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# Presence of carbaryl in the smoke of treated lodgepole and ponderosa pine bark

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ABSTRACT

Lodgepole and ponderosa pine trees were treated with a 2% carbaryl solution at recreational areas near Fort Collins, CO, in June 2010 as a prophylactic bole spray against the mountain pine beetle. Bark samples from treated and untreated trees were collected one day following application and at 4-month intervals for one year. The residual amount of carbaryl was determined, and bark samples were burned to examine the smoke for the active ingredient. Smoke recovered from spiked bark samples showed a very high correlation between the treated rate and the concentration recovered from the smoke. Residual carbaryl on the bark was relatively stable throughout the study and carbaryl was detected in the smoke throughout the duration of the test.

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## 1. Introduction

Periodic outbreaks of the mountain pine beetle (*Dendroctonus ponderosae*) can cause extensive mortality to preferred hosts, especially lodgepole pine (*Pinus contorta*) and ponderosa pine (*P. ponderosa*) (Leatherman et al., 2007). In the western United States, tourism and safety are affected because killed trees are unsightly and become health hazards in areas frequented by people, as the dead trees decay and fall to the ground. Insecticidal formulations are sometimes applied to high-value trees in order to prevent beetle infestation, consequent death of the tree, and tree-fall that might result in injury to people or damage to property. In the western United States, carbaryl formulations (e.g., Sevin) are preferred for this application. Many aspects of this use of carbaryl were reviewed by Hastings et al. (2001).

Despite insecticide treatment, treated trees are sometimes cut and removed to address hazardous conditions in developed areas. Treatments sometimes fail in areas of very high beetle pressure, because of an improperly applied treatment, or as a result of infestation above the height of the treated bark. The wood of dead trees might be disposed of in an air-curtain burner, in which air is forced into the burning chamber, thereby increasing the temperature and rate of burning as well as reducing the emission of smoke or the trees may be cut and utilized as firewood. A related issue concerns fire fighters and fire safety personnel, who have expressed concern about undertaking wildfire-suppression activities in areas containing insecticide-treated trees.

Previous studies have found that other pesticides, including the herbicides 2,4-D, picloram, hexazinone, dicamba, and dichloroprop (McMahon et al., 1985) and the insecticides chlorpyrifos and lindane (Bush et al., 1987), are present in the smoke of burned, treated wood and vegetation. This study therefore examined residual levels of carbaryl (Sevin SL) on the bark of lodgepole and ponderosa pines and in the smoke of treated pine bark burned in a laboratory furnace.

## 2. Materials and methods

### 2.1. Spike and recovery trials

Untreated bark samples were collected from near the study area (within 0.8–1.5 km) prior to treatment of the trees. All trees were of similar but undetermined age, being in a naturally generated stand. The solution holding capacity of the untreated bark was measured in order to determine approximate expected field residues for the development of the analytical methods. The solution holding capacity was determined by preparing 1 L of Sevin SL according to the label directions (39 ml Sevin SL concentrate and 31 µl Thoroughbred adjuvant in 1 L deionized water), and by applying the solution to pre-weighed bark samples to the point of run off by using an artist's airbrush. Treated bark was reweighed immediately after excess formulation stopped dripping from the samples, and the amount of solution retained by the bark was determined by subtraction of the dry weight from the treated weight.

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Untreated bark was ground in a Wiley mill with a 20 mesh (0.85 mm) screen. Samples (0.5 g) of each bark species were treated with 60 μl of Sevin SL at 100, 50, 10, 1% of the labeled rate (of 2% carbaryl) to constitute 2880, 1440, 288, and 28 $\mu g\,g^{-1}$ by weight of bark, respectively. The 60 μl amount on the 0.5 g sample was based on the results of the solution holding capacity procedure described in the previous paragraph. Water was used for the control. After allowing the solution to distribute throughout the bark sample for several hours, 5 ml of a methanol and water solution (1: 1) was added to the sample. Each sample was shaken and left to settle. The samples were filtered by using Bio-Rad PolyPrep gravity-flow chromatography columns (0.8 × 4 cm) with fritted disks prior to injection on high performance liquid chromatography (HPLC). All analyses were conducted based on Zhong et al. (1995) on a Waters 2695 high performance liquid chromatograph under the following conditions: 5 μl injection volume; column: 25-cm C-18 column at 30 °C; mobile phase: methanol + water 55 + 45 at a flow rate of 1.2 $ml\,min^{-1}$; detection: 217 nm on a Waters 996 photodiode array detector. A six-point standard curve was constructed from 0.1 to 100 ppm, and 0.1 ppm was used as the limit of quantitation, although traces of carbaryl were detectable in the field collected samples below this concentration.

