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Leaching characteristics of homologues of benzalkonium chloride from wood treated with ammoniacal copper quaternary wood preservative

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Abstract In Japan, ammoniacal copper quaternary wood preservatives type-1 (ACQ-1), which contains copper and benzalkonium chloride as its active ingredients, is among the most widely used wood preservatives in the pressure treatment of wood. Benzalkonium chloride (BAC) in commercial ACQ-1 products mainly comprises C12 and C14 homologues. In the present study, the leaching characteristics of these BAC homologues were investigated using the heartwood and sapwood portions of Japanese cedar, Japanese larch, and Sakhalin fir treated with ACQ-1 and 1% monoethanolamine (MEA) solution containing equimolar amounts of homologues. Distilled water (DW) and artificial seawater (SW) were used as leaching media. Consequently, it was observed that the leaching rate of the C12 homologue tended to be higher than that of the C14 homologue in DW. The leaching of C12 homologues was accelerated by using SW, resulting in a significantly higher leaching rate than the C14 homologue using SW. It was thought that the difference in the hydrophobicities based on alkyl chain lengths resulted in these phenomena. However, when the heartwood portion of Japanese larch was treated with the homologues in MEA, the leaching rate of the C14 homologue was significantly higher than that of the C12 homologue.

Key words Ammoniacal copper quaternary (ACQ) · Benzalkonium chloride (BAC) · Leaching · Seawater

Introduction

In recent years, growing environmental concerns have led to drastic modifications in the active ingredients of wood preservatives in many countries, such as eliminating or restricting the use of chromate copper arsenate (CCA).¹ Alternatively, wood preservatives containing copper and organic biocides as active ingredients are used in many countries.¹ In Japan, formulations that contain copper and triazole (CuAz) wood preservatives and ammoniacal copper quaternary (ACQ) wood preservatives are most widely used for pressure treatment among water-borne wood preservatives.² According to the JIS K 1570 standard,³ ACQ wood preservatives are classified into two types based on their compositions: ACQ-1 contains copper and benzalkonium chloride (BAC) and ACQ-2 contains copper and didecyldimethyl ammonium chloride (DDAC). In Japan, ACQ-1 is among the most widely used wood preservatives in the pressure treatment of wood.

Numerous studies investigated the leaching characteristics of copper from treated wood including the effects of acidity^{4–9} and seawater^{10–13} because copper has been most widely used as the active ingredient in various wood preservatives. On the other hand, only a few studies^{14,15} have investigated the leaching characteristics of ACQ-1 or BAC; furthermore, the factors affecting BAC leaching have not been investigated as thoroughly as those affecting copper.

Commercially available BACs mainly consist of C12, C14, and C16 alkyl chain homologues with differences in their compositions; they possess different physical, chemical and microbiological properties. Tsunoda¹⁶ reported that the fungicidal efficacy of the C14 homologue against *Trametes versicolor* (L. ex Fr.) Quel is higher than that of the C12 homologue, while those of the C12 and C14 homologues against *Fomitopsis palustris* (Berkeley et Curtis) Murrill are equal. The fixation mechanisms of BAC homologues and their bromide salts on beech sawdust depend on their hydrophobicities: among C8, C10, and C12 homologues, the C12 homologue achieves the highest fixation strength on wood.¹⁷

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BAC in commercial ACQ-1 contains approximately 74%, 26%, and less than 1% of C12, C14, and C16 homologues, respectively.¹⁸ Thus, the leaching characteristics of each BAC homologue from treated wood and the factors affecting their leaching behaviors are important in order to extend the service areas of wood treated with ACQ-1, such as marine services. Furthermore, this information is thought to be important for considering new quaternary ammonium compounds (QACs) as wood preservatives. However, the leaching characteristics of BAC homologues from wood treated with ACQ-1 or those of a reagent containing several homologues and the factors that affect their leaching have not been reported.

In the present study, we evaluated the effects of alkyl chain length and sea salts on the characteristics of the leaching of BAC homologues from wood specimens treated with ACQ-1 using two types of leaching mediums: distilled water and seawater.

