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Effect of components of leaching medium on the leaching of benzalkonium chloride from treated wood

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Abstract Different leaching media composed of water-soluble extracts from Sakhalin fir, Japanese cedar, and Japanese larch heartwoods and of taxifolin were used to characterize leaching of the C12 and C14 homologues of benzalkonium chloride from treated wood. The leaching medium of Sakhalin fir extract moderately accelerated the leaching rates of the two homologues. Japanese cedar extract accelerated the leaching of the C12 homologue at a similar rate and that of the C14 homologue at a higher rate. Japanese larch extract remarkably accelerated the leaching rates of both homologues, particularly that of the C14 homologue. Thus, the leaching rate of the C14 homologue was higher than that of the C12 homologue with the Japanese cedar and larch extracts. The media of taxifolin, a major phenolic extractive of Japanese larch, preferentially accelerated the leaching rate of the C14 homologue. The amounts of phenolic compounds in the different leaching media were in the following order: Japanese larch > Japanese cedar > Sakhalin fir. These results indicate a relationship between the amount of phenolic compounds and the leaching rates of the two homologues.

Key words Benzalkonium chloride · Homologue · Leaching medium · Taxifolin

Introduction

Since 1996, wood preservatives such as ammoniacal copper quat (ACQ) and copper azole (CuAz) have been mostly used as alternatives for chromated copper arsenate (CCA) in the pressure treatment of wood in Japan.^{1,2} According to the Japanese Industrial Standard (JIS) K1570,³ ACQ wood preservatives consist of copper and quaternary ammonium chloride as active ingredients and are classified into two

types, namely, ACQ-1 and ACQ-2. ACQ-1 contains copper and alkylbenzyltrimethylammonium chloride (benzalkonium chloride, BAC) and ACQ-2 contains copper and didecyltrimethylammonium chloride (DDAC) as active ingredients. The former is predominantly used in Japan.

Leaching of the active ingredients from preserved wood results in the loss of wood protection. The conditions prevailing at the place where the treated wood is utilized are considered to influence the leaching of the active ingredients from wood. Several studies have been conducted to discuss the effects of soil acidity^{4–9} and sea water (SW)^{10–13} on the leaching of copper because copper is the most widely used fungicidal element in various wood preservatives. On the other hand, although a few studies have been conducted to investigate the factors that affect the leaching of quaternary ammonium chlorides,^{14–17} they have not been completely understood. The BAC in commercial ACQ-1 formulations contains approximately 74%, 26%, and less than 1% of C12, C14, and C16 homologues, respectively.^{18,19} It has been observed that these homologues differ in their fungicidal activities,²⁰ while differences in their leaching characteristics remain to be determined.

Our previous study on the leaching of the two above-mentioned major homologues from ACQ-treated wood demonstrated that, in general, the C12 homologue is more easily leached than the C14 homologue and that leaching rate is accelerated by SW.²¹ The results suggested that the alkyl chain length of the BAC plays an important role in leaching resistance. However, when Japanese larch heartwood was treated with the C12 and C14 homologues dissolved in monoethanolamine (MEA), the leaching rate of the C14 homologue with distilled water (DW) was markedly higher than that of the C12 homologue.²¹

Crawford et al.⁸ reported that the acidity and organic components of soil affect the resistance of CCA wood preservatives against leaching from treated wood. Japanese larch contains relatively large amounts of organic wood extractives,²² so we assumed that the presence of readily removable wood extractives and changes in the properties of the leaching medium caused different patterns of the leaching of BAC homologues from the treated wood during

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leaching experiments. This means that leaching of the C14 homologue was higher than that of the C12 homologue from Japanese larch heartwood.

Various organic compounds present in soil²³ serve as important factors that affect the leaching of BAC homologues when treated wood is used in ground-contact conditions. Therefore, in the present study, leaching media of water-soluble wood components from Sakhalin fir, Japanese cedar, and Japanese larch heart wood were tested for their effects on the leaching of BAC homologues, and parameters such as the amounts of organic and phenolic components in the media and the pH of the media are subsequently discussed.

