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Toxicity of sodium fluoride to subterranean termites and leachability as a wood preservative

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Abstract Wood preservation is one of the most effective methods to prevent damage caused by termites. Sodium fluoride (NaF) is a well-known fungicide for preventing decay in timber due to its excellent diffusion in wood. In this study, the toxicity of NaF to the termites *Reticulitermes flaviceps* and its potential leachability as wood preservative were assessed. While termites were in contact with NaF-treated filter paper in a Petri dish for nine days, termites were found completely dead while the papers were treated by NaF at concentration of 0.5 % (wt/wt) or above. Wood blocks of *Pinus massoniana* were treated with five different concentrations of NaF (0.1, 0.25, 0.5, 1 and 2 %) respectively, and then exposed to a non-soil-contact field leaching experiment. After 4 weeks, retention levels of NaF in the wood blocks dropped from 0.075–0.834 % to 0.057–0.284 %. A choice test, in which NaF-treated and untreated wood blocks were exposed to the termites *R. flaviceps* was conducted. The results showed NaF, even at retention of 0.057 % (wt/wt), could significantly inhibit termite feeding in the treated blocks. The results suggest that NaF is a suitable wood preservative with anti-feedant activity against termites.

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1 Introduction

Subterranean termites are economically important insects which can cause serious damage to wooden structures and trees. One method of preventing subterranean termite damage is to establish a physical or chemical barrier around wooden structures. The physical barriers include the use of sand or stainless steel mesh to prevent termites entering the buildings (Su and Scheffrahn 1992). Chemical barriers consist of termiticides in the soil around the structures (Su et al. 1993; Pan et al. 2011).

An alternative method to protect timber from termite damage is to modify the internal structure of the wood. Wood modified with dimethyloldihydroxy-ethyleneurea (DMDHEU), or by acetylation or furfurylation was shown to be resistant to dry wood and subterranean termites (Militz et al. 2011; Rowell 2006; Hadi et al. 2005). The treatment of wood with the preservative CCA (chromated copper arsenate) effectively inhibits termite damage (Grace 1998). However due to environmental concerns CCA has been banned or its use has been limited in Europe, Japan and North America (Schultz et al. 2007). Wood treated with boron-based preservatives, such as disodium octaborate (DOT), boric acid and metaborates, is resistant to termite damage (Furuno et al. 2003; Usta et al. 2009). However, boron-based preservatives are generally ineffective when used to treat timber for outdoor use due to the ease of leachability from the wood.

Fluoride has been used for many years in Europe and the United States to treat wooden railway ties (Becker 1973, 1976). When fluoride was initially introduced as a wood preservative there were adverse reactions with nickel, zinc, or copper in double-diffusion treatments (Baechler 1953). Later on, bifluorides were introduced as wood preservatives in Germany to prevent damage on timber by the European House Borer *Hylotrupes bajulus* (L.) larvae (Becker 1974).

Because of its effectiveness against fungal attack, fluoride became an important component of many remedial treatment systems (Morrell and Love 1995). In the USA, Flurods (98 % sodium fluoride, Osmose Utilities Services, Inc.) was registered by the EPA (Registration Number 3008-63) for internal remedial treatments of wood poles. In Australia, fluoride rods were also used for remedial treatment of internal decay in hardwood power poles. To date, research on sodium fluoride as a wood preservative has focused on its spread, fungal inhibition and methods of analysis in preservative treated wood (Chen et al. 2003; Freitag and Morrell 2005; Cabrera and Morrell 2009). However, the efficacy of sodium fluoride against termites is poorly documented and requires further investigation. The objectives of this paper were to evaluate the toxicity of NaF to the termites *Reticulitermes flaviceps* and investigate its leachability as a wood preservative.