Materials and methods

Reagents

Benzyltrimethylammonium chloride (C12 homologue, 99%) and benzyltrimethylammonium chloride (C14 homologue, 99%) (Fig. 1) were purchased from Fluka (Tokyo, Japan). Methanol (MeOH), acetonitrile (CH₃CN), ethanol (EtOH), and dichloromethane (DCM), all of which were high-performance liquid chromatography (HPLC) grade, were purchased from Kanto Chemicals (Tokyo, Japan). Formic acid (HCOOH), 1 M ammonium hydroxide solution (NH₄OH), ammonium perchlorate (NH₄ClO₄), and monoethanolamine (MEA) were also purchased from Kanto Chemicals (Tokyo, Japan). Hydrochloric acid (HCl) was purchased from Wako (Tokyo, Japan). Aquamarine (artificial seawater) was purchased from Yashima Pure Chemicals (Osaka, Japan). A commercial ACQ-1 product, which contained 9.0% copper (as CuO) and 7.2% BAC, was kindly supplied by Koshii Preserving (Osaka, Japan). From the preliminary experiment, it was confirmed that the ACQ-1 mainly comprised C12 and C14 homologues (3.3:1, w/w).

Wood specimens

The heartwood and sapwood portions of Japanese cedar (*Cryptomeria japonica* D. Don), Japanese larch (*Larix lep-*

tolepis Gord), and Sakhalin fir (*Abies sachalinensis* Masters) were used. Three wood specimens with dimensions of 2 (T) × 2 (R) × 1 (L) cm were continuously cut from six different wood stakes [2 (T) × 2 (R) × 70 (L) cm] of each species. The intermediate specimen was used as unleached control and the other two on the sides were used for leaching procedures involving distilled water (DW) and artificial seawater (SW). All the specimens were dried at 60°C for 48 h and stored at 26°C and 55% relative humidity (RH). Later, six sets of matched wood specimens from six different stakes of each species were placed in a small vessel. Thereafter, 4% or 8% of the ACQ-1 solution or 1% MEA solution containing 3.75 mM or 7.5 mM of both C12 and C14 homologues was added. The solution was subjected to vacuum at 96 kPa for 30 min and then stored for 2 h at atmospheric pressure. After this pressure treatment, the specimens were placed in bags and the bag was sealed for 1 week to avoid drying. Subsequently, each of these specimens was dried at room temperature for 72 h and then at 50°C for 72 h.

Leaching procedure

Leaching was performed by the following method. Six wood specimens were placed in a 300-ml conical flask and 240 ml of DW (pH 6) or SW (pH 8 adjusted with 1 M NaOH) was added to it as a leaching medium. After the solution was subjected to 96 kPa vacuum for 1 h, the flask was set on a horizontal shaker and shaken at 125 rpm at 25°C for 240 h. The leaching medium was collected after intervals of 24 h, 72 h, and 144 h; the leaching medium was then changed. After the leaching experiment, the wood specimens were dried at room temperature for 72 h and then at 50°C for 72 h and then milled using a Wiley mill for the quantitative analyses of BAC and copper. The resultant leaching rate in the wood specimens was expressed by the following equation:

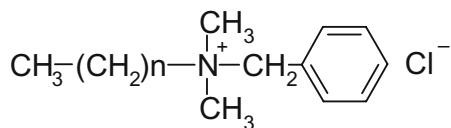
$$\text{Leaching rate (\%)} = \frac{m_B}{m_A} \times 100$$

where m_A is the amount of each BAC homologue (or copper) in the matched wood specimen (unleached control), m_B is the amount of residual each BAC homologue (or copper) in the exposed wood specimen.

The statistical difference was determined by using two paired *t*-tests (Excel 2003, Microsoft), and Bonferroni correction was used for multiple testing within each portion of the species treated with each concentration.

Quantitative determination of BAC in wood

The quantitative determination of BAC homologues in wood was carried out in accordance with previously reported methods.¹⁸ To confirm the recovery of BAC homologues from wood treated with ACQ-1, wood powders of all the above-mentioned species were prepared using a Wiley mill (2-mm mesh) and mixed with ACQ-1 solutions and employed in these methods.



C12 homologue : $n=11$

C14 homologue : $n=13$

Fig. 1. Structure of the homologues of benzalkonium chloride (BAC)

Quantitative analysis of BAC in leachate from wood treated with ACQ-1

The amounts of BAC homologues in the leachate from wood specimens treated with ACQ-1 were analyzed by HPLC. In order to remove the water-soluble wood components and to concentrate the homologues, the collected leaching mediums were subjected to solid-phase extraction (SPE). Leaching mediums (30–50 ml) were loaded in SPE cartridges (Oasis WCX) conditioned with 2 ml of MeOH followed by 2 ml of H₂O. After loading, each of the cartridges was washed with 3 ml of 0.1 M HCl, H₂O, and 1 M NH₄OH and subsequently with 3 ml of MeOH and DCM/MeOH (1:1, v/v). Finally, the remaining BAC on the cartridge was eluted using 5 ml of CH₃CN/H₂O/HCOOH (70:28:2, v/v/v), and the eluent was analyzed by HPLC with an ultraviolet (UV) detector.¹⁸

Analysis of copper in wood specimens treated with ACQ-1

Wood specimens were milled in a Wiley mill; then, approximately 0.5 g of the powder was transformed to ash in a muffle furnace at 600°C for 5 h. The resultant residue was dissolved in 2 ml of 8 M nitric acid (HNO₃). The solution was then diluted with DW up to 100 ml and filtered through a 0.45- μ m filter. Then the copper content of the filtrate was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, ICP SPS7800, Seiko).

