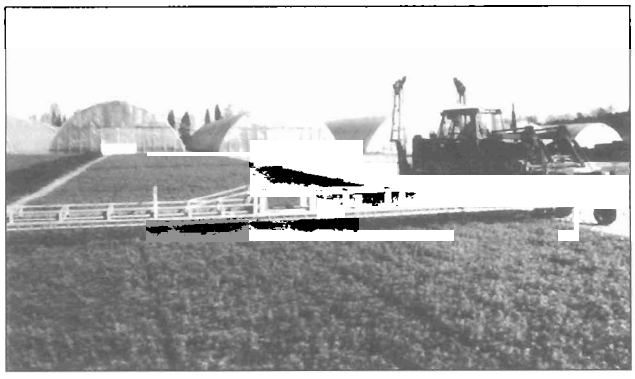

Figure 1. The tractor sprayer used in the study

At nursery A, the commercial permethrin solution was F-permethrin® (Berner, active ingredient 250 g/kg, cis/trans isomeric ratio 25/75). Nursery B used Gori 920® (Gori, active ingredient 250 g/l, cis/trans ratio 25/75). The final concentration of the spray liquid at both nurseries was 2 %. This solution was diluted in water. The application of permethrin was done at two time periods during the same day at nursery A; the first period took three hours and the second period one and a half hours. Thereafter, the applicator washed and cleaned the sprayer for 45 min. At nursery B, the application period took 43 min and the washing of the sprayer 20 min.

The permethrin concentration was determined separately from the needles and stems of the sprayed pine and spruce seedlings. The residues in the seedlings were followed for a two-week period at both nurseries. The seedling samples were taken randomly from the seedling boxes (2-3 seedlings/sampling time) and they were stored at - 20 °C before analysis. One sample contained about 4 g of needles or stem, which was eluted in petroleum ether (3 x 30 ml), evaporated and purified with a commercially available Florisil column. The samples were analyzed in a gas chromatograph (Hewlett Packard 5890) equipped with a capillary column (HP-1, 25 m) and an electron capture (EC) detector. The run program was the following: initial temperature 180 °C, rate 5 °C/min, and final temperature 220 °C. The injection volume was 1 µl and the temperature of the detector was 380 °C. The permethrin standard used in the analyses was from Dr. Ehrenstorfer (Germany). It contained both cis and trans forms at a ratio of 25/75, and in the final results the concentration of these isomers has been calculated together.

A small laboratory experiment was also done to determine the permethrin concentration in the stems of one-year-old container seedlings of pine after dipping them into 2 % permethrin spraying solution for 1 min in a beaker. The seedlings were then stored and analysed for permethrin as described above.

At the nurseries, the workers (two men) were practised into the spraying operations. At nursery A the applicator wore cotton coveralls and a cotton cap, leather boots and neoprene gloves. When preparing the spray liquid he wore a half-mask respirator with a gas filter. At nursery B the applicator wore jeans, leather boots, a short cotton jacket and rubber gloves. The exposure of workers to permethrin during application and the washing of the sprayers was evaluated by occupational hygienic measurements and biological monitoring. Air samples were taken at the workers' breathing zone into XAD-2 adsorption tubes (SKC Inc., PA, USA) with portable pumps (SKC Inc., PA, USA). The sampling times were equivalent to the work periods. The contents of the XAD-2 tubes were added to 3 ml of ethyl acetate and analyzed as earlier described by Kangas *et al.* (1993). The potential and actual exposure of the workers to permethrin was estimated by