2 Materials and methods

2.1 Materials

Sodium fluoride (NaF) as a fluoride was tested in this paper (Aladdin-reagent). Filter papers ($\Phi = 90$ mm, Whatman) were prepared with various concentrations of sodium fluoride and presented to termites in a no-choice toxicity test. Sapwood blocks ($t = 20 \times r = 30 \times l = 50\ mm^3$) of *Pinus massoniana* were prepared for impregnation and subsequently used for laboratory and field tests.

Reticulitermes flaviceps is one of the most economically important subterranean termites in China. In this study, workers of *R. flaviceps* were collected by trapping at the campus of Zhejiang A&F University and maintained in a rearing room at 25 °C and 65 % relative humidity (RH).

2.2 Toxicity tests

A piece of filter paper was placed in a Petri dish ($\Phi = 90$ mm). The filter paper was evenly wetted with 1 ml of NaF solution at concentrations of 0, 0.1, 0.25, 0.5, 1 and 2 % (wt/wt) respectively. Four replicates were prepared for each treatment. Thirty termite workers were introduced into each Petri dish. The Petri dishes were placed in a dark incubator maintained at 25 °C and 65 % RH. Dead termites were recorded daily for nine days. Termites which did not respond to prodding with a pencil tip were considered moribund or dead (Pan et al. 2011).

2.3 Wood impregnation

Wood blocks were vacuum-treated at 0.9 Mpa for 30 min, and then impregnated with the NaF solutions for 5 days at atmospheric pressure. Five NaF concentrations (0.1, 0.25, 0.5, 1 and 2 %) were prepared. The impregnated wood blocks were cleaned with blotting paper and stored in a climatic chamber for 2 weeks at 25 °C and 65 % RH. Impregnated blocks were used for field leaching and termite resistance tests. Twenty replicates were prepared for each treatment. These blocks were subsequently weighed prior to being oven-dried at 103 °C for 48 h.

Fig. 1 Thirteen blocks of *Pinus massoniana,* from each NaF treated group, exposed to the field for 4 weeks to assess leachability

2.4 Field leaching

Field leaching was performed in order to imitate sodium fluoride runoff from wood exposed to the weather. Thirteen blocks from each NaF-treated group were put in a plastic frame which was perforated at sides and sealed at the top and bottom (Fig. 1). Then, the plastic frame was buried 20 cm belowgound in the campus of Zhejiang A&F University (119.73°E, 30.26°N) on March 5th, 2012. There were on average 20 rainy days with average rainfall and temperature for the month of March of 266.5 mm and 9.2 °C, respectively (data from Hangzhou Meteorological Bureau, China). After 4 weeks, blocks were collected and assessed to determine NaF retention level and mass loss.

2.5 Termite resistance tests

Untreated and treated (impregnated and impregnated/leached) blocks were exposed to *R. flaviceps* in choice feeding tests. A pair of control and treated blocks (1/4 of the original block size) was placed into a cylindrical container (6 × 9 cm). A total of 150 termite workers and 15 soldiers were introduced into each container. The containers were placed on damp cotton pads and kept at 25 °C under high humidity in the dark for 2 months. Termite mortality and mass loss of wood blocks were determined at the conclusion of the tests. Seven test blocks were used for each treatment.

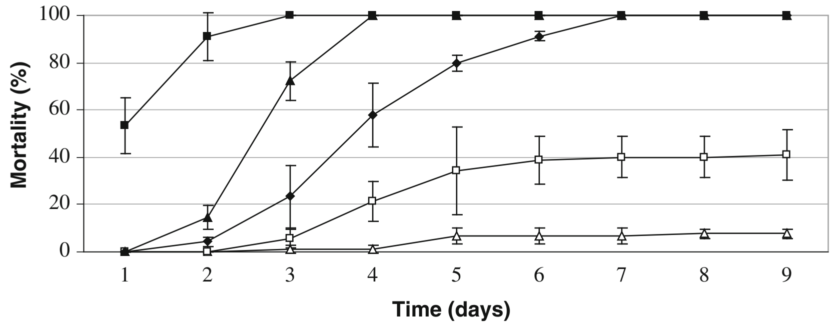

Fig. 2 Bioassay of NaF to *Reticulitermes flaviceps*. The termites were placed on filter papers treated with *open triangle* 0.1; *open square* 0.25; *filled circle* 0.5; *filled triangle* 1; *filled square* 2 % of NaF. Thirty termite workers per concentration of NaF were tested during a 9-day trial

