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Residues from Organic Arsenical Herbicides in Chemically Thinned Forests

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ABSTRACT

Conifers in four Pacific Northwest locations and forest types were stem-injected with the organic arsenicals cacodylic acid and monosodium methanearsonate (MSMA), herbicides used for forest thinning and insect control. Concentrations and locations of As residues in tree stems, twigs, foliage, and in litter and soil were determined. Within each forest type, spring treatment led to somewhat higher concentrations in crowns than did fall application; differences were larger with cacodylic acid than with MSMA. Most residue concentrations were in the range of 20 to 60 mg As/kg (dry-weight basis). Trees killed 5 yr earlier showed As concentrations of 122 to 670 mg/kg in the phloem just above the injection sites, 10.9 to 25.0 mg/kg in the xylem, and 34.7 to 77.8 mg/kg in upper lateral twigs and terminal leader shoots. Residues in litter were lowest (5–9 mg/kg) in Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] stands and highest (27–46 mg/kg) in lodgepole pine (*Pinus contorta* Engelm.) stands. Surface soil concentrations below the litter traps increased 0 to 3.7 mg As/kg over native soil concentrations of 1 to 7 mg/kg. Most observations were within the range of naturally occurring As in these sites. Persons using fuel from treated stands probably would not receive measurable exposure to toxic forms of As. Residues in fuelwood would be minimized if wood at the point of injection and bark on the lower stem were excluded from the fuel. Bark removal is made easy by injecting arsenicals in the fall.

Additional Index Words: **soils, fuel quality, human exposure, forest thinning, defoliation, translocation.**

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Two organic arsenical herbicides monosodium methanearsonate (MSMA) and cacodylic acid (dimethylarsinic acid), have been effective in thinning forest stands in the Pacific Northwest, Northeast, and South (Newton, 1970; Bovey, 1976; Newton and Smith, 1976; McCavish and Smith, 1978). Unwanted trees are killed by direct injection of these chemicals to make room for crop trees. The same compounds have been useful in controlling forest insects in western forests in a variety of circumstances where control is not readily achievable by other means (Buffam, 1971; Newton and Holt, 1971). Thus, their potential use in forests is extensive.

The degree to which herbicide residues are present and biologically active determines their environmental significance. Although the direct responses to the injected chemicals are well documented, less is known about the movement of residual chemicals after injection, the presence of residues in wood that may be utilized by humans (e.g., for fuel), or the deposition of residues in soil and, potentially, in groundwater.

Previous studies have shown varying levels of As residues in foliage of treated pine (*Pinus* spp.) and Engelmann spruce (*Picea engelmannii* Parry ex Engelm.) (Greaves, 1974; Lister et al., 1976; Frye et al., 1977). Studies on As distributions in fresh litter below treated Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] and tulip-poplar (*Liriodendron tulipifera* L.) have shown a wide range of values (Holt, 1967; Macklin and Witkamp, 1973).

Reported levels of As in soil also vary. Norris et al. (1983) found that As levels in soil and in herbs near treated trees generally were slightly higher after treatment with arsenicals; As levels in litter from treated trees also were higher than in litter from controls. This finding indicates a possible transfer of As from litter to soil. However, Macklin and Witkamp (1973) found As levels in soils near tulip-poplar treated with cacodylic acid to be no higher than in soil near controls. The variation in reported levels of introduced and naturally occurring As residues complicates their interpretation. The importance of As in soil is related to mobility and transfer to water or its uptake by roots.

This paper examines As residues from MSMA and cacodylic acid in treated forest ecosystems. Levels of As residue in foliage, twigs, litter, and soil were determined in stands in four forest types after treatment with these arsenicals. Transfer of residues from treated trees to soil also was followed. The forest types studied are typical of western coniferous forests where these chemicals would reach maximum intensity of use.

METHODS

Site and Treatment

The study ws conducted in stands of four distinct forest types.

1. Lodgepole pine (*Pinus contorta* Engelm.), age 65 yr, Frater Lake, Stevens, County, Washington; about 600-mm annual precipitation.
2. Mixed conifer, age 50 yr, Twelve Mile Creek, Stevens County, Washington; about 600-mm annual precipitation.
3. Ponderosa pine (*Pinus ponderosa* Dougl. ex Laws.), age 65 yr, Pringle Falls, Deschutes County, Oregon; about 500-mm annual precipitation.
4. Douglas-fir, age 30 yr, Mt. June, Linn County, Oregon; about 1800-mm annual precipitation.