Results and discussion

Retention amounts of copper and BAC in treated wood

The amounts of BAC homologues in wood treated with ACQ-1 were analyzed by using a previously reported method. However, in this study, the recoveries of BAC homologues from wood were confirmed by using wood treated with BAC in MeOH; consequently, the recovery of BAC homologues from the wood treated with ACQ-1 was confirmed. The resulting recovery is summarized in Table 1. This recovery appeared to vary according to the wood species. However, we used the present method for the determination of BAC homologues levels in wood samples because the recovery of them at the two spiking levels of the same homologue in each wood species was insignificant.

In the present study, wood specimens treated with equal amounts of C12 and C14 homologues in MEA were also used to study leaching of them. The results of the retention of copper and BAC in treated heartwood and sapwood portions of each species of wood are summarized in Tables 2 and 3.

Leaching of copper from wood treated with ACQ-1

The leaching rates of copper are shown in Fig. 2. For the heartwood portion, the leaching rates of copper from

Table 1. Recovery of C12 and C14 homologues from wood treated with ammoniacal copper quaternary wood preservatives type-1 (ACQ-1)

Wood	BAC in wood (mg/cm ³)	Recovery (%) ^a	
		C12	C14
Japanese cedar			
Heartwood	5.5	91 (1.4)	94 (1.6)
Sapwood	5.5	88 (2.2)	92 (1.2)
Heartwood	0.28	90 (1.8)	92 (2.0)
Sapwood	0.28	89 (0.7)	92 (0.9)
Japanese larch			
Heartwood	5.5	84 (0.7)	89 (1.2)
Sapwood	5.5	83 (1.1)	87 (1.3)
Heartwood	0.28	89 (2.5)	89 (5.6)
Sapwood	0.28	85 (1.2)	89 (5.1)
Sakhalin fir			
Heartwood	5.5	96 (0.3)	95 (0.7)
Sapwood	5.5	93 (0.8)	92 (0.8)
Heartwood	0.28	98 (1.1)	94 (2.2)
Sapwood	0.28	95 (0.3)	94 (4.8)

Values in parentheses are standard deviations

BAC, benzalkonium chloride

^a Average of three replicate samples

Table 2. Retention levels of BAC in wood treated with ACQ-1

Wood	ACQ concentration (%)	ACQ retention (g/cm ³) ^a		
		Cu	C12	C14
Japanese cedar				
Heartwood	8	4.9 (0.24)	5.0 (0.19)	1.4 (0.05)
Sapwood	8	5.1 (0.10)	4.7 (0.36)	1.4 (0.11)
Heartwood	4	2.6 (0.08)	2.9 (0.20)	0.8 (0.06)
Sapwood	4	2.7 (0.06)	2.8 (0.18)	0.8 (0.09)
Japanese larch				
Heartwood	8	4.0 (0.21)	3.5 (0.18)	1.0 (0.10)
Sapwood	8	5.0 (0.23)	4.2 (0.15)	1.2 (0.04)
Heartwood	4	2.2 (0.12)	2.1 (0.22)	0.6 (0.05)
Sapwood	4	2.6 (0.08)	2.6 (0.09)	0.7 (0.04)
Sakhalin fir				
Heartwood	8	4.8 (0.17)	4.6 (0.14)	1.3 (0.05)
Sapwood	8	5.0 (0.15)	4.5 (0.22)	1.3 (0.06)
Heartwood	4	2.5 (0.04)	2.8 (0.16)	0.8 (0.04)
Sapwood	4	2.7 (0.05)	2.7 (0.08)	0.8 (0.04)

Values in parentheses are standard deviations

^a Average of six replicate samples

Japanese cedar treated with 4% and 8% ACQ-1 and from Sakhalin fir treated with 8% ACQ-1 were significantly higher in SW than those in DW. Although significant difference was not observed in other species, the same trend was observed. On the other hand, for the sapwood portion, only the leaching rate of copper from Japanese cedar was significantly higher in SW than that in DW; the leaching rates of copper were slightly higher (statistically insignificant) in the other cases. A similar result has been reported using southern yellow pine treated with ACQ.¹⁵ Thus, it can be assumed that SW accelerates copper leaching from wood treated with ACQ-1.

