

Prediction and evaluation of borate distribution in Eastern black spruce (*Picea mariana* var. *mariana*) wood products

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Abstract Borate distribution and content in re-wetted brush-treated Eastern black spruce (*Picea mariana* var. *mariana*) blocks were investigated by near-infrared spectroscopy (NIRS). Samples were brush-treated with 40 % glycerol-based DOT ($\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$) and then conditioned for different durations (5, 9, 20, and 30 days) at high relative humidity (approaching 100 %). The effect of a glue-line on the borate distribution and content was also evaluated. Borate penetration depth was estimated in the radial direction in wood block samples. The evaluation of borate's diffusion gradient in terms of boric acid equivalent was conducted on the whole radial plane of the other portion of wood samples that were sliced every 0.4 cm in the radial direction. The effect of glue-lines was evaluated using two wood strips glued together. Calibration models achieved R^2 ranging from 0.4 to 0.5 and root-mean-square error (RMSE) ranging from 0.28 to 0.31 %. The statistic for validation achieved R^2 ranging from 0.3 to 0.4 and RMSE ranging from 0.31 to 0.34 %. NIRS had some predictive abilities for borate distribution and borate concentration using the projection to latent structures-PLS regression method.

Introduction

Borate formulations are generally considered to be safe and effective fungicides and insecticides. Their efficacy is not constrained by their poor resistance to water leaching when they are used in the interior of buildings (Thevenon and Pizzi 2003;

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Freitag and Morrell 2005). Borate preservatives can easily be applied to critical components of buildings by several methods prior to construction to provide latent protection in case the area becomes wet (Grace and Yamamoto 1994; Obanda et al. 2008). They can also be applied in situ in response to observed moisture penetration or biological deterioration (Blow and Summers 1985; Lebow et al. 2013). Borates can diffuse into vulnerable areas when they become wet. They can penetrate refractory wood such as Douglas fir heartwood which cannot easily be penetrated by pressure treatment (Morrell et al. 1990; Lloyd et al. 1999; Rhatigan et al. 2002). Borate in waterborne preservative solutions can easily penetrate wet solid wood by diffusion to achieve adequate penetration and retention to protect wood, with minimal effect on wood mechanical properties (Drysdale 1994; Mounanga 2008; Piao et al. 2009). The effect of glue-lines on borate movement in solid wood composites, such as glued-laminated timbers and cross-laminated panels, is also of interest (Dirol 1988; Felix and Gatenholm 1991; De Groot et al. 2000; Lebow et al. 2010). Different techniques have been used to monitor the borate distribution and borate concentrations of treated wood; however, the majority of them are either qualitative or require elaborate analytical techniques (AWPA 1996, 2000, 2005; Awoyemi et al. 2009; Saadat 2012). Quantitative analysis methods are destructive and time-consuming (Watanabe et al. 2011; Tsuchikawa and Schwanninger 2013; Leblon et al. 2013). Alternative nondestructive radiation techniques, such as near-infrared spectroscopy (NIRS), coupled with multivariate statistical methods have been investigated to quantitatively estimate boron-based preservative concentrations in treated pine (*Pinus spp*) sapwood (Taylor and Lloyd 2007). NIRS has been used as a quality assurance tool for the wood preservation in the industry (Stirling 2013) to predict wood moisture content and chemical composition of wood surfaces (Koumbi-Mounanga et al. 2014), to predict stiffness of radiata pine (*Pinus radiata* D. Don) veneers (Meder et al. 2002), and to predict surface color, contact angle and adhesive bond strength of Douglas fir (*Pseudotsuga menziesii* var. *menziesii*) veneers and trembling aspen (*Populus tremuloides* Michx.) strand products (Koumbi-Mounanga et al. 2013, 2015).

In this study, the potential of NIRS to estimate borate distributions and borate concentrations in Eastern black spruce (*Picea mariana* var. *mariana*) wood products is assessed. Boron penetration depth and boron-based preservative concentrations are estimated by partial least square regression models of NIRS measurements. The effect of glue-lines in a solid wood composite on borate diffusion is also studied. Such a study may help in the development of an easy-to-operate and portable analytical tool to determine borate distributions and borate concentrations of wood products by the industry.

Materials and methods

Sample preparation for borate distribution and for glue-line effect

Samples of Eastern black spruce (*Picea mariana* var. *mariana*) lumbers were acquired green from a local lumber supply store Midway Lumber Mills LTD

(Thessalon, ON, Canada). They were kept in conditioning chamber at 15 °C and relative humidity (RH) >95 % until surface-planed and cut into forty wood blocks with $3.5 \times 6 \times 9 \text{ cm}^3$ dimensions in tangential, longitudinal and radial directions, respectively. These samples were used to study the borate distribution, borate content and effect of a glue-line (Fig. 1). Twenty of the blocks were bonded to $1 \times 3.5 \times 6 \text{ cm}^3$ (radial/tangential/longitudinal) wafers with liquid phenol–formaldehyde (PF) resin supplied by Momentive Specialty Chemicals Canada, Inc. (Edmonton, AB, Canada) to study the glue-line effect. Manufacturer specifications for PF physical and chemical properties are described by Momentive (2011). All samples (without and with glue-line) were pressure-treated with water until they reached the target moisture content (approaching 100 %) with a vacuum pressure process cylinder using vacuum at 11 kPa absolute pressure for 30 min, pressure at 689 kPa overnight (24 h) and a final vacuum at 11 kPa for 15 min. Individual samples were then brush-treated on the top (tangential) area of the $3.5 \times 6 \text{ cm}^2$ surface using a solution of 40 % disodium octaborate tetrahydrate (DOT) in propylene glycol commercially available from the SANSIN Corporation (Strathroy, ON, Canada).