Materials and methods

Reagents

The following chemicals were purchased from Kanto Chemicals (Tokyo, Japan): high-performance liquid chromatography (HPLC)-grade methanol (MeOH) and acetonitrile, 1 M ammonia solution, ammonium perchlorate, MEA, 10 mM hydrochloric acid (HCl), and formic acid. Benzyltrimethylammonium chloride (C12 homologue, 99%) and benzyltrimethylammonium chloride (C14 homologue, 99%) were purchased from Fluka (Tokyo, Japan). (+)-Taxifolin was purchased from Extrasynthese (Genay, France).

Wood specimens and treatment

Wood specimens with dimensions of 2 (R) × 2 (T) × 1 cm (L) were cut from the sapwood of Japanese cedar (*Cryptomeria japonica*), dried at 60° ± 2°C for 48 h, and then stored at 26° ± 1°C and 55% ± 3% relative humidity (RH). Thereafter, the specimens were placed in a small vessel with an MEA solution containing 3.75 mM each of the C12 and C14 homologues. The specimens in the vessel were subjected to vacuum (5 kPa) for 1 h and then kept at atmospheric pressure for 2 h to allow complete absorption of the treatment solution into the specimens. After impregnation of the specimens with the treatment solution, they were placed in sealed bags for 1 week to prevent them from drying, following which they were dehydrated at room temperature for 72 h and then at 50° ± 2°C for 72 h. The amount of BAC in the treated wood was chemically determined by a previously reported method.¹⁹

Preparation of the leaching media

To prepare leaching media of wood extracts, heartwood specimens of Japanese cedar, Japanese larch (*Larix leptolepis*), and Sakhalin fir (*Abies sachalinensis*) were treated by the above-mentioned method, without the BAC. Fifty MEA-treated heartwood specimens each of Japanese cedar, Japanese larch, and Sakhalin fir were placed in conical

Table 1. Composition of solution for leaching media

| Name | Composition |
|------|---|
| LM-1 | Extractable components from Sakhalin fir |
| LM-2 | Extractable components from Japanese cedar |
| LM-3 | Extractable components from Japanese larch |
| LM-4 | 0.1 mM HCl in distilled water |
| LM-5 | 10 mM HCl in distilled water |
| LM-6 | 0.01 mg ml ⁻¹ taxifolin in distilled water |
| LM-7 | 0.1 mg ml ⁻¹ taxifolin in distilled water |
| DW | Distilled water |

flasks containing 2000 g DW. The flasks were then subjected to vacuum (5 kPa) for 1 h, following which they were shaken on a rotary shaker at 125 rpm at 25° ± 1°C for 24 h. The resultant solutions were filtered and stored at 5° ± 1°C until use. A leaching medium of 0.1 mM HCl was prepared by diluting 10 mM HCl solution with DW. Media of 0.01 mg/ml and 0.1 mg/ml taxifolin were prepared by dissolving a specific amount of (+)-taxifolin in DW. All the media used in this study are listed in Table 1.

Leaching experiment

The leaching experiment was performed according to a method reported previously²¹ with a modification in the total leaching time (144 h). Three BAC-treated wood specimens were placed in a 200-ml conical flask together with 120 g of a leaching medium. The flask was then subjected to vacuum (5 kPa) for 1 h and shaken on a rotary shaker (125 rpm) at 25° ± 1°C for 144 h. The leaching medium was recovered after 24, 72, and 144 h and replaced with fresh medium at 24 and 72 h.