### 2.2. Burning

Ground bark samples (0.5 g) were treated with 60 μl of Sevin SL solution at the concentrations noted above. Bark was burned by using a method modified from McMahon et al. (1985). A Lindberg Blue M tube furnace (Fig. 1) was equipped with a quartz glass burning tube, 100 cm in length and 7.5 cm inside diameter. The entire 0.5-g bark sample was placed in a crucible, which was placed onto a burning stage and the stage was pushed to the middle of the burning tube by using a push rod. The samples were burned at 500 °C and burning continued for five minutes following the start of combustion. The smoke was collected by using a vacuum pump to pull air through a sorbent cartridge (XAD-2, SKC Inc., Eighty Four, PA USA). The carbaryl was extracted by cutting open the cartridges, removing the sorbent and glass wool packing, and extracting in 5 ml of 1:1 methanol: water. A portion (1 ml) of each sample was passed through a gravity feed chromatography column prior to HPLC analysis.

### 2.3. Analysis of field-collected samples

Ponderosa and lodgepole pine trees in or near the Belleaire Lake Campground area of the Roosevelt National Forest in Larimer County, CO, were treated with 2% carbaryl (Sevin SL, Bayer) by a forestry contractor according to label directions. Tree boles were sprayed on all sides to the point of run off to a height of about 12 m (40 feet). The trees were in a naturally generated stand and were of similar but undetermined age. Untreated trees were located from 0.8 to 1.5 km from the treated trees in the same area. Bark was collected for analysis of carbaryl residues by scraping a 7.5 × 7.5 cm sample from within the treated area by using a draw knife. The bark samples were placed in resealable plastic bags and shipped to our laboratory in Mississippi for extraction and analysis. All bark samples were stored at −40 °C and then air dried for >24 h prior to grinding in a Wiley mill with a 20 mesh (0.85 mm) screen. Untreated bark samples were ground first, and the mill cleaned thoroughly with acetone between sampling points. Unused portions of the bark were stored at −40 °C. Carbaryl was extracted from treated bark by placing 0.5 g of ground bark sample into a 20-ml liquid scintillation vial and following the extraction and analysis methods described in section 2.1. Bark samples (0.5 g) were burned in the tube furnace as described in section 2.2.

Residues of carbaryl in the bark and smoke were evaluated for differences due to bark species and time since treatment by subjecting data to a repeated measures analysis of variance (SAS for Windows, v. 8.1., SAS Institute, 2001).

## 3. Results and discussion

### 3.1. Recovery of carbaryl from spiked bark samples

This extraction method provided a linear response between the applied and recovered carbaryl from 28.8 to 2880 $\mu g\,g^{-1}$ ($y = 2.2x - 0.73$, $R^2 = 0.996$, where $x$ = the applied dose and $y$ = the recovered concentration). When treated bark was burned and the smoke collected on the cartridges, the carbaryl recovered followed a linear relationship from 288 to 2880 $\mu g\,g^{-1}$ ($y = 0.04x - 0.69$, $R^2 = 0.965$). Carbaryl was not readily detected in the smoke of bark treated with less than 288 $\mu g\,g^{-1}$. This is likely due to the relatively poor sensitivity of HPLC-UV detection of carbaryl versus other methods of detection, such as LC-MS. Naphthol, a known