patch tests (Chester *et al.* 1995). Alpha cellulose patches (11 x 11 cm) were attached over and under the workers' clothes at arms, chest, back and thighs. Exposure through the skin of the hands was measured by hand wash samples taken immediately after a work period (Zweig *et al.* 1985). The hand wash samples (in ethanol) and adsorbent pads were analyzed according to a method modified by Durham and Wolfe (1962) and Kangas *et al.* (1993). The urine samples for biological monitoring were collected from the operators immediately after the work periods and stored at - 20 °C (as well as the occupational hygienic samples) until analysis. A pentafluorobenzyl bromide derivative was formed from permethrin metabolites in the workers' urine samples (Manninen *et al.* 1986). Briefly, the urine sample was first hydrolyzed with acid, purified in commercially available C-18 columns and then derivatized in the presence of tetrabutyl ammonium hydroxide and pentafluorobenzyl bromide. All these samples were analysed with the above mentioned gas chromatograph and run program.

Results

The permethrin residues in the pine and spruce stems were followed for two weeks after the spraying (Figure 2) and those in the needles for 3 or 10 days (Figure 3). At nursery A the permethrin residues in the spruce stems fell to about 77 % of the initial levels in two weeks. In the pine stems the residues fell to 44 %. At nursery B the initial level of permethrin fell to about 54 % during the two-week time. Furthermore, in the pine needles, the residues diminished to 60 % on average in 10 days, and in the pine needles to about 9 % during the three days of follow-up.

The spreading of the permethrin solution from the tractor sprayer was also determined in the seedlings

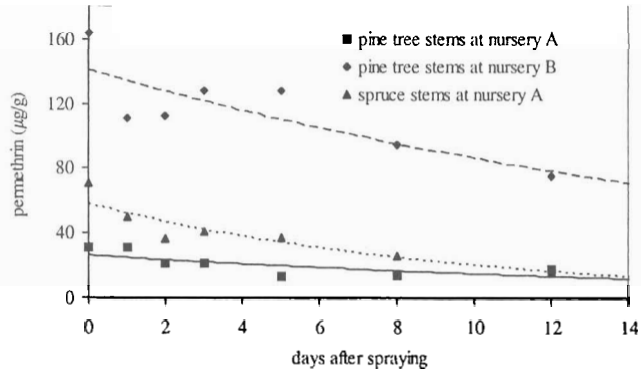

Figure 2. The permethrin residues (µg/g) after spraying in the stems of seedlings at nurseries A and B. The concentrations are the mean of two to four different measurements.

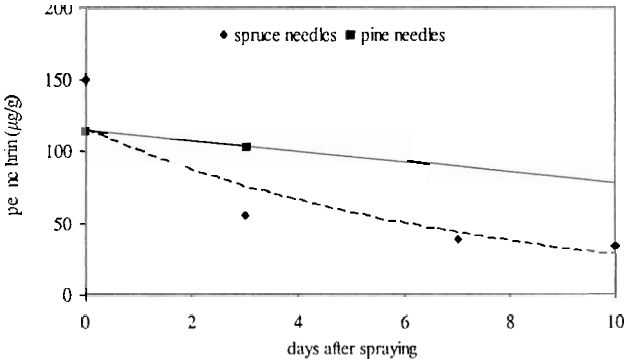

Figure 3. The permethrin residues (µg/g) after spraying in the needles of seedlings at nursery A. The concentrations are the mean of two or three different measurements

at nursery A shortly after the application. The concentrations of permethrin in the different stems and needles of spruce were about 24 % and 18 %, respectively. In the pine seedlings, the figures were 35 % and 45 %, respectively.

In the pine seedlings dipped into 2 % permethrin solution in the laboratory experiment, the concentration of permethrin in the stems was higher (360 µg/g) than in the seedlings sprayed with permethrin (about 40-160 µg/g).