Ten plots (two replicates of the following five treatments) were established in each forest type; cacodylic acid applied in the fall and spring, MSMA applied in the fall and spring, and untreated control plots. Fall treatments were in early December; spring treatments were in late April for the lodgepole pine and mixed-conifer stands, and in early June for the ponderosa pine and Douglas-fir stands. Trees in the ponderosa pine and Douglas-fir stands were treated with 1.0-mL chemical/5-cm stem diameter at breast height (dbh, 135-cm aboveground), applied with a tree injector. Trees in the lodgepole pine and mixed-conifer stands received 1.0-mL chemical/2.5-cm dbh applied with a "hack and squirt" technique: a small cut was made through the bark, and approximately 1 mL of solution was applied in the cut with a squeeze bottle. Cacodylic acid was applied in a solution containing 367 g As/L; MSMA was applied in a solution with 373 g As/L. The amounts of elemental As applied to each forest type, determined from the actual preparation used in the field, are shown in Table 1.

Sample Collection and Analysis

Samples of trees, litter, and soil were collected in June and July and again in September and October. One tree from each plot was sampled in June/July and another in September/October. For each tree sample, a 28-cm section was taken from the trunk just above

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Table 1. Amounts of elemental As applied at each stand, based on actual preparations used.

Chemical and time of treatment	Stand: Lodgepole pine†	Mixed-conifer†	Ponderosa pine‡	Douglas-fir‡	Mean
	As, kg/ha				
Cacodylic acid, fall	1.42	0.94	0.97	1.36	1.18
Cacodylic acid, spring	1.03	0.94	0.97	1.48	1.11
MSMA, fall	1.51	0.65	0.87	0.93	0.99
MSMA, spring	1.43	1.03	0.84	0.60	0.97
Mean	1.36	0.90	0.91	1.10	

† Trees received 1 mL chemical/2.5-cm stem diam.
‡ Trees received 1 mL chemical/5.0-cm stem diam.

the injection point, and twigs and foliage were collected from the crown. Each of the species studied forms a nodal group of branches at the base of each year's annual height growth. These "whorls" of branches are dependable indicators of branch age. Branch-whorl 1 was designated the tip of the crown and whorl 12 the base, below which there are few live branches. The foliage and twigs from branch-whorls 1, 4, 6, 9, and 12 were sampled as follows:

1. Whorl 1, which contained only growth from the current year, was used in its entirety as a single sample.
2. In samples from whorl 4, which contained 4 yr of growth along the branches, foliage and twigs from each year's growth were combined.
3. All samples from whorls 6 and 9 were combined.
4. In samples from whorl 12, all ages within the branches (12-yr-growth) were combined, but foliage and twigs were separated.

Litter was collected from two 0.21-m^2 litter traps randomly placed in each plot. Fifty soil plugs, 1.9 cm in diameter and 15.0-cm deep, were randomly selected from each plot and combined for analysis. Organic debris was removed before inserting the soil tool. Soil plugs were occasionally shallower, when rocks hampered penetration, and occasionally deeper, when the presence of animal burrows required penetration of up to 20 cm to obtain a 15-cm plug. Treatment replicates were combined for As analysis, so that each treatment on each site was represented by one analysis of a sample consisting of a 100-plug composite.

The general analytical procedure was adapted from Manning and Fernandez (1970). Samples were prepared for analysis with a wet-ash digestion, as follows. Each sample was ground through a 0.5-mm (50-mesh) screen and mixed thoroughly. A 1.0-g sample was placed in a 100-mL Kjeldahl flask and 6-mL concentrated HNO_3 was added. Samples were heated until foaming ceased and concentrated to 1.0 mL; 3-mL concentrated HNO_3 was added and the samples were again concentrated to 1.0 mL. Three milliliters of HNO_3 were added again and the samples were concentrated to near dryness (about 0.25 mL). Thirty milliliters of deionized water were added to the cooled samples. Triplicate samples from trees and litter were analyzed for As with a Perkin-Elmer model 70A graphite tube furnace on a Perkin-Elmer model 303 atomic absorption spectrophotometer. Quantitative determinations were reliable at the 1.0 mg/kg level. Analysis of soil samples with this technique proved ineffective; therefore, these samples were sent to the Washington State Div. of Health, Wenatchee, for analysis by colorimetric techniques.