Yamamoto et al.¹⁴ reported that 400 μ g/cm³ of copper leached from Japanese cedar treated with ACQ-1 at a retention level of 5.7 mg/cm³ with the leaching method according

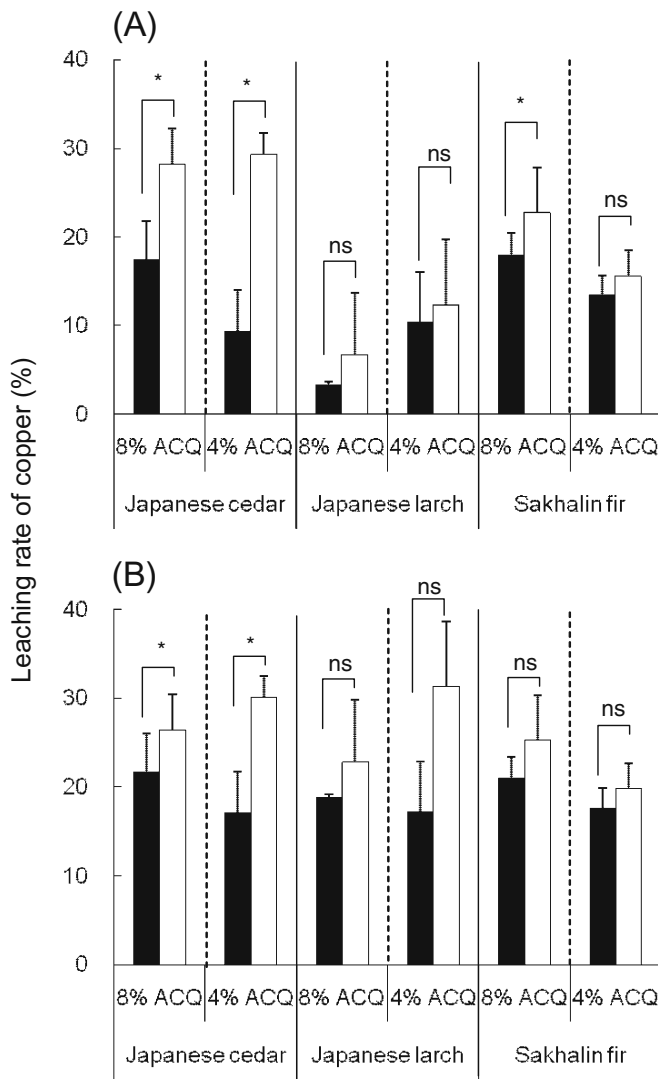


Fig. 2A, B. Average leaching rates of copper in distilled water (DW) (filled bars) and artificial seawater (SW) (open bars) from **A** the heartwood portion and **B** the sapwood portion treated with ammoniacal copper quaternary wood preservatives type-1 (ACQ-1). Asterisk, significant difference; ns, no significant difference (according to paired *t*-tests; $P < 0.05$). Error bars denote standard deviations

to JIS K 1571.¹⁹ By using the present leaching method, about $460\mu\text{g}/\text{cm}^3$ of copper leached from the Japanese cedar sapwood portion at a retention level of $6.0\text{mg}/\text{cm}^3$ (as ACQ). Thus, the present leaching procedure is considered to have the same potential for acceleration of the leaching process as the standard JIS method.¹⁹

Amount of BAC in leachate

To confirm the safe recovery of BAC from the collected leaching mediums by using the SPE method, 0.1 mg each of C12 and C14 was added to the leaching mediums after 24h, and the resultant solutions were subjected to the SPE method described in *Materials and methods*. Consequently,