2.6 Fluorine analysis

Both impregnated and leached blocks were analyzed for fluoride content respectively. Fluoride was analyzed according to procedures described by Li and Xu (1999). Blocks from each treatment were dried and ground to pass through a 60 mesh (sieve size 0.25 mm) stainless steel screen. Half a gram of ground wood was distilled using sulphuric acid and hydrogen peroxide. Then, fluoride was separated in a dry air steam. The fluoride content was analysed by a spectrophotometric method of the La (III)–F^- alizarin complexone system (Wada et al. 1985). Percentage of fluoride in the block is recorded as wt/wt (%).

2.7 Statistical analysis

Probit analysis was used to calculate LC_{50} values (lethal concentration of NaF required to kill 50 % of the termites) in toxicity assay. One-way ANOVA was used to assess wood mass loss and termite mortality caused by NaF at different concentrations in tests. The significance of the *F*-statistic was tested at $\alpha = 0.05$ level. All analyses were performed with SPSS 16.0 for Windows Software (SPSS Inc, Chicago, IL, USA) (Gerber and Finn 2007).

3 Results and discussion

3.1 Toxicity of NaF to termites

In this paper, toxicity of NaF to subterranean termites was evaluated. Average mortalities of termites to different concentrations of NaF during the 9-day trial are shown in Fig. 2. Dead termites were not observed in the control. Concentrations of NaF tested showed dose–response curves for termites (Fig. 2). Dead termites were recorded only at 2 % concentration after the first day. Within 7 days, all termites had died at concentrations of 0.5, 1 and 2 %. However, termite mortality tended to stabilize after 5 days at concentrations of 0.1 and 0.25 %, and reached 7.78 % and 41.11 % on the last observation day, respectively. The results showed termite mortality did not occur at ≤1 % NaF after the first day of treatment and the LC_{50} value only reached a maximum of 0.26 % after 6 days (Fig. 2; Table 1), which suggested the mode of action of NaF was slow and less toxic than other commercial termiticides (Mao et al. 2011; Pan et al. 2011). Boric acid is a common chemical used for wood preservative currently. It has similar character to NaF, such as slow acting against termites, water soluble etc. The LC_{50} of boric acid is 0.026 % (wt/wt) to *Reticulitermes flavipes* (Su et al. 1994), which showed that NaF is less toxic to termites than boric acid. NaF, especially at low concentrations, would not be a suitable termiticide.

Table 1 LC_{50} of NaF to workers of *Reticulitermes flaviceps* during a 9-day bioassay

Period of treatment (day)	LC_{50} (95 % confidence interval) (%, wt/wt)
1	–
2	1.30 (1.13–1.51)
3	0.68 (0.51–0.93)
4	0.40 (0.35–0.46)
5	0.29 (0.26–0.32)
6	0.26 (0.24–0.29)
7	–
8	–
9	–

Thirty termite workers were tested for each treatment

A large number of literature reported that fluoride as a wood preservative expressed an excellent ability to prevent wood-rot fungi attack even at low dosage (Baechler and Roth 1956; Fahlstrom 1964; Freitag and Morrell 2005). Johanson and Howick (1975) considered that retention of NaF at 6 kg/m^3 could prevent the termites *Nasutitermes exitiosus* consuming over 5 % wood. However, the termiticidal effectiveness of fluoride was still poorly documented, although fluorine has been used against insects and termites in wood preservation for a long time (Becker 1973). This study demonstrates that the concentrations of NaF in filter paper need to be above 0.5 % to kill *R. flaviceps* workers in a no-choice test (Fig. 2). Meanwhile, retention of 0.057 % (wt/wt) NaF in wood could significantly inhibit termites feeding in a choice test (Table 2).