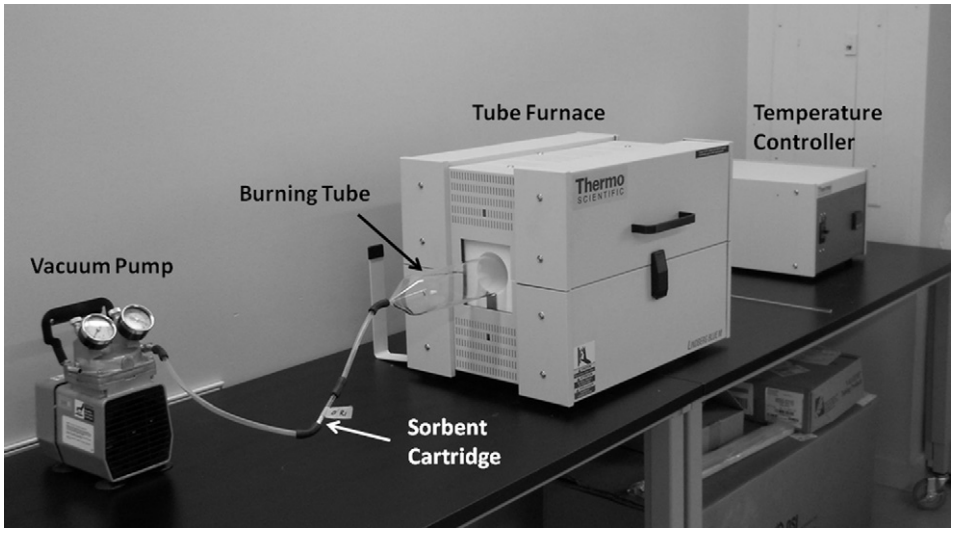


**Fig. 1.** Tube furnace apparatus for collecting smoke.

degradation product of carbaryl, was readily detected in smoke as well as bark samples but was not quantified.

### 3.2. Residue analysis of field-treated bark samples

Considering each species separately, time significantly affected the concentration of carbaryl residue detected (lodgepole pine: $F = 40.32$, df = 3, 39, $p < 0.0001$; ponderosa: $F = 4.68$, df = 3, 41, $p = 0.0067$) (Fig. 2). When the residue data for both species were analyzed together, there was a significant species by time interaction ($F = 20.30$, df = 3, 80, $p < 0.0001$), indicating that the effect of time depended upon which species was considered. There was an initial increase in carbaryl in lodgepole pine bark. About 1308 $\mu g\, g^{-1}$ was detected one day after treatment, and this increased to 2176 $\mu g\, g^{-1}$ after 4 months and then declined to 1866 and then 1465 $\mu g\, g^{-1}$ at 8 and 12 months, respectively. A smaller but similar increase at 4 months was seen on ponderosa pine, with 542 $\mu g\, g^{-1}$ detected initially, increasing to 711 at 4 months and then declining to 637 and 563 $\mu g\, g^{-1}$ at 8 and 12 months, respectively. It has been postulated by the authors that the increase after time = 0 was due to a refinement of the bark sampling technique. The samples were taken to the phloem layer at time = 0 but only to include the exposed bark surface at later times to prevent mortality of the trees, resulting in a dilution effect caused by the larger initial sample. This was due to administrative suggestions related to stand management than to scientific considerations.

The differences in residues between lodgepole and ponderosa are likely due to the morphology of the bark of the respective species. Bark samples were taken to include the entire exposed surface area. The outer bark of lodgepole pine is considerably thinner and less deeply furrowed than ponderosa bark, requiring a shallower sample to be taken. If the applied solution penetrated the two barks similarly, the thicker samples required of ponderosa bark would dilute the active ingredient.

Our residue results are consistent with those published previously using carbaryl. In 1983, the residue of carbaryl on lodgepole pine in Colorado sprayed one year previously was 359 $\mu g\, g^{-1}$, while those sprayed in that year had initial residues of 890 $\mu g\, g^{-1}$, which declined to 531 $\mu g\, g^{-1}$ 16 months later (Page et al., 1985). Page et al. (1989) observed carbaryl at 241–1418 $\mu g\, g^{-1}$ on ponderosa pine bark at initial treatment, but the longevity was not examined. Zhong et al. (1995) found rapid dissipation (within 60 days) of carbaryl on the bark of white spruce at high temperature and humidity, but carbaryl was more stable at lower humidity over the tested range of temperatures. Dissipation on loblolly pine disks was not significant in 60 days (Zhong et al., 1995). The bark samples in the cited study were treated in the laboratory, and the experiment was conducted in a dark incubator. However, it seems that exposure to precipitation and sunlight did not significantly increase carbaryl dissipation, as the levels detected in our study remained constant or dissipated only slowly. In northern California, Haverty et al. (1985) estimated that the labeled rate of carbaryl provided protection from western pine beetles (*Dendroctonus brevicomis*) for only one flight season, but other studies determined it remained effective for two seasons in the mountain West (Haverty et al., 1998; Fettig et al., 2006a,b). In the Southwest, treatment with carbaryl was effective at preventing attack by engraver beetles for at least 13 months (DeGomez et al., 2006). In Georgia, carbaryl residues dissipated from 3200 to 4100 $\mu g\, g^{-1}$ to below detection within 8 months (Hastings and Coster, 1981). The longer residual time in Colorado in our study might be the result of several factors, including lower precipitation and colder winter temperatures, both of which slow microbial activity and therefore microbial degradation of the compound.