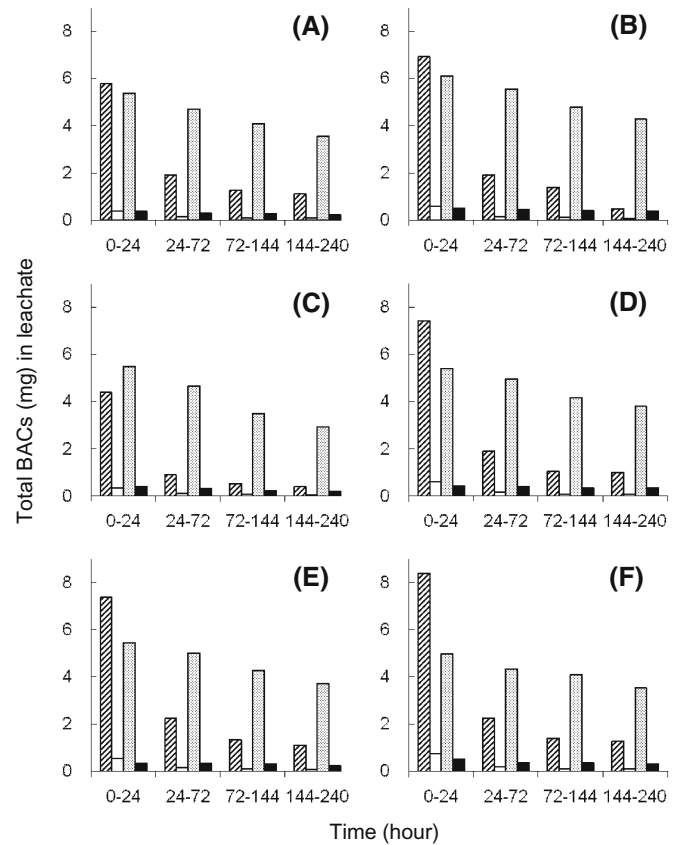


Fig. 3A–F. Total amount of each BAC homologue leached from specimens treated with 8% ACQ-1. **A** Heartwood and **B** sapwood of Japanese cedar; **C** heartwood and **D** sapwood of Japanese larch; and **E** heartwood and **F** sapwood of Sakhalin fir. Hatched bars, C12 homologue in DW; open bars, C14 homologue in DW; dotted bars, C12 homologue in SW; filled bars, C14 homologue in SW

Table 3. Retention levels of BAC in monoethanolamine (MEA)-treated wood in MEA solution

Wood	BAC concentration (mM)	BAC retention (g/cm^3) ^a	
		C12	C14
Japanese cedar			
Heartwood	7.5	3.4 (0.09)	3.2 (0.07)
Sapwood	7.5	3.7 (0.28)	3.7 (0.37)
Heartwood	3.75	2.4 (0.13)	2.1 (0.12)
Sapwood	3.75	2.1 (0.18)	2.3 (0.28)
Japanese larch			
Heartwood	7.5	2.8 (0.06)	2.5 (0.07)
Sapwood	7.5	3.2 (0.17)	3.0 (0.13)
Heartwood	3.75	2.0 (0.07)	1.7 (0.12)
Sapwood	3.75	2.0 (0.08)	2.0 (0.09)
Sakhalin fir			
Heartwood	7.5	3.2 (0.03)	3.1 (0.03)
Sapwood	7.5	3.4 (0.23)	3.4 (0.21)
Heartwood	3.75	1.9 (0.10)	1.9 (0.10)
Sapwood	3.75	2.0 (0.08)	2.2 (0.10)

Values in parentheses are standard deviations

^a Average of six replicate samples

the additional BAC could be recovered (>93% recovery) from all the species of wood in both DW and SW.

The amounts of BAC homologues leached in DW and SW decreased with time (Fig. 3). The amounts of the C12

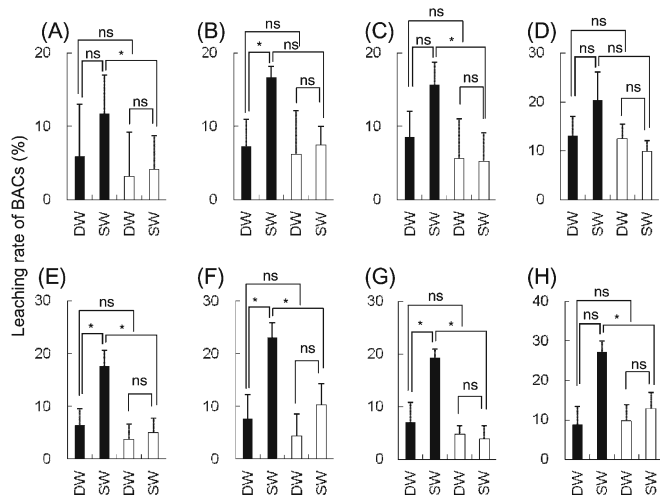


Fig. 4A–H. Average leaching rate of C12 (solid bars) and C14 (open bars) homologues in DW and SW from Japanese cedar heartwood treated with 8% ACQ-1 (A) and 4% ACQ-1 (B), sapwood treated with 8% ACQ-1 (C) and 4% ACQ-1 (D), heartwood treated with 7.5 mM BAC in monoethanolamine (MEA) (E) and 3.75 mM BAC in MEA (F), and sapwood treated with 7.5 mM BAC in MEA (G) and 3.75 mM BAC in MEA (H). Asterisk, significant difference; ns, no significant difference (according to paired *t*-tests with Bonferroni correction; $P < 0.05/4$). Error bars denote standard deviations