Fifth-year Sampling of Single Larch and Lodgepole Pine

In a related experiment, lodgepole pine and a larch (*Larix occidentalis* Mill.) near the lodgepole pine stand were sampled in early spring. Both were 7.6 cm in diameter and had been killed with two injections of cacodylic acid 5 yr earlier. Both were completely defoliated, thus no foliage samples could be taken. Upper branches and xylem and phloem of the trunks were sampled as in the fresh trees; the trunk sample was divided into phloem, the outer 0.30 cm of xylem, and the remaining xylem. After the samples were dried and ground through a 1.25-mm (20-mesh) screen, they were analyzed for As by neutron activation at the Oregon State Univ. Radiation Center, using a TRIGA IV reactor and gamma ray spectrometer.

Table 2. Mean defoliation index values by stand, treatment, and time of sampling.

Parameter	Defoliation index†
Stand type	
Lodgepole pine	3.8a‡
Mixed-conifer	4.1a
Ponderosa pine	3.6a
Douglas-fir	3.6a
Treatment (season)	
Cacodylic acid (fall)	4.1a
Cacodylic acid (spring)	3.8a
MSMA (fall)	3.7a
MSMA (spring)	3.6a
Sampling time	
Summer	3.4a
Fall	4.1b

† Index is based on a 5-point scale, in which 1 = a healthy tree and 5 = a completely defoliated tree, considered dead.
‡ Within the same parameter type, defoliation values followed by the same letters are not statistically different at the $P \leq 0.05$ level of probability; those followed by different letters are statistically different at $P \leq 0.05$ according to Tukey's HSD test.

RESULTS

Defoliation

The effectiveness of cacodylic acid and MSMA for thinning is summarized in Table 2. Analysis of variance showed that defoliation levels increased with time between treatment and observation, but neither chemical nor seasonal effects differed significantly at $P \leq 0.05$. There were no differences within treatments among forest types. No mortality from transfer of chemicals between trees (through grafted roots) was observed in untreated trees.

Foliage and Twigs

An estimate of As distribution within trees was first obtained from the raw tissue data. From these estimates, statistical differences among the treatments were determined, e.g., spring vs. fall application and MSMA vs. cacodylic acid injection. First, the model form

$$Y = B_0 + B_1X_1 + B_2X_1^2 + B_3X_2$$

was used, where Y is As concentration in tissue (mg/kg), X_1 is whorl position, and X_2 is proportion of foliage in the foliage-plus-twig tissue sample. The effect of tree size was corrected with covariance, adjusting each observation to an average tree size. The quadratic whorl equation provides the best fit of a number of models tested, and gives an unbiased weighted average concentration when evaluated for the sixth-branch whorl. The predicted As concentration for whorl 6, in an intermediate crown position, was then expanded to the tree population to estimate As concentration on the plot.

Average As concentrations in the foliage and twigs from lodgepole pine, ponderosa pine, and mixed-conifer stands were nearly equal, but concentrations in Douglas-fir stands were significantly lower according to Tukey's

Table 3. Mean As concentrations in whorl 6 foliage and twigs, from weighted mean trees with average defoliation, by chemical and season of application.

Treatment	Time of application		
	Fall	Spring	Combined
	As, mg/kg†		
Cacodylic acid	38	54	46a
MSMA	40	52	46a
Combined	39a	53b	

† Average As concentrations followed by the same letters are not statistically different at $P \leq 0.05$ by Tukey's HSD test.

HSD test. (Numbers followed by the same letter were not significantly different at $P \leq 0.01$).