All samples were wrapped in plastic to minimize drying during the test and stored at 22 °C and RH >98.9 % in a Drytech kiln (USA series 3900MC). All samples were conditioned for different durations (5, 9, 20 and 30 days). In order to analyze the borate distribution, samples were sawn in half, lengthwise in the radial direction; one portion was used for measuring the penetration depth and the other portion, for measuring the borate gradient along the grain.

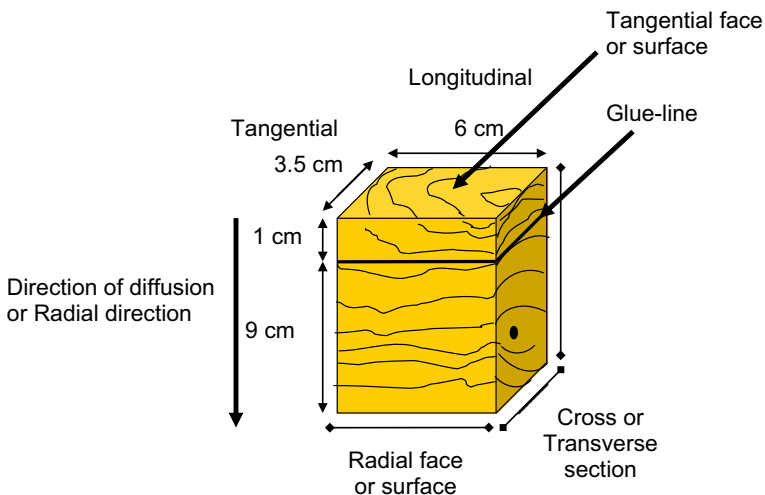


Fig. 1 Example of a wood block sample with glue-line sawn longitudinally (lengthwise) from boards radially generated from logs that were cut longitudinally at the saw mill

Sample preparation for penetration depth analysis

Samples used for borate penetration depth analysis were prepared from black spruce strips which measured 90–100 mm radially, 35 mm tangentially (widthwise) and 10 mm along the grain. The top (tangential) surfaces of the wood strip samples were brush-treated with DOT glycerol, and penetration depths in the radial direction were determined. The borate penetration depth of the whole section was revealed by spraying a curcumin reagent (0.25 g curcumin, 10 ml concentrated hydrochloric acid and 10 g salicylic acid in 100 ml ethanol as described in Williams 1968) on the split surface of three replicate boron-treated samples. A red/pink coloration develops at a level of concentration of preservative equivalent to more than 0.2 % boric acid (Murphy and Tuner 1989), while untreated wood zones are pale yellow. The duration for revealing coloration ranged from 5 to 20 min, and measurements were expressed in % of penetration depth (% borate coverage of the exposed surface). The whole section (radial face) was analyzed to determine the boron retention in wood by ICP spectroscopy. The ICP spectroscopy measurement was expressed in % boric acid equivalent (e.g., Williams 1968; Cockcroft 1974). Both borate measurements were then related to the scanned NIR spectra.

Sample preparation for gradient analysis

The gradient of borate diffusion was conducted by analyzing thin wood wafers cut from one portion of wood blocks sawn radially every 0.4 cm starting at the borate-treated surface. The whole wafer was analyzed. Wood wafer samples were ground to powder with a Thomas-Wiley laboratory mill grinder (USA model 4) and screened with a 2-mm mesh Tyler equivalent filter (USA series equivalent NO 18). Borate was extracted from about 0.5 g of sawdust in 40 ml of hot (90 °C) distilled water for 4 h in a Blue M water bath (USA model MW1165C-Serial No M71211), and the resulting extracted solution was diluted 50 times (about 250 ml of final volume) and then analyzed by ICP spectroscopy as described in AWP standard A21-00 (AWPA 2000) and AWP standard A03-05 (AWPA 2006).

Spectral measurements

Samples were bagged and kept in conditioned ambient temperature storage in a chamber at 23.5 °C under drying conditions (relative humidity = 0–2 %) prior to scan. NIR spectral data were acquired from different wood wafer samples in the direction of borate diffusion at 2-min intervals with an Ocean Optics Inc. Labspec[®] 256-HL-2000 NIR spectrophotometer (Ocean Optics Inc., 830 Douglas Ave, Dunedin, FL34698 USA) equipped with an optical probe positioned on the top of the sample with a 2-mm-diameter beam. The instrument has a spectral resolution of 2 nm and was calibrated manually for white/dark after every performed triplicate measurement. Each wafer sample was scanned three times on both top and bottom surfaces (bark-side up and bark-side down) particularly on flat zones that bordered the sample. The measurement procedure was done with all samples including for the

configuration of glue-line samples where scans were additionally conducted around the glue-line's zone.