homologue in the leachates were clearly higher than that of the C14 homologue. After the second leaching cycle (24–48 h), the amounts of C12 and C14 homologues in SW were clearly higher than those in DW. Thus, it was thought that the leaching of the C12 homologue was higher than the C14 homologue, and leaching of C12 and C14 homologues was accelerated by SW.

Leaching rate of BAC from treated Japanese cedar

Most of the average leaching rates of the C12 homologue in DW were higher than those of the C14 homologue; however, there was no significant difference between their leaching rates from specimens treated with ACQ-1 in DW (Fig. 4A–D). In SW, the leaching rate of the C12 homologue from heartwood and sapwood treated with 8% ACQ-1 was significantly higher than that of the C14 homologue. Although significant differences were observed only in the heartwood portion treated with 4% ACQ-1, the average leaching rates of the C12 homologue from specimens treated with ACQ-1 were higher than those in SW.

By using the specimens of Japanese cedar treated with equimolar amounts of C12 and C14 homologues in MEA, there was an insignificant difference between the leaching rates of C12 and C14 homologues in DW (Fig. 4E–H). However, the leaching rates of the C12 homologue from the specimens were significantly higher than those of the C14 homologue in DW. Additionally, the leaching rate of the C12 homologue in SW was significantly higher than that in DW, except for the sapwood portion treated with 3.75 mM BAC in MEA.

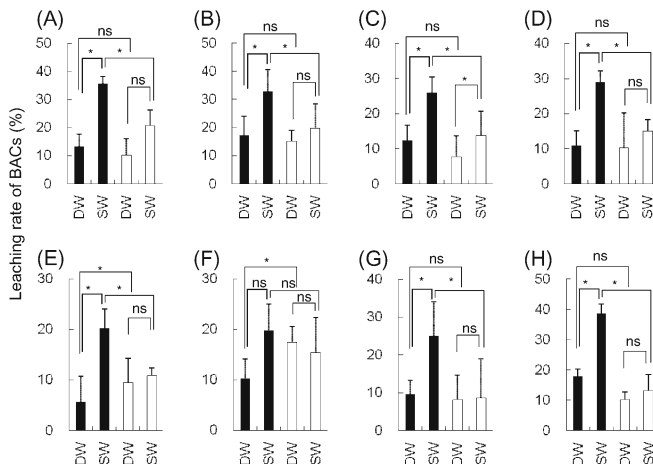


Fig. 5A–H. Average leaching rates of C12 (solid bars) and C14 (open bars) homologues in DW and SW from Japanese larch heartwood treated with 8% ACQ-1 (A) and 4% ACQ-1 (B), sapwood treated with 8% ACQ-1 (C) and 4% ACQ-1 (D), heartwood treated with 7.5 mM BAC in MEA (E) and 3.75 mM BAC in MEA (F), and sapwood treated with 7.5 mM BAC in MEA (G) and 3.75 mM BAC in MEA (H). Asterisk, significant difference; ns, no significant difference (according to paired *t*-tests with Bonferroni correction; $P < 0.05/4$). Error bars denote standard deviations

Leaching rates of BAC homologues for treated Japanese larch

Similar to Japanese cedar, there was no significant difference between the leaching rates of C12 and C14 homologues from specimens treated with ACQ-1 in DW (Fig. 5A–D). In SW, the leaching rates of the C12 homologue from the specimens treated with 8% and 4% ACQ-1 were significantly higher than those of the C14 homologue in SW. Furthermore, the leaching rate of the C12 homologue from the specimens in SW was significantly higher than those in DW.

For the heartwood portion treated with BAC in MEA, the leaching rate of the C14 homologue was significantly higher than that of the C12 homologue in DW, while in most of the other cases, the leaching rates of the C12 homologue were similar to or higher than those of the C14 homologue with or without significance (Fig. 5D–H). However, the leaching rates of the C12 homologue were higher than those of the C14 homologue with no significance only in the heartwood portion treated with 3.75 mM BAC.