Stand	Smoothed As concentrations, mg/kg
Lodgepole pine	52a
Mixed-conifer	50a
Ponderosa pine	52a
Douglas-fir	29b

Arsenic concentrations in whorl 6, as calculated by this model, were compared by treatment, time of application, and chemical (Table 3). Trees treated with cacodylic acid in the spring had a mean As concentration 16 mg/kg higher than that of trees treated in the fall. Although this was the only significant difference among individual treatments ($P \leq 0.05$), the As concentration in trees treated with MSMA in spring was greater by 12 mg/kg than that in trees treated with MSMA in fall. The cacodylic acid treatments resulted in the highest mean concentration, 54 mg/kg for spring treatment, and the lowest mean concentration, 38 mg/kg for fall treatment. These values, however, do not differ significantly from the corresponding mean MSMA treatment values and merely show a trend. When data from all forest types were combined, As concentrations in crowns after spring treatment were 14 mg/kg higher than those after fall treatment, a highly significant difference ($P \leq 0.01$). Differences in mean concentration response to cacodylic acid and MSMA treatment were generally nonsignificant.

The mean concentration of all standardized observations from trees sampled in the spring did not differ perceptibly from trees sampled the following fall; both values were 46 mg As/kg.

A pronounced difference between upper and lower crown concentrations of As was observed in foliage and twigs from trees injected with either chemical during the spring and fall. The quadratic term was significant in regression ($P \leq 0.05$), indicating that the gradients were most pronounced in the lower crowns, reaching the upper asymptotes in small branches and foliage. In general, highest concentrations were in the tops, but there were appreciable differences in vertical gradients (Fig. 1). When injected in the spring, MSMA had the steepest gradient; conversely, MSMA injected in the fall had a very weak gradient. The order is reversed for cacodylic acid, with a steep gradient for the fall injection. Gradients differ more between fall and spring for MSMA than for cacodylic acid. The quadratic effect, although weak, is consistent among treatments and improves our ability to integrate the total crown residue level.

Arsenic concentrations in foliage and twigs after spring applications were from 40 to 60 mg/kg; concentrations

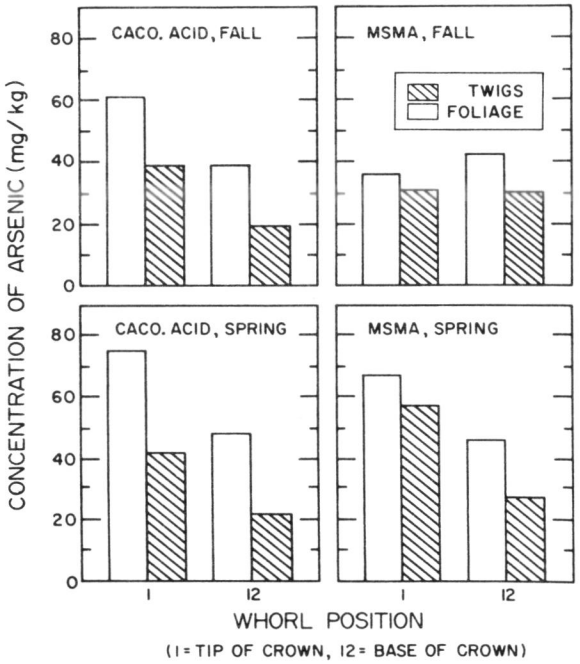

Fig. 1. Vertical distributions of As in the crown, by treatment, for spring and fall samplings combined. Values based on standardized observations corrected for proportion of foliage and diameter variation among trees.

after fall applications were from 30 to 40 mg/kg. Integration of the equations in Fig. 1 confirmed that trees treated in the spring had about 40% more As in the crowns than those treated in the fall ($P \leq 0.05$). This finding indicates by difference that spring treatments should deposit less As in stems and roots than fall treatments.

Without exception, As concentrations were highest in the youngest foliage and twigs and decreased in older tissue (Fig. 1). Trees injected in spring had higher concentrations in foliage and twigs and produced steeper gradients than those injected in the fall. This corresponds to the season of most rapid sap flow upward and least flow downward. Trees treated with MSMA had a much steeper vertical gradient in crowns for spring than for fall injections, but spring and fall treatments with cacodylic acid showed similar horizontal gradients. In mixed conifers and lodgepole pine, As concentration gradients along the branches within whorls appeared steeper along the horizontal (Fig. 2) than along the vertical axis (Fig. 1 and 2). Vertical and horizontal gradients did not differ in Douglas-fir and ponderosa pine.