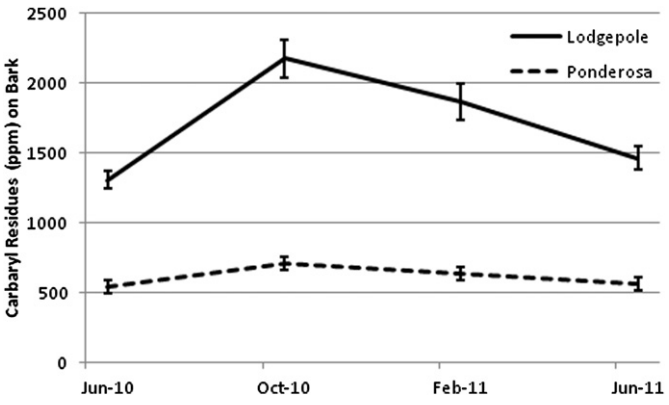


**Fig. 2.** Carbaryl recovered from treated bark.

### 3.3. Smoke analysis

Species and time (main effects) significantly affected the amount of carbaryl recovered in the smoke produced from treated bark (species: $F = 36.54$, df = 1, 12, $p < 0.0001$; time: $F = 15.16$, df = 3, 76, $p < 0.0001$), but the species by time interaction did not ($F = 2.43$, df = 3, 76, $p = 0.0717$) (Fig. 3). When species were subjected independently to the ANOVA model, time had a significant effect on the recovery of carbaryl in the smoke of both lodgepole ($F = 6.66$, df = 3, 36, $p = 0.0011$) and ponderosa ($F = 19.26$, df = 3, 40, $p < 0.0001$) pine barks. The reduction in the amounts recovered from smoke over time roughly followed that determined in the respective bark residues. This is as expected since we found such a high correlation (see Section 3.1) between the amount of carbaryl present on the bark and that recovered from the sorbent cartridges.

Bush et al. (2000) noted, in a review based largely on McMahon et al. (1985), that more pesticide was recovered in smoke below 500 °C, and that little to none was recovered at 600 °C. Since fireplaces and air curtain burners operate at temperatures exceeding 500 °C, it is possible that less of the insecticide would have been recovered using these incineration methods. The boiling point of carbaryl is 315 °C. Therefore, it was initially thought that volatilization of the compound prior to combustion (and therefore decomposition) was responsible for the amounts recovered and that burning at a higher temperature might not have any effect. However, the boiling points of chlorpyrifos and lindane are 160 and 323 °C, respectively, and the increased temperature did result in loss of the compound from the smoke. Therefore, it is likely that carbaryl would be absent from the smoke of hotter fires as well.

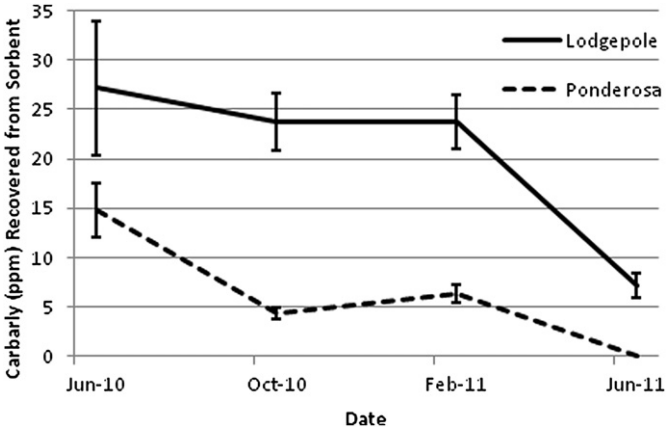


**Fig. 3.** Carbaryl recovered from the cartridge sorbent following burning of treated bark samples.

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## References

Bush, P.B., Neary, D.G., McMahon, C.K., 2000. Fire and pesticides: a review of air quality considerations. In: Moser, W.K., Moser, C.F. (Eds.), Fire and Forest Ecology: Innovative Silviculture and Vegetation Management. Tall Timbers Ecology Conference Proceedings, No. 21. Tall Timbers Research Station, Tallahassee, FL, pp. 132–136.