Quantitative determination of BAC homologues in leaching medium

HPLC with ultraviolet detection (HPLC-UV; LC-10A system; Shimadzu, Kyoto, Japan) was used for the quantitative analysis of BAC homologues in the leaching medium. Before the analysis, the leaching medium was purified and concentrated by performing solid-phase extraction (SPE).²¹ SPE of the leaching media LM-1 to LM-3 and LM-7 was conducted using Oasis mixed cation-exchange (MCX) cartridges (Waters, Tokyo, Japan) because it was anticipated that the components present in excess in the leaching medium would interfere with the recovery of the C12 and C14 homologues if Oasis weak cation-exchange (WCX) cartridges (Waters, Tokyo, Japan) were used for SPE. The leaching medium (5 ml) was mixed with 3.3 ml of MeOH and 0.5 ml of HCl (0.1 M). The resultant solution was loaded on SPE cartridges (Oasis MCX) conditioned with 2 ml of MeOH, followed by 2 ml of water. After loading, the cartridge was washed with 0.1 M HCl (3 ml), 1 M NH₄OH (3 ml), and MeOH (3 ml). Finally, the BAC that remained on the cartridge was eluted with 5 ml of 0.5 M NaClO₄ in CH₃CN/H₂O (70:30, v/v), and the eluent was analyzed using HPLC-UV according to a previously reported method.¹⁹

Calculation of the leaching rates

The amounts of each BAC homologue in the different leaching media were analyzed as follows. The total leaching rates (TLRs; %) of the homologues were calculated using the following equation:

$$\text{TLR} = \frac{m_{\text{total}}}{m_c} \times 100 \quad (1)$$

where m_{total} is the total amount (mg) of the C12 (or C14) homologue in the recovered leaching medium, and m_c is the amount (mg) of the C12 (or C14) homologue in the three treated specimens.

The rate of acceleration was calculated using the following equation:

$$\text{RLR} = \frac{\text{TLR}_{\text{lm}}}{\text{TLR}_{\text{DM}}} \times 100 \quad (2)$$

where RLR is the relative leaching rate, TLR_{lm} is the TLR for the leaching medium under consideration, and TLR_{DM} is the TLR in distilled water. Three replicates were used for each medium. The TLR was statistically analyzed by Tukey's multiple comparison test, using Excel 2003 (Microsoft, USA) with the add-in software Statcel 2.²⁴ A *P* value of less than 0.01 was considered significant.

Content of organic and phenolic compounds in leaching media and measurement of pH

The amount of organic compounds in a leaching medium was determined on the basis of the residual dry weight of each leaching medium after dehydration at 100°C for 24 h. The amount of phenolic compounds in a leaching medium was determined by the Folin-Ciocalteu method.²⁵ (+)-Taxifolin was used as the calibration standard. The pH of the test medium was measured using a pH meter (D-21; Horiba, Kyoto, Japan) at room temperature.

Results and discussion

Effect of heartwood components on leaching characteristics of BAC homologues

The retention levels of the C12 and C14 homologues in the treated specimens were 1.8 kg/m³ (standard deviation, 0.08 kg/m³; *n* = 6) and 1.9 kg/m³ (standard deviation, 0.05 kg/m³; *n* = 6), respectively. The results of the leaching of homologues with DW and leaching media (LM-1, LM-2, and LM-3) are shown in Table 2.

With LM-1, the TLR of the C12 homologue was higher than that of the C14 homologue, while the RLR of the latter was higher than that of the former (Table 2). The leaching rate of the C14 homologue was further accelerated by LM-2; consequently, the RLR and TLR of the C14 homologue were higher than those of the C12 homologue. The leaching rates of the two homologues were significantly accelerated by LM-3, with the TLR of the C14 homologue being higher

Table 2. Leaching rate and relative leaching rate of C12 and C14 homologues in media containing wood components

| Leaching medium | Total leaching rate (%) | | Relative leaching rate | |
|-----------------|-------------------------|---------------|------------------------|------|
| | C12 | C14 | C12 | C14 |
| DW | 3.1 (0.25) A | 1.5 (0.10) D | – | – |
| LM-1 | 5.6 (0.28) B | 3.7 (0.30) A | 1.8 | 2.4 |
| LM-2 | 5.9 (0.27) B | 9.2 (0.50) E | 1.9 | 6.1 |
| LM-3 | 15.1 (0.41) C | 29.6 (0.55) F | 4.9 | 19.6 |