The gradients of As in foliage and twigs measured from whorls 1 through 4 for each forest type are shown in Fig. 2. The gradient for the mixed-conifer stand was clearly the steepest, while the other three were nearly identical. All gradients were consistent in form. The lodgepole pine and the mixed-conifer stands had substantially higher concentrations than either the Douglas-fir or ponderosa pine stands, reflecting the difference in initial dosage almost proportionally.

Figure 3 shows the partitioning of As between foliage and twigs at the top and the base of the crown. In all cases, the foliage exhibited higher concentrations than the twigs. However, trees injected in the fall with MSMA had nearly equal concentrations in twigs and foliage, while

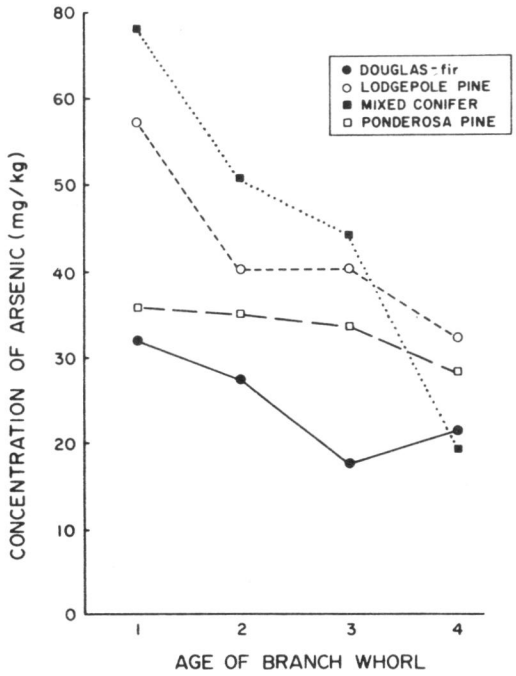

Fig. 2. Arsenic concentrations in branch whorls 1 through 4 for each forest type. Each line is mean of all treatments. Error bar indicates ±1 standard error.

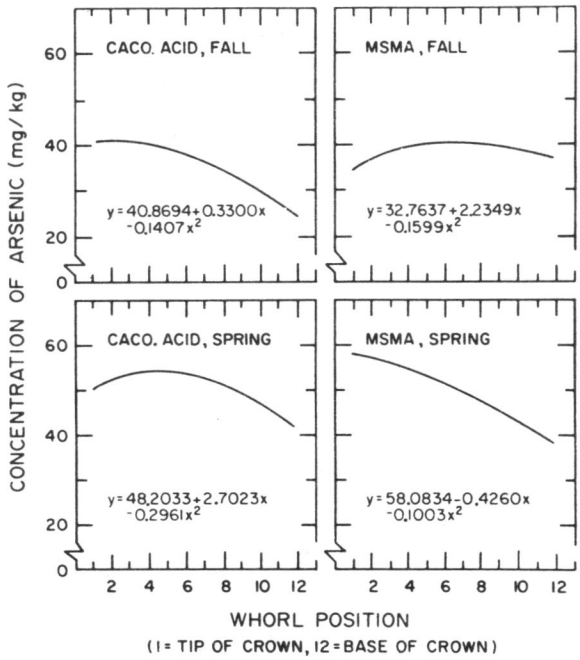

Fig. 3. Concentration of As in foliage and twigs at top and base of crown, by treatment. Error bars indicate ±1 standard error.

trees injected in the spring with cacodylic acid had twice as much arsenic in the foliage as in the wood. Other observations from Fig. 3 also support results already discussed: concentrations were higher in the top of the tree, and trees treated with MSMA showed greater difference in As concentrations between spring and fall injections.

Arsenic concentrations were low inside the bark (woody xylem material) in stems of freshly sampled trees. Over 80% of the values were between 0 and 3 mg/kg. No significant differences among sites or treatments could be determined.

Fifth-year Larch and Lodgepole Pine

In the fresh samples, only total and xylem As content were determined; phloem was not sampled. However, samples from trees that had been treated 5 yr earlier illustrate in a general way the distribution of the arsenicals between xylem and phloem. Because these samples were not replicated, they serve only as an example of distribution among tissues in the parts of the trees having the highest concentrations. Unfortunately, the amount of cacodylic acid injected in the two trees is not known, and the old-tree samples inadvertently were collected near the injection wounds.