Leaching rates of BAC homologues from Sakhalin fir

A significant difference between the leaching rates of C12 and C14 homologues in DW was observed only in the sapwood portion treated with 4% ACQ-1 (Fig. 6A–D). In SW, the leaching rates of the C12 homologue from the specimens treated with ACQ-1 were significantly higher than those of the C14 homologue, except for the heartwood portion treated with 4% ACQ-1. The leaching rate of the C12 homologue from specimens treated with ACQ-1 in SW was significantly higher than that in DW with significance

Table 4. Ratio of amounts of C12 to C14 homologues in wood specimens unexposed and exposed to distilled water (DW) and artificial seawater (SW)

Wood	ACQ concentration (%)	C12/C14 (w/w)		
		Unexposed	Exposed to DW	Exposed to SW
Japanese cedar				
Heartwood	8	3.53 (0.08) a	3.43 (0.11) b	3.25 (0.06) c
Sapwood	8	3.36 (0.05) a	3.26 (0.07) a	2.99 (0.03) c
Heartwood	4	3.59 (0.05) a	3.55 (0.13) ab	3.23 (0.06) b
Sapwood	4	3.53 (0.11) ab	3.50 (0.05) a	3.11 (0.07) b
Japanese larch				
Heartwood	8	3.55 (0.07) a	3.43 (0.10) a	2.89 (0.03) b
Sapwood	8	3.47 (0.10) a	3.29 (0.01) a	2.98 (0.03) c
Heartwood	4	3.38 (0.14) a	3.29 (0.03) a	2.82 (0.06) b
Sapwood	4	3.55 (0.03) a	3.55 (0.26) ab	2.96 (0.07) b
Sakhalin fir				
Heartwood	8	3.51 (0.01) a	3.38 (0.04) a	3.22 (0.08) b
Sapwood	8	3.46 (0.05) a	3.33 (0.04) b	3.11 (0.09) c
Heartwood	4	3.55 (0.06) a	3.38 (0.10) a	3.13 (0.15) a
Sapwood	4	3.53 (0.04) a	3.43 (0.08) a	3.05 (0.04) b

Within each row, ratios of C12/C14 with the same letter denote no significant difference (*t*-tests with Bonferroni correction; $P < 0.05/3$)

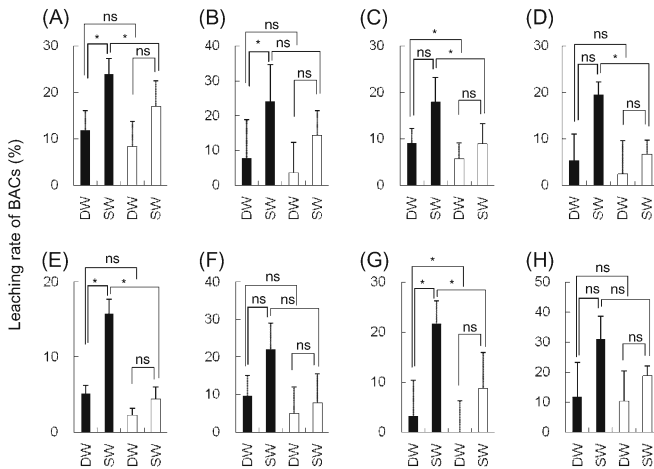


Fig. 6A–H. Average leaching rate of C12 (*solid bars*) and C14 (*open bars*) homologues in DW and SW from Sakhalin fir heartwood treated with 8% ACQ-1 (A) and 4% ACQ-1 (B), sapwood treated with 8% ACQ-1 (C) and 4% ACQ-1 (D), heartwood treated with 7.5 mM BAC in MEA (E) and 3.75 mM BAC in MEA (F), and sapwood treated with 7.5 mM BAC in MEA (G) and 3.75 mM BAC in MEA (H). Asterisk, significant difference; *ns*, no significant difference (according to paired *t*-tests with Bonferroni correction; $P < 0.05/4$). Error bars denote standard deviations

in the heartwood portion and without significance in the sapwood portion.

The leaching rate of the C12 homologues in DW was significantly higher than those of the C14 homologue only in the sapwood portion treated with 3.75 mM BAC in MEA (Fig. 6E–H). A significantly higher leaching rate of the C12 homologue than that of the C14 homologue in SW was observed in specimens treated with 7.5 mM BAC in MEA. The leaching rates of the C12 homologue in SW from the sapwood and heartwood portions treated with 7.5 mM BAC were higher than those in DW.

Leaching characteristics of BAC homologues

From the above-mentioned results, we thought that the leaching of the C12 homologue was accelerated by SW. Consequently, the leaching rate of the C12 homologue became higher than that of the C14 homologue. However, to confirm these hypotheses, the above-mentioned results are considered to be statistically insufficient. To confirm the hypotheses, we compared ratios of amount of C12 to C14 homologues in unexposed specimens and in those exposed to DW and SW.