Values in parentheses are standard deviations. Total leaching rates with same capital letter are not significantly different (Tukey's test, *P* < 0.01)

Table 3. Amount of organic and phenolic compounds and pH of leaching media

| Leaching medium | Amount (mg/g leaching medium) | | pH |
|-----------------|-------------------------------|-----------|----|
| | Organics | Phenolics | |
| LM-1 | 0.72 | 0.08 | 7 |
| LM-2 | 0.64 | 0.14 | 6 |
| LM-3 | 2.01 | 0.30 | 5 |

than that of the C12 homologue. These results indicate that wood components could accelerate the leaching rate of the C14 homologue, and, in some cases, a higher leaching rate of the C14 homologue than that of the C12 homologue was recorded.

Properties of leaching media based on wood extracts

To further discuss the effects of organic compounds on the leaching characteristics of the two homologues, some properties of the three leaching media (LM-1 to LM-3), such as the amount of organic and phenolic compounds in the media and the pH of the media, were determined (Table 3).

Relationships between the amount of organic components and TLR, the amount of phenolic components and TLR, and that between the pH and TLR are shown in Fig. 1. The TLRs of the two homologues in LM-1, LM-2, and LM-3 appeared to increase with an increase in the amounts of organic and phenolic compounds and a decrease in pH. This was particularly evident in the case of the TLR of the C14 homologue. Thus, an increase in the amount of organic or phenolic compounds and/or a decrease in pH induced by wood components were considered as the reasons for the higher leaching rate of the C14 homologue.

Effect of acidity and amount of phenolic components on leaching

The leaching media of HCl (LM-4 and LM-5) or those of taxifolin (LM-6 and LM-7), a representative phenolic compound present in the Japanese larch heartwood,²¹ were used in the leaching experiments in the present study in order to

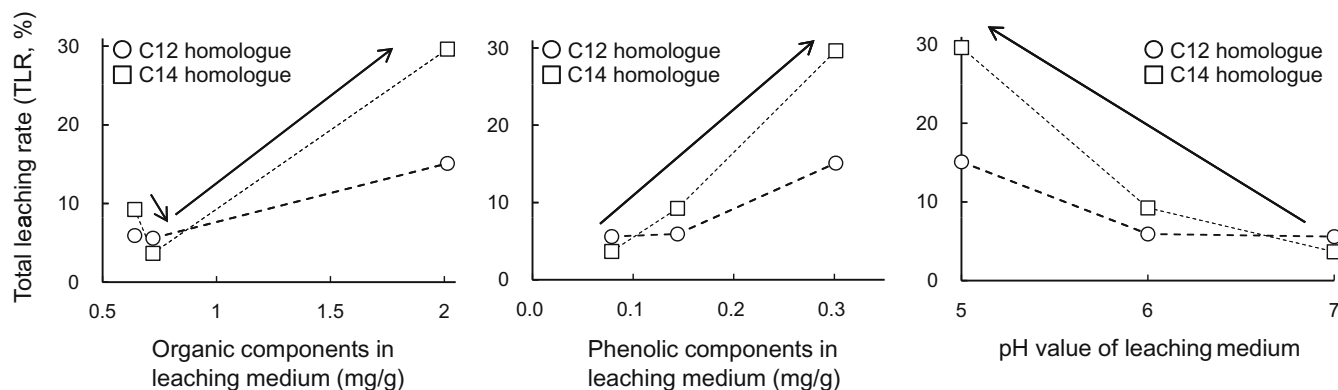


Fig. 1. Relationships between the properties of the leaching media and the total leaching rate (TLR) of the C12 and C14 homologues of benzalkonium chloride from treated wood