With two exceptions, As concentrations near the point of injection in the single larch and lodgepole pine were similar to those found in fresh tissue (Table 4). As would be expected, relatively high concentrations were found in the phloem near the injections, with 670 mg/kg in larch and 123 mg/kg in lodgepole pine. Complete trunk sections displayed concentrations from 16.5 to 46.4 mg/kg, reflecting the low concentrations in xylem and the small proportion of phloem tissue in a cross-section. The amounts in the trunk were considerably higher than the 0 to 3 mg/kg found in the trunk of trees treated in the present study. However, the concentrations in the old trunks were about equal to those of the branches, while freshly treated trees in this study showed bole-to-branch ratios of As residue concentrations to be about 0.05. The proximity of the sampling site to the point of injection probably accounts for the difference and may also explain the location of much of the As not found in the crowns. The above values may be compared with the natural background concentrations of 1 to 5 mg/kg (depending on site) found in whorls 1 through 12 of living tree crowns.

Litter

Arsenic in litter (including fresh fall of foliage from treated trees) from the lodgepole pine and mixed-conifer stands was twice that in litter from the ponderosa pine and Douglas-fir stands (Table 5). This again reflects that

Table 4. Concentration of As in trees treated 5 yr before present study.

Tree species	Sample description	Concentration of As, mg/kg
Larch	Complete trunk section	46.4
	Phloem	670.0
	Outer xylem	24.9
	Inner xylem	18.8
	Terminal shoot	77.8
	Upper lateral twigs†	35.2
Lodgepole pine (lower trunk)	Trunk section	16.5
	Phloem	122.0
	Outer xylem	18.3
	Inner xylem	10.9
Lodgepole pine (upper trunk)	Trunk section	27.6
	Phloem	124.3
	Outer xylem	25.0
	Inner xylem	24.0
	Terminal shoot	34.7
	Upper lateral twigs†	35.8

† Upper lateral twigs are current year's growth of uppermost side branches.

Table 5. Means of As concentrations in the litter by stand and by treatment (mean of both sampling times).

Chemical and time of treatment	Stand: Lodgepole pine	Mixed-conifer	Ponderosa pine	Douglas-fir	Mean
	As, mg/kg				
Cacodylic acid, fall	30	23	26	8	22a†
Cacodylic acid, spring	53	40	19	18	33a
MSMA, fall	48	25	25	7	26a
MSMA, spring	52	57	22	22	38a
Mean	47a	37a	24b	15b	30

† Treatment or standmeans followed by different letters are significantly different at the $P \leq 0.01$ level, by Tukey's HSD test.

Douglas-fir and ponderosa pine were injected with about one-half as much arsenical per tree of a given size as were the lodgepole pine and mixed-conifer.

Litter from ponderosa pine injected in the fall had As concentrations of 23mg/kg; litter after spring injections had concentrations of only 8 to 9 mg/kg. This large difference is not apparent in litter from the other three stands. Litter collected in June/July had a mean concentration of 15 mg/kg; that collected in September/October had a mean concentration of 30 mg/kg. Differences between species (sites) was highly significant ($P \leq 0.01$) but choice of treatment did not appear to affect litter ($P > 0.05$).

Soil

In general, differences in As concentrations between treated and untreated soils were low and invariant among treatments and sites (Table 6). The apparently greater concentrations in treated plots reasonably reflect the introduction of As-based materials into the ecosystem 1 yr earlier. The interaction between microsite and treatment precludes statistical analysis in the absence of background samples from each treated plot. The values shown primarily indicate the trend in residue increases. Each kilogram of As introduced per hectare apparently leads to a temporary increase of about 1.0 mg/kg soil above background levels of 1 to 7 mg/kg in soil in control plots, but persistence of the residue and reliability of the sample could not be determined.