Tables 4 and 5 list the ratios of C12 to C14 homologues (C12/C14, w/w) of the specimens unexposed and exposed to DW and SW. The ratio for the specimens exposed to SW were significantly lower than that for the unexposed specimens, except for the heartwood portion of Sakhalin fir treated with 4% ACQ-1 and the sapwood portion of Japanese larch treated with 7.5 mM BAC. These results suggest that the leaching rate of the C12 homologue is significantly higher than that of the C14 homologue in SW. Additionally, the ratios of C12 to C14 homologues for the specimens exposed to SW were significantly lower than those in DW, except for the heartwood portions of Japanese cedar and Sakhalin fir treated with 4% ACQ-1 and the sapwood portion of Sakhalin fir treated with 3.75 mM BAC. These results suggest that the leaching of C12 homologues is accelerated by SW.

The cation exchange interactions with carboxylic and phenolic hydroxyl groups of wood are thought to be the dominant mechanism in the fixation of QACs on wood.^{17,20–24} Additionally, the “ion-pair mechanism” (the clustering of ion pairs on the exchanged ion)^{25,26} is thought to be important for the fixation of QACs on wood. The formation of micelle-like aggregations of QACs plays an important role in the adsorption of QACs on cellulose fibers and the alkyl chain length of QACs influences the aggrega-

Table 5. Ratio of amounts of C12 to C14 homologues in wood specimens unexposed and exposed to DW and SW

Wood	BAC concentration (mM)	C12/C14 (w/w)		
		Unexposed	Exposed to DW	Exposed to SW
Japanese cedar				
Heartwood	7.5	1.06 (0.01) a	1.03 (0.01) b	0.92 (0.01) c
Sapwood	7.5	0.93 (0.01) a	0.94 (0.01) a	0.78 (0.02) b
Heartwood	3.75	1.01 (0.02) a	0.98 (0.01) a	0.86 (0.02) b
Sapwood	3.75	1.12 (0.04) a	1.09 (0.01) a	0.96 (0.01) b
Japanese larch				
Heartwood	7.5	1.08 (0.03) a	1.12 (0.03) b	0.96 (0.01) a
Sapwood	7.5	1.00 (0.03) a	0.91 (0.06) b	0.72 (0.04) c
Heartwood	3.75	1.07 (0.04) a	1.16 (0.04) b	1.02 (0.04) c
Sapwood	3.75	1.04 (0.03) a	1.00 (0.04) a	0.85 (0.02) b
Sakhalin fir				
Heartwood	7.5	1.03 (0.01) a	1.00 (0.01) a	0.90 (0.02) b
Sapwood	7.5	0.92 (0.02) a	0.91 (0.04) a	0.78 (0.05) a
Heartwood	3.75	1.00 (0.03) a	0.95 (0.00) a	0.84 (0.03) b
Sapwood	3.75	1.02 (0.02) a	0.98 (0.03) b	0.88 (0.01) c

Within each row, ratios of C12/C14 with the same letter denote no significant difference (*t*-tests with Bonferroni correction; $P < 0.05/3$)

tion process: an increase in the number of CH₂ groups in the alkyl chain of QACs created a more pronounced hydrophobic interaction among the alkyl chains and promoted self-aggregation.²⁷

Based on the results of our study, we present the following mechanisms: BAC retained on wood from cation exchange was exchanged with inorganic cations in SW and this exchanged BAC became available. Thus, the leaching rate of the C12 homologue was higher than that in SW. On the other hand, the leaching of the C14 homologue was less affected by SW probably because of its lower solubility in water [octanol–water partition coefficients of C12 and C14 homologues are 2.93 and 3.91 (calculated online <http://www.syrres.com>)] or its strength in forming self-aggregates based on the alkyl chain length. Therefore, the leaching rate of the C12 homologue was significantly higher than the C14 homologue in SW.

By simply comparing the average leaching rates (Figs. 4–6) and literature results,²⁰ it can be considered that the leaching rate of the C12 homologue is higher than that of the C14 homologue in DW and the leaching rate of the C14 homologue is accelerated with seawater. However, further studies are needed to confirm these speculations. Furthermore, in the case of Japanese larch, the leaching rate of the C14 homologue was significantly higher than that of the C12 homologue in DW. This discrepancy cannot be explained in the present article. Further experiments are required to clarify this phenomenon.

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