Data processing

The data processing was done using the Unscrambler[®] 9.8 (CAMO software. Inc., 1 North Cir., Woodbridge, NJ 07095-2105, USA). The NIR absorbance spectra acquired at the wavelength 1100–2400 nm region were smoothed by applying a second derivative 10pt Savitzky–Golay transformation and then related by the projection to latent structures-PLS regression method to various DOT glycerol contents obtained from wood wafer samples. PLS regressions were computed with full cross-validation. There were sufficient number of scans recorded for the Unscrambler[®] program to be used for model development and to be classified as independent calibration and validation sets within two factors determined based on RMSE values, to give an optimal prediction for the modeling (Boulesteix and Strimmer 2006; Rosipal and Kramer 2006; Esbensen et al. 2002; Geladi and Kowalski 1986). Performance of PLS models was calculated with the relative percent difference (RPD) in order to estimate the ratio of the standard error of performance (SEP) to the standard deviation (SD) of the reference data of DOT glycerol as described by Williams and Norris (1987) and Natsuga and Kawamura (2006). In addition, the sample-specific standard error of prediction was computed using the Unscrambler program to separate the performance of treated and non-treated wood specimens (control samples) at different durations. Confidence bands of standard deviation (SD) were associated with specific data samples of the prediction performance following the method described in Faber et al. (2003).

Results

Radial penetration depth of wood block portions: borate penetration depth versus borate retention by treatment durations

The borate distribution was analyzed for the penetration depth and the borate diffusion gradient. Observations regarding the borate diffusion gradient are examined in the second part of the study. Glue-line effects are analyzed in both study sections. It is noted that some illustrations are accessible as electronic supplementary material. The % of borate coverage and the % of boric acid equivalent (BAE) related to the whole radial plane of wood block samples after different diffusion times are shown in Fig. 2. The influence of the glue-line on the boron diffusion was demonstrated by simple comparison of observations obtained from samples without and with glue-line. Regardless of whether samples were with or without a glue-line, preservative penetration depths increased significantly and in a similar way with treatment durations. The % BAE significantly increased as a function of treatment durations with maximum values after 30 days. For the samples without glue-line, percentage values of coverage yielded progressively 34 % at 5 days, 38 % at 9 days, 40 % at 20 days and 42 % at 30 days. Similarly, the %

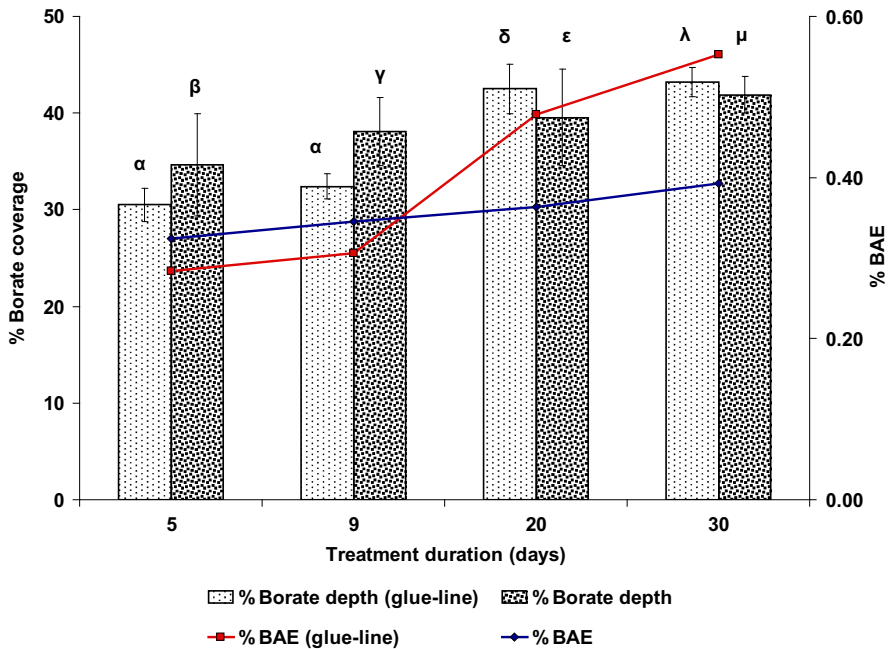


Fig. 2 Distribution of the borate coverage and borate diffusion expressed in boric acid equivalent (BAE) at different treatment times and for constant moisture content. For each probe, values having the *same* letter (α , β , γ , δ , ϵ , λ , μ) are not significantly different at the 5 % level of confidence

BAE retention increased as a function of treatment duration. Thus, values yielded 0.32 % at 5 days, 0.35 % at 9 days, 0.36 % at 20 days and 0.39 % at 30 days. The progressive evolution of % BAE was almost the same with glue-line samples, although the samples with the glue-lines had lower values for earlier treatment durations but higher values later on. The standard deviations ranged from 1.3 to 2.54 for samples without glue-line and from 1.9 to 5.31 for samples with glue-line. There should be no influence of the moisture content (MC) because the MC was kept constant at 100 % during the phase of brush treatment of samples. At 5 days, borate retention reached about 0.32 % BAE for samples without glue-line and 0.28 % BAE for samples with glue-line. For both sample configurations, this was approximately double the value of the minimum level required to protect wood of around 0.15 % BAE. However, further experiments should be conducted for treatment durations within 24 h. The related borate coverage or penetration depth was 35 % for samples without glue-line and 31 % for samples with glue-line.