DISCUSSION

Arsenic levels in treated forests are determined by additions to and losses from background levels. Location of a chemical after injection depends largely on its initial distribution in the tree and the movement of injected substances into rapidly cycled foliage and twigs. Residual As in the ecosystem can be minimized by determining and using the lowest effective dose of arsenical herbicide. These data show that the lower injection level of 1.0 mL/5-cm stem diam is sufficient to remove trees from the canopy layer. Newton and Smith (1976) reported that effective and consistent killing of trees in a range of sizes required dosages following the 3/2 power of the diameter. Our dosing scheme was on a linear scale adequate to kill the larger trees and, therefore, overdosed small trees. Equipment capable of applying fractional doses would be helpful in this regard.

Table 6. Soil As concentrations in surface 15 cm of soil (dry-weight basis).

Chemical and time of treatment	Stand: Lodgepole pine	Mixed-conifer	Ponderosa pine	Doublas-fir	Mean
	As, mg/kg				
Cacodylic acid, fall	8.2	2.6	2.5	12.6	6.5
Cacodylic acid, spring	3.0	2.9	1.4	3.8	2.8
MSMA, fall	2.3	4.2	3.2	9.0	4.7
MSMA, spring	2.2	4.4	2.7	7.0	4.1
Control	1.0	2.0	1.0	7.0	2.8
Mean	3.3	3.2	2.2	7.9	4.2

Trees injected in the spring had about 40% more As in the foliage and branches than those injected in the fall, presumably reflecting the upward flush of sap in xylem. Of the two chemicals, cacodylic acid is more likely to end up in the foliage, and MSMA in bark and stems. As a result, the short-term potential for As concentrations to reach the forest floor after chemically induced defoliation is highest when cacodylic acid is injected in the spring. Residues remaining in the trunk are least after spring treatment, and these residues are concentrated in bark and the outer few millimeters of xylem. These data indicate that season of injection is not critical to the chemicals' effectiveness, so their use could be scheduled to minimize certin types of residues in sensitive areas, e.g., firewood cutting lots.

Initial concentrations of As in the litter on the forest floor depend on initial concentrations in the foliage, proximity of litter to treated trees, and litter dilution from untreated trees and preexisting litter. Norris et al. (1983) found higher concentrations of As in litter at distances of one-half times the crown radius of treated trees than at distances of two and four times the crown radius. This distance factor is not expected to be important in stands dense enough to require thinning, where crowns of treated trees normally overlap. Because leaf area is related to basal area of stems in young stands (Grier and Waring, 1974; Cole, 1984), the proportion of stand basal area treated should give a reliable indication of expected dilution and, hence, of net concentration.

Most of the foliage on treated trees in this study was deposited in the litter within the 1st yr after injection. Litterfall was estimated at 5620 kg/ha from both treated and untreated trees. Assuming 10^4 kg/ha of foliage for a 30-yr-old Douglas-fir stand (Webb et al., 1983), with approximately 25% of annual litterfall from untreated trees (Silver, 1962), then a one-time-only excess of 4370 kg ha was deposited by the approximately 1260 thinned trees per hectare. The foliage was weighted according to Silver's (1962) age-class distribution, and the As concentration in the foliage was similarly weighted by needle-age class and amount of As in the foliage relative to that in wood. The average weighted As concentration in foliage of injected trees was estimated at 41.4 mg/kg. About one-fifth of the crown volume of the stand was in untreated trees. Since foliage from untreated trees dilutes the treated litter, the average As concentration in litter should be approximately 32 mg/kg. This estimate agrees well with the 30 mg/kg for litter collected in the fall from all stands (Table 5). The Douglas-fir and

ponderosa pine sites received lower dosages and had stands of greater tree size and a lower proportion of treated crowns than the others. The resulting lower As concentrations in the litter were highly significant ($P \leq 0.01$). The total As in the "average" litter for all stands was 0.18 kg/ha, approximately 16% of the average amount injected (from Table 1).