Table 4. Leaching rates and relative leaching rates of C12 and C14 homologues in media containing HCl

| Leaching medium | Total leaching rate (%) | | Relative leaching rate | |
|-----------------|-------------------------|---------------|------------------------|------|
| | C12 | C14 | C12 | C14 |
| DW | 3.0 (0.22) A | 1.4 (0.09) A | – | – |
| LM-4 | 2.8 (0.36) A | 1.5 (0.37) A | 0.9 | 1.0 |
| LM-5 | 77.4 (3.30) B | 49.9 (1.81) C | 26.0 | 34.4 |

Values in parentheses are standard deviations. Total leaching rates with same capital letter are not significantly different (Tukey's test, $P < 0.01$)

Table 5. Leaching rates and relative leaching rates of C12 and C14 homologues in media containing taxifolin

| Leaching medium | Total leaching rate (%) | | Relative leaching rate | |
|-----------------|-------------------------|--------------|------------------------|-----|
| | C12 | C14 | C12 | C14 |
| DW | 3.0 (0.22) A | 1.4 (0.09) C | – | – |
| LM-6 | 2.6 (0.08) A | 1.6 (0.08) C | 0.9 | 1.1 |
| LM-7 | 4.8 (0.21) B | 8.9 (0.17) D | 1.6 | 6.1 |

Values in parentheses are standard deviations. Total leaching rates with same capital letter are not significantly different (Tukey's test, $P < 0.01$)

examine the effects of acidity and phenolic components on the leaching of homologues. The TLRs of the homologues with LM-4 were similar to those with DW, while the TLRs of the homologues with LM-5 were drastically higher than those with DW (Table 4). In addition, the TLR of the C12 homologue was higher than that of the C14 homologue with LM-5, while the RLR of the latter was higher than that of the former. These results were in accordance with the pH values of LM-1, LM-2, and LM-3 and suggested that the acceleration of the leaching rates of homologues with the three media was not caused by the pH of the media alone.

With LM-6, the leaching rates of the two homologues remained unaffected (Table 5). However, the higher amount of taxifolin present in LM-7 resulted in the higher leaching rate of the C14 homologue with this medium (Table 5). It is interesting to note that the amounts of phenolic com-

pounds in LM-2 and LM-3 were higher than 0.1 mg/g but lower than 0.1 mg/g in LM-1. These results indicated that the amounts of phenolic compounds in the leaching media were responsible for the different leaching rates of the two homologues: the leaching rate of the C14 homologue was higher than that of the C12 homologue.

Because phenolic compounds such as taxifolin react with copper leading to precipitation²⁶ within the wood and given that the reduced amount could not be readily extracted during the experimental leaching process, the compounds are not considered to be key factors involved in the leaching of the C12 and C14 homologues from ACQ-1-treated or BAC-treated Japanese larch and cedar heartwoods.²¹ Such a phenomenon could partly account for the discrepancy in the leaching characteristics of the two homologues under identical leaching conditions in the laboratory.

Conclusions

The presence of water-extractable organic components of Sakhalin fir, Japanese cedar, and Japanese larch in the leaching media accelerated the leaching rates of both the C12 and C14 homologues. As compared with the leaching rate of the C12 homologue, that of the C14 homologue was accelerated in the following order: Japanese larch > Japanese cedar > Sakhalin fir. These results indicated a close relationship between the amounts of phenolic compounds in the leaching media with the leaching of homologues. Because soil contains various organic components²³ and various phenolic compounds,²⁷ it should be noted that the leaching rates of BAC homologues in the soil are aided by precipitation and are higher than in DW. In addition, the amount of the leached BAC homologues in the soil is thought to differ from that in DW and SW. Further studies are currently underway to better understand the leaching characteristics of BAC homologues from treated wood under simulated service conditions.

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