Study of borate diffusion gradient along the diffusion direction of wood block portions: borate diffusion as a function of treatment durations

The borate gradients in black spruce samples by treatment duration are shown in Fig. 3. Apart from the wafer closest to the treatment point, where the concentrations tended to decrease with treatment duration, the gradients were similar for the

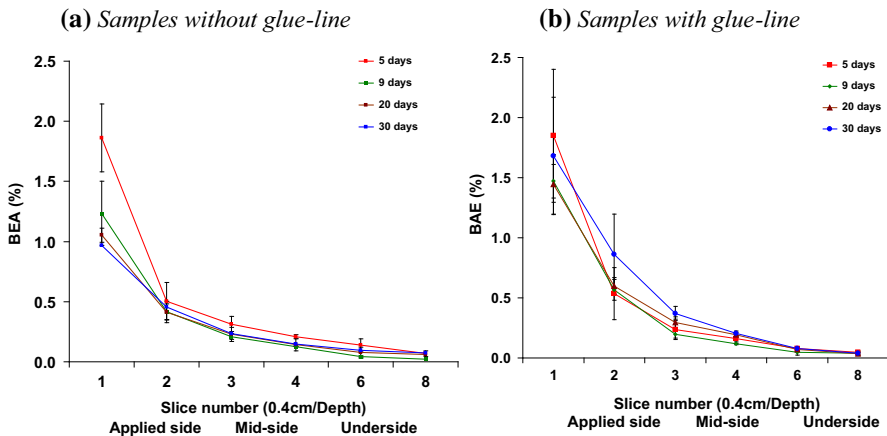


Fig. 3 Gradient of borate diffusion in radial direction from the edge grain of the wood block for samples conditioned at different durations and at constant moisture content. Each *dot* represents an average of three replicate samples

different durations. It is evident that the glue-line did not inhibit borate movement relative to the sample without a glue-line. After 30 days, the borate level in both cases was close to 0.15 % BAE, the level to control decay, to a depth of 1.6 cm.

Prediction of borate diffusion gradient

The NIRS predictions of borate retention (% BAE) for the different treatment durations and locations in the samples are presented in Fig. 4. Absorbance data acquired in the 1100–2400 nm region (three scans averaged per point) were used for the prediction (spectral data results not shown). PLS models of DOT concentrations were built for both sample configurations (without and with glue-line). The regression in both samples was able to provide reasonably good correlations between the measured and predicted values. The correlation of DOT glycerol values was 0.688 and 0.716 for specimens without and with glue-lines, respectively. R^2 values for calibration models were 0.474 and 0.513 successively for samples without and with a glue-line. Validation regressions of samples without and with a glue-line yielded R^2 of 0.362 and 0.445, respectively. RMSE (calibration/validation) ranged from 0.2832 to 0.3120 % and 0.3174 to 0.3396 %, respectively. For both sample configurations, PLS regression models were significant at p value < 0.0001 (Fig. 4).

Comparison of measured values versus predicted values of borate diffusion gradient by treatment durations

Comparison between measured and predicted borate retention at different treatment durations is reported in Figs. 5 and 6, showing differences in each individual gradient of borate prediction with treatment duration.