The concentrations of permethrin measured at the workers' breathing zone and in the hand wash samples during the application and sprayer cleaning, as well as the amount of permethrin metabolite (3-PBA) in the workers' urine samples collected after the work period are presented in Table 1. The potential and actual exposure of the workers to permethrin during the work periods was measured with the adsorbent

Table 1. The concentration of permethrin at the workers' breathing zone (µg/m³) and in hand wash samples (µg/h, both hands calculated together) during the tractor spraying and the sprayer washing, and the concentration of 3-phenoxybenzoic acid (3-PBA, µmol/l) in the workers' urine samples collected after the work period

	Worker 1* (nursery A)	Worker 1** (nursery A)	Worker 2*** (nursery B)
Breathing zone (µg/m³)	14.0	6.3	4.2
Hand wash (µg/h)	19.2	67.6	57.0
Urine 3-PBA (µmol/l)	-	<0.03	0.05

* spraying of permethrin solution for 3 h
** spraying of permethrin solution for 1 h 30 min and thereafter washing of the sprayer for 45 min
*** spraying of permethrin solution for 43 min and thereafter washing of the sprayer for 20 min
- not measured

patch technique (Figures 4 and 5). The total contamination of the clothes by permethrin was 150 µg/h during the first spraying period and 346 µg/h during the second spraying and spray washing at nursery A. Inside the clothes the concentrations of permethrin were 14 and 42 µg/h, respectively. At nursery B, the workers' clothes contained 2782 µg/h of permethrin after the spraying; inside the clothes the concentration was 25 µg/h. The skin exposure was calculated by summing the concentrations inside the workers' clothes and those in the hand wash samples. The exposure through the skin was 34 µg/h after the first spraying and 109 µg/h after the second spraying and sprayer washing at nursery A. At nursery B, the actual skin exposure was 82 µg/h.

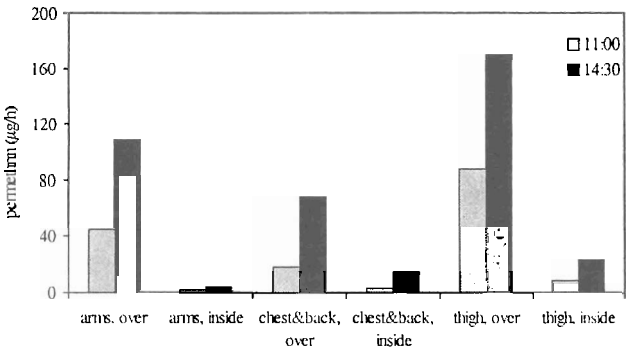

Figure 4. The contamination of clothes and skin by permethrin (µg/h) at nursery A during the two spraying operations, at 11:00 and 14:30. The last period included also the washing of the tractor sprayer. Over = permethrin contamination over the clothes, inside = permethrin contamination inside the clothes

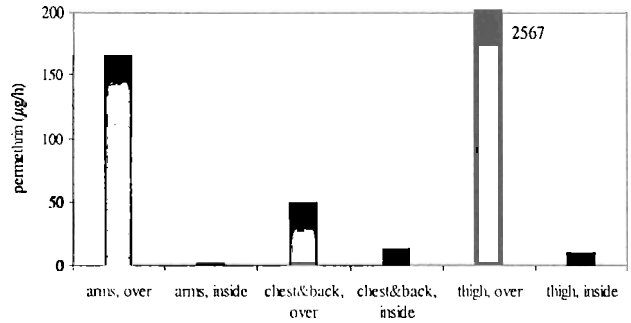

Figure 5. The contamination of clothes and skin by permethrin (µg/h) at nursery B during the spraying period and washing of the tractor sprayer. Over = permethrin contamination over the clothes, inside = permethrin contamination inside the clothes

Discussion and conclusions

There were differences in the spreading of permethrin solution by the tractor spraying technique used at the two nurseries. Firstly, the sizes of the seedlings were not similar; at nursery A the seedlings were higher than at nursery B. Secondly, the seedling densities affect the spreading of permethrin spray; at nursery A the seedling density was higher. This explains why the concentration of permethrin in the pine seedlings was about five times higher soon after the spraying period at nursery B than at nursery A. In the future, the development of the sprayer machines is very important for producing a uniform spraying outcome. This study revealed no differences in the retention of residues in the seedlings between the two permethrin preparations used (powder and liquid form). The residues in the stems were followed up for a two-week period after the spraying. The permethrin residues fell to about 44 % and 77 % in the stems of pine and spruce, respectively. Spraying with permethrin should preferably be done in spring just before sending the seedlings into the field, because in the southern and central parts of Finland, the pine weevil is active in May.