Bush, P.B., Taylor, J.W., McMahon, C.K., Neary, D.G., 1987. Residues of lindane and chlorpyrifos in firewood and wood smoke. Journal of Entomological Science 22, 131–139.

DeGomez, T.E., Hayes, C.J., Anhold, J.A., McMillin, J.D., Clancy, K.M., Bosu, P.P., 2006. Evaluation of insecticides for protecting southwestern ponderosa pines from attach by engraver beetles (Coleoptera: Curculionidae: Scolytinae). Journal of Economic Entomology 99, 393–400.

Fettig, C.J., Allen, K.K., Borys, R.R., Christopherson, J., Dabney, C.P., Eager, T.J., Gibson, K.E., Herbertson, E.G., Long, D.F., Munson, A.S., Shea, P.J., Smith, S.L., Haverty, M.I., 2006a. Effectiveness of bifenthrin (Onyx) and carbaryl (Sevin SL) for protecting individual, high-value conifers from bark beetle attack (Coleoptera: Curculionidae: Solytinae) in the western United States. Journal of Economic Entomology 99, 1691–1698.

Fettig, C.J., DeGomez, T.E., Gibson, K.E., Dabney, C.P., Borys, R.R., 2006b. Effectiveness of Permethrin Plus-C (Masterline®) and carbaryl (Sevin SL®) for protecting individual, high-value pines (Pinus) from bark beetle attack. Arboroculture and Urban Forestry 32, 247–252.

Hastings, F.L., Coster, J.E., 1981. Field and Laboratory Evaluations of Insecticides for Southern Pine Beetle Control. General Technical Report SE-21. United States Department of Agriculture, Forest Service, Southeastern Forest Experiment Station, Asheville, NC, 39 pp.

Hastings, F.L., Holsten, E.H., Shea, P.J., Werner, R.A., 2001. Carbaryl: a review of its use against bark beetles in coniferous forests of North America. Environmental Entomology 30, 803–810.

Haverty, M.I., Shea, P.J., Hall, R.W., 1985. Effective residual life of carbaryl for protecting ponderosa pine from attack by the western pine beetle (Coleoptera: Scolytidae). Journal of Economic Entomology 78, 197–199.

Haverty, M.I., Shea, P.J., Hoffman, J.T., Wenz, J.M., Gibson, K.E., 1998. Effectiveness of Esfenvalerate, Cyfluthrin, and Carbaryl in Protecting Individual Lodgepole Pines and Ponderosa Pines from Attack by *Dendroctonus* Spp. Research Paper PSW-RP-237. Pacific Southwest Research Station, Forest Service, U.S. Department of Agriculture, Albany, CA, 12 pp.

Leatherman, D.A., Aguayo, I., Mehall, T.M., 2007. Mountain Pine Beetle. Fact Sheet No. 5.528. Colorado State University Extension, Fort Collins, CO, 4 pp.

McMahon, C.K., Clements, H.B., Bush, P.B., Neary, D.G., Taylor, J.W., 1985. Pesticides Released from Burning Treated Wood. In: Proceedings: Eighth Conference on Fire and Forest Meteorology, April 19 to May 2, 1985. Society of American Foresters, Bethesda, MD, pp. 145–152.

Page, M., Haverty, M.I., Richmond, C.E., 1985. Residual Activity of Carbaryl Protected Lodgepole Pine against Mountain Pine Beetle, Dillon, Colorado, 1982 and 1983. Research Note PSW-375. Pacific Southwest Forest and Experiment Station, Forest Service, U.S. Department of Agriculture, Berkely, CA, 4 pp.

Page, M., Haverty, M.I., Richmond, C.E., 1989. Insecticide residues on pine bark: influence of trees, sample volume and size on variability. Journal of Entomological Science 24, 180–185.

Zhong, H., Hastings, F.L., Hain, F.P., Monahan, J.F., 1995. Carbaryl degradation on tree bark as influenced by temperature and humidity. Journal of Economic Entomology 88, 558–563.