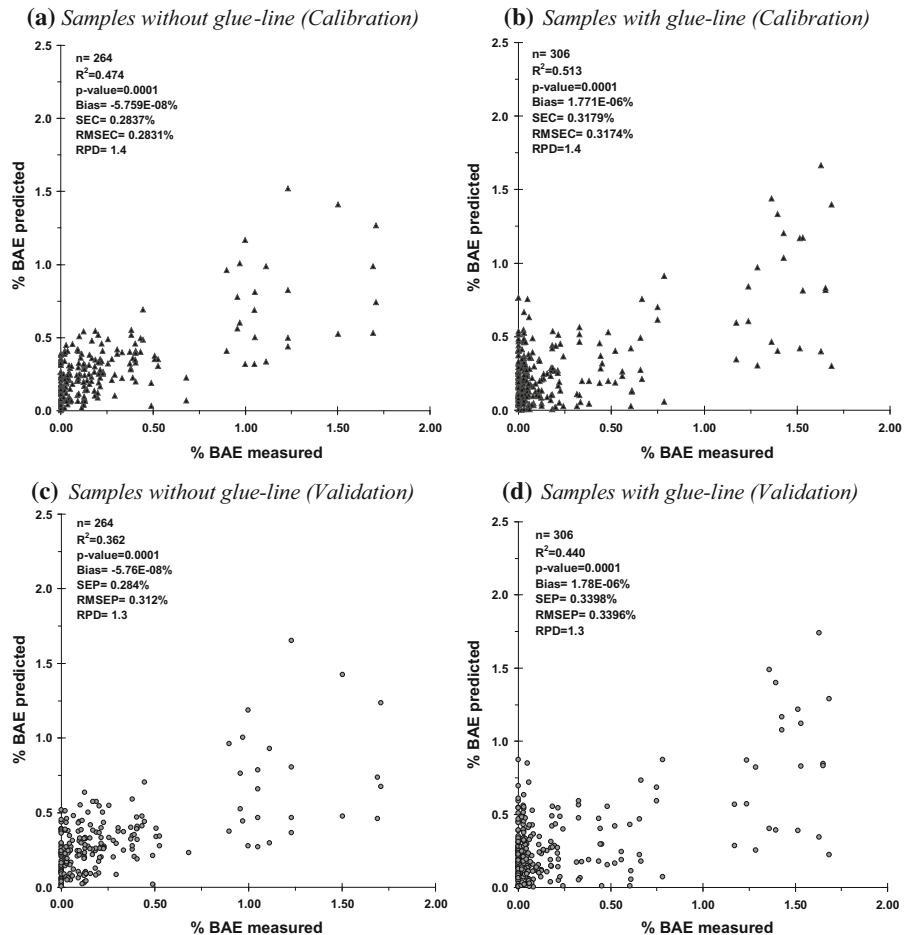


Fig. 4 PLS regression models of boron contents (BAE in %) for the whole sample conditioned at various treatment times. Each *dot* represents an average of three spectra for calibration and validation

After 5 days of diffusion time, NIRS tended to underestimate higher borate concentrations and overestimate lower concentrations (Fig. 5a, b). After 9 days duration (Fig. 5c, d), low borate values deeper in wood samples were again overestimated. Thus, NIRS prediction tends to indicate that levels are above the decay toxic threshold when in fact they are not. For the longer durations (Fig. 6a, b, c, d), predicted concentrations were closer to the analyzed values, although at 30 days, the predicted levels were also higher than the measured ones for lower concentrations.

Sample-specific standard errors of borate prediction

Sample-specific standard errors of borate prediction were different for all treatment durations and for both samples without a glue-line (Fig. 7a) and samples with a

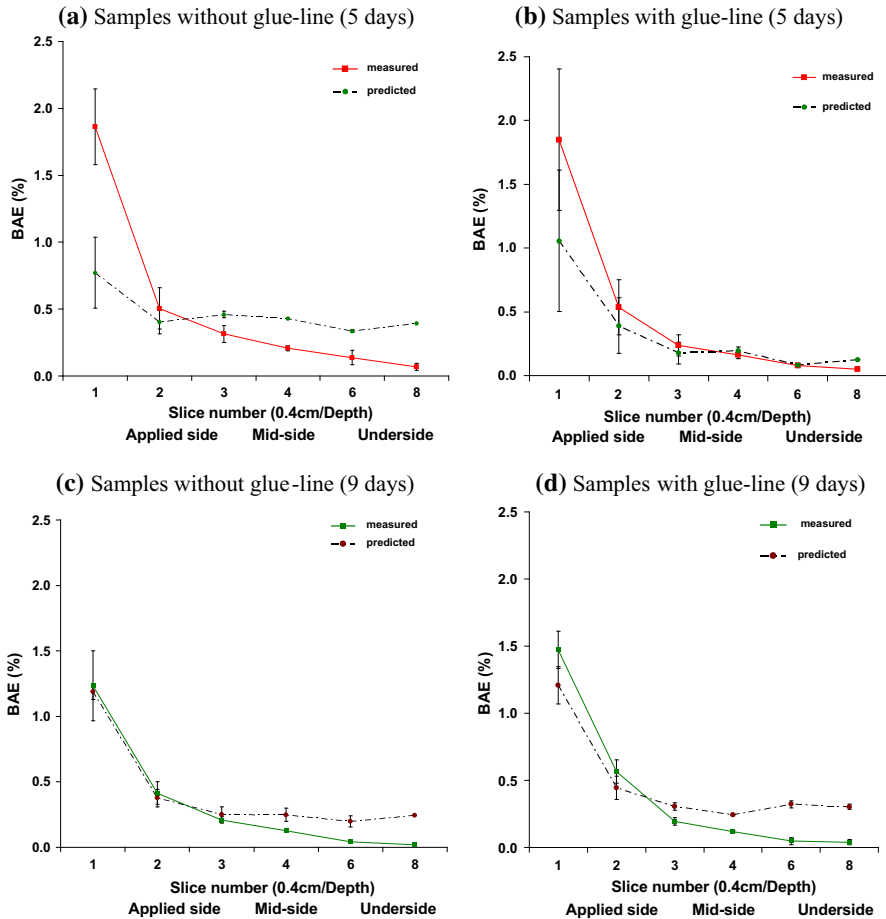


Fig. 5 Predicted versus measured values of boron contents (BAE in %) for individual conditioning at 5 and 9 days. All measurements were performed in triplicate

glue-line (Fig. 7b). Sample-specific standard errors of DOT prediction were differentiated when measurements were done at around 5 and 9 days (Fig. 7). When measurements were done on samples without a glue-line, sample-specific standard errors of DOT expressed clearly the borate prediction by grouping the differentiation of specimens at 5 and 9 days (Fig. 7a) in contrast to when measurements were done with glue-line samples for the same period (Fig. 7b). Average standard deviation values were in a similar range for samples both without and with a glue-line; they were: 0.276 and 0.295 at 5 days; 0.227 and 0.376 at 9 days; 0.197 and 0.353 at 20 days; 0.326 and 0.376 at 30 days.