The exposure of nursery workers to permethrin was quite low according to the measurements at the breathing zone of the workers and the biological monitoring studies. However, the contamination of clothes, skin and hands confirmed that exposure to permethrin did occur. The contamination level of clothes and skin was much lower at nursery A after the first spraying than after the second one, which also included the washing of the tractor sprayer equipment. At nursery B, the contamination of the workers's clothes was higher than at nursery A. The worker at nursery B had a very high amount (over 2500 µg/h) of permethrin in the patch sample collected over his thigh. The washing and cleaning of the tractor sprayer is a work phase in which this kind of high exposure can easily occur, if the worker is not careful. However, the actual dermal exposure to permethrin was at the same level at both nurseries, i.e. about 0.5 mg/day. In animal tests, permethrin has the NOEL value (no observed effect level) of 5 mg/kg (five-year rat test). Permethrin is not classified to be carcinogenic; therefore the safety factor used in the assessment of human exposure is 100. Then, the AOEL (acceptable operator exposure level) is 0.05 mg/kg, which means an AOEL value of about 3 mg for a person weighing 70 kg. If we assume that all the permethrin would be adsorbed into the human body, the amounts of permethrin, which were measured in this study, are much lower than the AOEL value.

In practice, the level of exposure to pesticides can vary significantly owing to a number of factors, such

as the method of application, treatment time, application rate, the circumstances under which the pesticide is applied, protective equipment used, etc. The correct use of personal protective equipment (coveralls, rubber gloves, rubber boots, cap, respirator) is important in this kind of work in order to minimize the exposure, especially via the skin. Especially, the washing of spraying equipment is a work phase in which considerable exposure via the hands and other skin areas can occur.

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ИСПОЛЬЗОВАНИЕ ПЕРМЕТРИНА В ПИТОМНИКАХ: НАЛИЧИЕ ОСТАТКОВ В САЖЕНЦАХ И ВЛИЯНИЕ НА РАБОТАЮЩИХ

А. Туомайнен, Ю. Кангас, Л. Терво

Резюме

Перметрин – широко используемый инсектицид. В данном исследовании перметрин использован против большого соснового долгоносика (*Hylobius abietis L.*) в двух питомниках. Целью исследования было выяснение наличия остатков перметрина в саженцах сосны и ели после опрыскивания трактором, а также подверженность работающих во время опрыскивания и во время мытья и уборки опрыскивателя.

На основании результатов исследования зоны дыхания и проб мочи установлено, что подверженность работающих воздействию перметрина незначительна. Работающие подвергались воздействию перметрина через кожу рук и прочие кожные покровы. Соответствующие защитные средства (комбинезон или брюки и куртка, резиновые перчатки, головной убор, резиновые сапоги и респираторы), которые регулярно очищаются и стираются необходимы для такой работы, чтобы воздействие, происходящее через одежду свести к минимальному.

В течение двух недель после опрыскивания саженцев сосны и ели перметрином его содержание в стволе саженцев сосны снизилось и составило 44-54 %, а ели 77%. В хвое саженцев ели содержание перметрина снизилось примерно на 60 % в течение 10 дней и у сосны 9 % за 3 дня. Имеются различия в равномерности опрыскивания. Главным образом это зависит от величины и частоты посадки саженцев. В будущем для получения хороших результатов по опрыскиванию необходимо усовершенствовать технические свойства опрыскивающих устройств.

Ключевые слова: перметрин, большой сосновый долгоносик, питомник, подверженность, остатки