Total As in the branches of Douglas-fir can be estimated as follows. If 1.4% of the total tree biomass is fine branches (Smith, 1971), the average As concentration is 40 mg/kg (Fig. 3), and the stand biomass is 170×10^3 kg/ha (Webb et al., 1983), then the total As in fine branches is 0.10 kg/ha. A similar computation, for medium branches that are 1.2% of total tree biomass and 25 mg/kg As concentration (Fig. 3), yields an estimate of 0.05 kg/ha. Total As in the fine and medium branches is 0.15 kg/ha, or about 14% of that initially injected (Table 1). Total As estimated in the crown (foliage and small branches) is 0.3 kg/ha, or about 34% of the total amount injected. Although these are estimates, >50% of the elemental As injected is apparently retained in large branches, trunks, and roots of the treated trees. Unfortunately, the data do not permit an estimate of disappearance rate in trunks, because of the differences in treatment of the older trees. Due to their large size and phenolic contents, all of these larger components decompose more slowly than foliage and small branches; hence, they tend to prolong the period of As-enriched litter. By extending the period of deposition, rate of deposition is reduced. From the work of Woolson (1977), it is probable that alkylation and volatilization as arsines occur while these residues remain in an organic matrix, as long as moisture is sufficient for microbial activity. Although the rate at which such degradation may proceed has not been measured, rates are obviously slow.

The highest As concentrations were found in the phloem, or inner bark. This is the site of activity for many insects, of which scolytid (*Coleoptera: Scolytidae*) and burprestid (*Coleoptera: Buprestidae*) beetles are especially abundant. These insects typically feed on inner bark of stressed, dying, or dead trees. If trees are stressed from climatic or other causes, bettles may become epidemic, to the detriment of healthy trees. These insects cannot breed successfully in trees treated with organic arsenicals (Newton and Holt, 1971; Newton, unpublished data), although they do succeed in trees treated with other herbicides (Newton, unpublished data). These findings indicate that insect reproductive failure results directly from the arsenical, rather than indirectly from tree death. Some buprestids may be found in treated trees; presumably, the live larvae contain nonlethal levels of As. There was no evidence that birds were feeding on these larvae. This is the only food-chain link in which we might expect warm-blooded animals to be exposed significantly to active residues.

The large volume of soil and the variability of native As concentrations limit our ability to generalize about As transfer to the soil from the litter. Norris et al. (1983) reported an increase in As concentration in browse vegetation and soil after tree injections, but differences between pre- and posttreatment levels were small and restricted to the area immediately below a treated crown. Arsenic reportedly often occurs in agricultural soils repeatedly treated with organic arsenicals. Woolson and Kearney (1973) reported that As levels in soil after treatment with cacodylic acid declined with time. In a later paper, Woolson (1977) reported that volatile arsine compounds were produced from soils under both aerobic and anaerobic conditions, providing evidence for the cycling of As from soil to air.

Arsenic applied as an organic arsenical herbicide adds a small amount of naturally occurring forms of As to the forest ecosystem. Foliage is quickly dumped as litter; twigs become litter during the next several years; and trunk residues, amounting to perhaps half or more of the total, may require more than a decade to reach the soil. Metabolism of the arsenicals to volatile arsines will probably cause some losses (Woolson, 1977). The remainder probably will oxidize to pentoxide, in which form it will be indistinguishable from the background, but this study did not distinguish among forms. There will be a real, but probably unmeasurable, increase in total As, largely as As_2O_5, on the site until oxidation, reduction, volatilization, and precipitation bring the levels to their pretreatment equilibrium. It cannot be estimated from the data in this study how long this will take, but it is reasonably certain that nearly all the introduced residues will be in a form that will probably not influence ecosystem function.

Treatments of this type were observed to weaken the cambial cells. As the trees died, the bark loosened; peeling the bark became easy within 24 to 32 weeks after treatment. This phenomenon was most pronounced after treatment with MSMA, and when herbicides were applied in the fall. Thus, treatment can be managed so as to permit removal of most of the residue from usable parts of the tree.

The results of this study have practical implications for at least two aspects of the human environment, other than efficient forest management. First, fuel wood from treated stands is almost certainly safe to burn, especially if the wood is collected from dead trees from which the bark is fallen, and the injection treatment zone is not used. Bark drops off fall-treated logs readily after a season of drying. The low levels of residues in the fuel may include a minor component of volatile arsines, which would either oxidize in the fire or escape with the smoke to oxidize in the open air. The insoluble, nonvolatile oxides would remain in the ash. Dermal contact should be negligible and physiological exposure not measurable. Second, large amounts of As occur naturally in the soil through which water moves. No measurable increases in As resulting from soil-borne residues should be found in water as the result of silvicultural As use. Because forests seldom will be treated more than once a century, no chronic effects on any part of the ecosystem are anticipated.

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