Maximum standard deviation (SD) values and the related % BAE were the following for samples without and with glue-line:

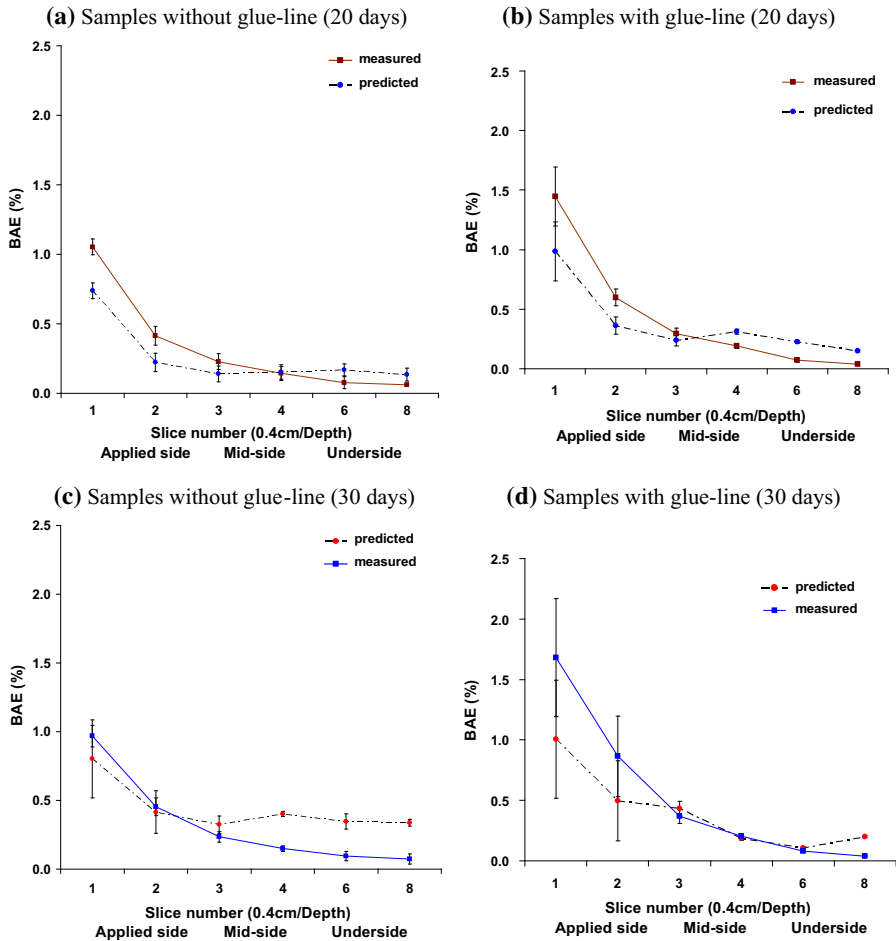


Fig. 6 Predicted versus measured values of boron contents (BAE in %) for individual conditioning at 20 and 30 days. All measurements were performed in triplicate

0.312 (SD) obtained at 0.335 % BAE and 0.327 (SD) obtained at 0.349 % BAE from 5 days;

0.227 (SD) obtained at 0.376 % BAE and 0.433 (SD) obtained at 0.322 % BAE from 9 days;

0.287 (SD) obtained at 0.737 % BAE and 0.457 (SD) obtained at 0.033 % BAE from 20 days;

0.448 (SD) obtained at 0.825 % BAE and 0.583 (SD) obtained at 0.134 % BAE from 30 days.

All predicted concentrations were obtained from the core zone before the center of wood block samples. They were in most cases around 0.30–0.35 % BAE, which was about double the minimum level for protection against biodegradability of wood borate-treated components.

