Development of a New Analytical Method for Quantifying Benzalkonium Chloride in Treated Wood and Evaluation of its Leaching Characteristics under Different Ambient Conditions

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Type-1 ammoniacal copper quaternary (ACQ-1) wood preservatives, which comprise copper and benzalkonium chloride (BAC) as active ingredients [1] are among the most widely used wood preservatives for pressure treatment in Japan as alternatives to chromated copper arsenate (CCA) wood preservatives [2]. BAC in ACQ-1 comprises homologues having different alkyl chain lengths (C12, C14, and C16 homologues), which possess different physical, chemical, and microbiological properties. Thus, it is important to elucidate the leaching characteristics of each BAC homologue in order to guarantee the protection of wood and to improve the performance of ACQ-1-treated wood. Furthermore, it is also important to eliminate the effects of environmental factors on the leaching of each BAC homologue from treated wood in order to improve the performance and extend the applications of ACQ-1-treated wood.

To investigate the leaching characteristics of each BAC homologue, a quantitative determination method was required, which could be used to quantify each BAC homologue in treated wood. Thus, during the first stage of this study, a method involving high-performance liquid chromatography with ultraviolet detection (HPLC-UV) and solid-phase extraction (SPE) was developed for the quantitative determination of each homologue in treated wood [3-5]. This method is applicable for the inspection of treated wood in keeping with official standards.

Next, by using the method developed, the leaching characteristics of the BAC homologues and the environmental factors affecting these characteristics were investigated [6]. The leaching rate of the BAC homologues from treated wood in distilled water (DW) was in the order of C12 > C14 > C16. This order of the leaching rates was identical to the order of the homologues with regard to water solubility (C12 > C14 > C16). The leaching rates of the homologues from treated wood were higher in seawater (SW) than in DW and the order of leaching rates in SW was C12 > C14 > C16. Thus, the leaching rate of the homologue having a shorter alkyl chain is higher than that of the homologue having a longer alkyl chain in both DW and SW. This tendency of the C12 homologue to exhibit a higher leaching rate than the C14 homologue was observed in a field experiment in which ACQ-1-treated wood specimens were exposed to marine conditions.

The retention of BAC homologues on wood occurs mainly via cation-exchange mechanisms by the carboxylic and phenolic hydroxyl groups in wood [7, 8]. The BAC homologues retained by these mechanisms can be replaced by inorganic cation species such as Na^+ and Mg^{2+} in SW or H^+ in acidic media. These replaced BAC homologues then undergo leaching easily; thus, SW and acidic media accelerate leaching, and the resulting leaching rates of the homologues depend on their hydrophobicities.

When the specimens were treated with 2 of the 3 homologues (C12, C14, and C16) in combination, the leaching rate of the C14 and C16 homologues from the specimens in SW was lower on treatment with a mixture of these homologues than on treatment with a mixture of C12 and either of these homologues. The leaching rates of the C14 and C16 homologues from the high-retention-level specimens were lower than those from the low-retention-level specimens in SW. The adsorption isotherms plotted for the homologues indicated that lateral hydrophobic interactions among adsorbed BAC homologues became more pronounced as the alkyl chain length increased. The ratio of aggregated BAC to the total BAC adsorbed on the wood increased as the concentration of C14 and C16 in the treatment solution increased. This ratio is considered to be higher for the mixture of C14 and C16 than for other combinations. Thus, it is assumed that the leaching behaviour of the homologues is affected by not only their hydrophobicity but also the formation of BAC aggregates on the treated wood.

Further, the leaching rate of the C12 and C14 homologues in soil (fungus cellar) was higher than that in DW. In general, soil contains inorganic cationic species such as K^+ , Na^+ , Mg^{2+} , and H^+ that also affect the leaching of BAC homologues in soil. In addition, the leaching rates of the C12 and C14 homologues were higher in leaching medium containing water-extractable wood components than in DW. Thus, it was assumed that the organic matter in the soil also affected the leaching of the homologues.

However, a critical difference was observed between the leaching characteristics in soil and in other

ABSTRACTS (PH D FOR GRADUATE SCHOOL OF AGRICULTURE)

leaching media in that the leaching rate of the C14 homologue from the treated wood was higher than that of the C12 homologue in the former. This result indicates that the leaching characteristics of BAC homologues in soil cannot be reproduced in distilled water, seawater, and acidic water. The leaching rate of the C14 homologue was also higher than that of the C12 homologue when leaching medium containing water-soluble wood components was used, and the rates recorded correlated with the concentration of phenolic compounds in the medium. Furthermore, taxifolin (phenolic compound) induced the higher leaching rate of C14 as compared to C12. Thus, phenolic compounds present in soils or generated during the decay of wood may be responsible for this discrepancy between the results obtained when soil was used and when other media were used.

Based on the results of the present study, the leaching mechanisms of BAC homologues and the effects of environmental factors on these mechanisms have been summarized in Fig. 1. The results indicate that leaching experiments should be conducted to evaluate the performance of wood treated with preservatives containing BAC as the active ingredient under different environmental conditions in which wood is used and with consideration to the various environmental factors it is exposed to. To prevent the leaching of BAC, the appropriate formulation of BAC homologues in wood preservatives should be selected depending on the environments in which the treated wood is used. For wood used in environments exposed to water or SW, BAC that mainly comprises homologues having longer alkyl chains should be used. On the other hand, for wood used in contact with the ground, BAC that mainly comprises homologues having shorter alkyl chains should be used.

For the further improvement of ACO-1-treated wood, future investigations should focus on the effects of combinations of homologues having different alkyl chain lengths on leaching in soil and in media containing phenolic compounds.



Fig1. Interactions of benzalkonium chloride (BAC) with wood and environmental factors.

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