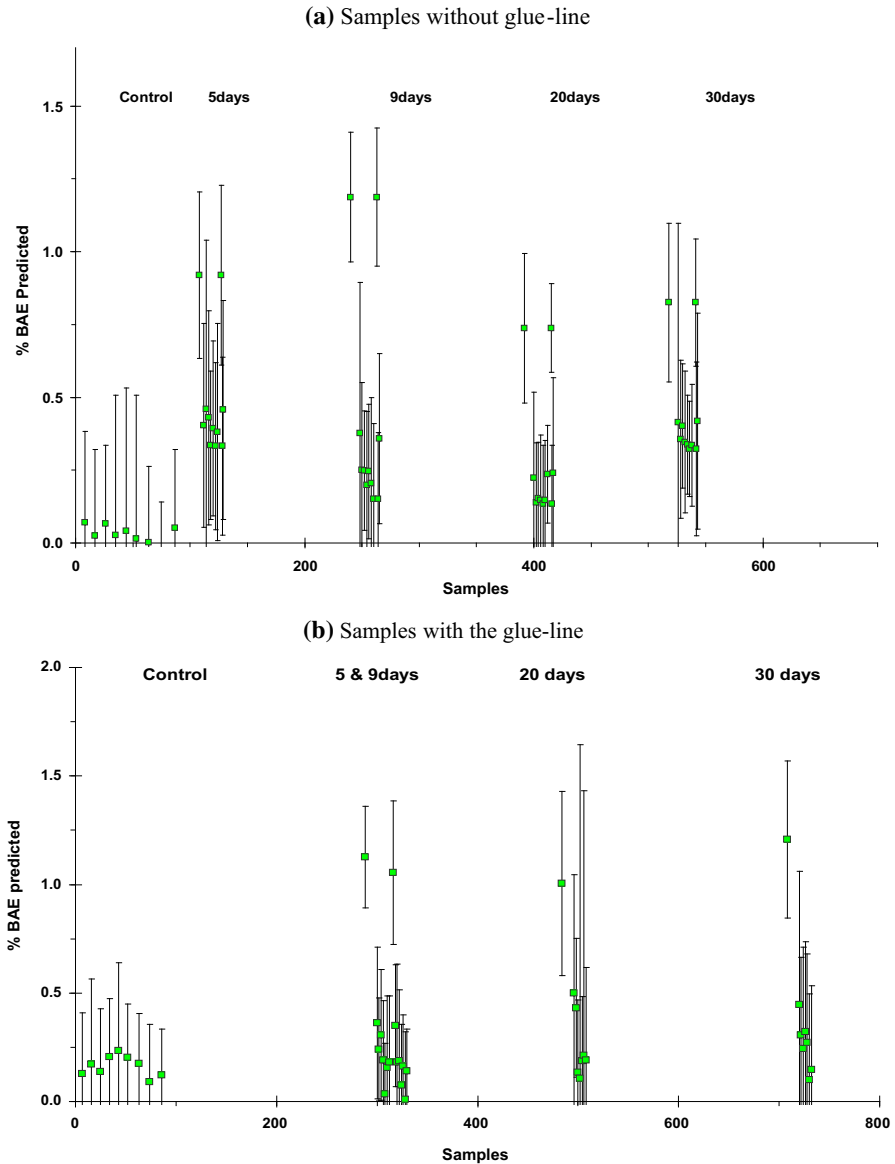


Fig. 7 Sample-specific standard error of prediction for boron content of predicted values versus measured values of Eastern black spruce. Each *dot* represents an average of three spectra, and the *error bars* are calculated by incorporating the standard deviation of measurement error into the predicted data values

Relative percent differences (RPD) in both sample configurations (without and with glue-line) were about 1.4 for DOT glycerol reference values and about 1.3 for predicted values.

Discussion

Study of penetration depth from radial surfaces of wood block portions: borate penetration depth versus borate retention by treatment durations

The % BAE concentrations significantly increased with treatment durations and penetration depths. Lebow et al. (2010, 2013) and Colak and Colakoglu (2004) reported similar results on borate distributions studies in samples from Southern pine (*Pinus* spp) lumber and beech (*Fagus* spp) veneers. Both experiments showed an improved penetration depth that increased proportionally with borate retentions and treatment durations. The present study showed similar results for borate diffusion from both sample configurations. It seems that there was no significant effect of the glue-line on the borate diffusion through the specimen because, although a glue-line appears as a monolithic barrier, any effect to slow down the borate migration flow through the treated wood is more like a sieve (Colakoglu et al. 2003; Waldron and Cooper 2010). Thus, differentiation appeared more at around 5–9 days of treatment durations (Fig. 2). In addition, eventually glue-lines' gaps in structural laminated composites allow borate to diffuse laterally through those longitudinal interruption bands of wood glue-lines analogous to the effects of radial splits (crosswise). The study suggests that some of the treatment durations should be shorter and should require, before being boron-treated, the use of variable moisture contents as well as other treatment types than brush treatment, which should use for example boron rod inserted at the in situ active site of degradation in the building construction. Clearly, the low costs associated with any conditioning of the study would have to be incorporated into an assessment of the commercial variability of the method.

Study of borate diffusion gradient of the wood block portion: borate diffusion as a function of treatment durations

Borate distribution in the radial direction was assessed by the borate diffusion gradient that was described progressively with different treatment durations. The shape of borate distribution flow was the same along the grain for all treatment durations and for all wood sample configurations. Similar observations were performed in Tsunoda (2001) with regard to an estimation of preservative properties of vapor-boron-treated wood and wood-based composite.

Prediction of borate diffusion gradient

PLS regressions of borate distribution in % BAE over different treatment durations were reasonably well performed in terms of the calibration R^2 ranging from 0.474 to 0.513 and the validation R^2 ranging from 0.362 to 0.445 for samples without and with a glue-line. RMSE (samples without and with glue-line) ranged from 0.2832 to 0.3120 % and 0.3174 to 0.3396 %, respectively. It can be seen from Fig. 4 that NIRS could have some application as a rapid method for the estimation of the borate

distribution and the borate retention in small block areas of black spruce samples. This ability to rapidly evaluate the distribution of boric acid containing preservatives over small areas was also observed by Williams (1968). In addition, Taylor and Lloyd (2007) found good R^2 of 0.96 and 0.86 for calibration and validation, respectively, for an experiment conducted with wood cubes from southern pine (*Pinus spp*) sapwood samples that were treated with boron content DOT concentrations ranging from 0.01 to 15.0 %. RMSE for calibration and validation yielded 0.92 and 2.12 %, respectively.

The present study showed similar results to those performed with regard to moisture contents of black spruce (*Picea spp*) logs by Hans et al. (2013), Douglas fir (*Pseudotsuga menziesii* var. *menziesii*) and trembling aspen (*Populus tremuloides* Michx.) veneers by Koumbi-Mounanga et al. (2013, 2014), which have R^2 ranging from 0.46 to 0.86 and RMSE ranging from 4.47 to 23.35 %.

Comparison of measured versus predicted borate diffusion gradient by treatment durations

Relationships of measured and predicted DOT diffusion gradients by treatment durations are represented in Figs. 5 and 6. They were weaker than those found on southern yellow or loblolly pine (*Pinus taeda* L.) (Jordan and Wellons 1977), longleaf pine (*Pinus palustris* Mill.) (Lloyd and Manning 1995; Christiansen 1991) and Douglas fir veneers (*Pseudotsuga spp*) (Lloyd et al. 1999; Koumbi-Mounanga et al. 2013), which had correlations between measured and predicted values ranging from 0.69 to 0.78. It seems evident from Figs. 5 and 6 that individual treatment durations affected differently the flowing of the borate gradient in terms of depth distance to be achieved radially in samples.

The NIR absorbance bands involved (1250, 1620, 1820 and 2200 nm spectral regions) might be induced by the boron-based preservative concentration due to basicity influence of borate in the reaction with phenolic compounds of wood wafers. This is also observed in the degradation of the cell wall polymers as likely as not, the phenomenon occurring in case of thermal treatment of wood. The spectral regions previously mentioned are related to the overtones of fundamental vibrational transitions in infrared region, mainly C–H (hydrocarbons...), C=O (cellulose, hemicelluloses...), O–H (water, alcohol, phenol...) and N–H (lignin...) functional groups (Thygesen and Lundqvist 2000; Schwanninger et al. 2011; Cozzolino et al. 2003; Leblon et al. 2013). Other hypothesis explicative might involve the oxyanion reactions within complex chemical reactions in the wood sites. The boron-based preservative treatment reaction with the wood wafer components was also identified in different investigations as cause of carbohydrate degradation and deacetylation reactions of polyoses in case of thermal treatment of wood. However, future estimation should involve and incorporate more parameters (temperatures, etc.) within more factors for an easy interpretation of the data (Mitsui et al. 2008; Burns and Ciurczak 2008; Bächle et al. 2010).

Sample-specific standard errors of borate prediction

Sample-specific standard errors of prediction of DOT glycerol retention of black spruce wood samples were done according to experiments conducted at different treatment durations and for both configuration samples studied. They were assessed with an average margin of standard deviation ranging from 0.197 to 0.376 over all treatment durations. Williams (1968) showed similar variability results to Sitka spruce (*Picea sitka* spp) boards; the standard deviation was based on nine determinations from 0.018 to 0.4 % boric acid equivalent concentration levels.

Relative percent differences (RPD) computed in the present study were 1.3 and 1.4 for DOT glycerol predicted values and reference values, respectively. RPD values obtained were under-performed compared to results by Koumbi-Mounanga et al. (2015) who differentiated the quality of performance of three drying cycles of moisture content prediction. This study obtained RPD for calibration and validation from 5.3 to 12 and 5.3 to 11.2, respectively. In the same context, a qualitative study determining physicochemical properties of rice by Natsuga and Kawamura (2006) interpreted those RPD values as poor models for repeatability.

Conclusion

The present study assessed the potential of near-infrared spectroscopy (NIRS) for the prediction of borate distribution in Eastern black spruce (*Picea mariana* var. *mariana*) wood block samples at different conditioning durations. A modest correlation between measured and predicted DOT glycerol values was found, and NIR scans could detect the slight effects of a glue-line on borate distribution. Glue-line effects on the distribution of boric acid equivalent need to be investigated further in products like cross-laminated timber (CLT) structures. Further developments of the experiment need to target different wood species as well as other preservative formulations using NIRS. This approach may also have important implications for the treatment of solid wood for CLT and other composites using refractory wood species. Borate distribution related to PLS regression models of various treatment durations that induced progressively the boric acid equivalent content-based DOT glycerol in the Eastern black spruce was presented. Such an approach is still empirical, and physics-based models needed to be developed to explain chemical reactions and other mechanism influences involved in borate treatment of structural composites. Further, the study was based on laboratory measurements, and an operational method that can be used in the manufacturing plant environment is still to be developed.

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