3.2 Leachability of NaF

Wood blocks impregnated with different concentrations of NaF (0, 0.1, 0.25, 0.5, 1 and 2 %) were used to investigate the leachability of NaF. Fluoride retention was raised as the concentration of NaF in the wood blocks increased. Maximum retention (0.834 % wt/wt) was reached when blocks were treated with 2 % NaF (Table 2). Similarly, fluoride retention of blocks was also raised as the concentration increased when they were leached in the field for 4 weeks. The retention rate varied from 34.05 to 76 % (Table 2). Weight of blocks decreased after leaching and mass losses were all less than 6 % except for the 0.1 % NaF treatment in which mass loss reached up to 14.91 % (Table 2). During leaching, no fungal attack was observed in NaF treated wood blocks except in those treated with 0.1 % NaF.

Fungal attack was observed at the wood blocks treated with low concentrations of NaF, therefore, the mass loss reached a maximum 14.91 %. This indicated that to fully protect timber from termite damage and fungal degrade, the concentration of NaF in the wood should be at least 0.1 % wt/wt (Table 2).

Fluoride can move through the heartwood of many refractory species and reach certain retentions in the wood blocks (Richards 1924; Becker 1976). Retentions of fluoride in wood increased associated with the concentration, the impregnated time, and the combined effect of these parameters (Morrell et al. 2005). Cabrera and Morrell (2009) found that fluoride movement tended to increase with increasing moisture content of wood. The results of this study here showed that the retention of fluoride in *P. massoniana* blocks treated with 2 % NaF wt/wt for 5 days was 0.834 % (wt/wt), which were similar to those in *P. ponderosa* wood (Morrell et al. 2005). With respect to leaching, there is limited evidence that fluoride can be easily leached from preservative treated timber. Morrell et al. (2005) demonstrated that fluoride was almost removed from pine block after leaching according to American Wood Preservers' Association (AWPA) Standard E10. However, retention rates of fluoride were more than 34 % in this study when the blocks were exposed in the field for 4 weeks. These variations of fluoride retention levels could be caused by the different leaching procedures. In AWPA, set of wood blocks are immersed in distilled water as described in the leaching procedures.

Table 2 Mean retention levels of NaF and mean mass losses of *Pinus massoniana* blocks

NaF-treated concentration (%)	Fluorine retention (%, wt/wt)		Mean fluorine retention (%)	Mean mass loss (%)
	Before leaching	After leaching		
0	0	0	N/A	15.87
0.1	0.075	0.057	76.00	14.91
0.25	0.174	0.099	56.90	5.29
0.5	0.189	0.109	57.67	3.02
1	0.311	0.130	41.80	4.16
2	0.834	0.284	34.05	3.66

The mass losses were calculated according to the differences in initial and final dry mass of the specimens. Thirteen blocks were used for each treatment

3.3 Resistance of NaF treated wood against termites

Termites prefer to feed on untreated wood as shown in Tables 3 and 4 and Fig. 3. For all concentrations of NaF, the mass loss in the treated blocks was significantly less than in the controls (Tables 3, 4). Mass losses were between 0.158 and 0.186 g in controls, while mass losses were around 0.04 g in treated wood. There was no significant difference in the mass losses between the treated and control blocks (Tables 3, 4). The mass losses in the treated blocks might be caused by natural factors rather than termites. Internal structure of wood might be damaged while the blocks were kept in moist environment during the experiments.

Termite mortalities raised as the concentrations of NaF increased (Tables 3, 4). Even before the leaching treatment, termite mortality reached a maximum of 47 % at the 2 % wt/wt NaF concentration. Leaching of the wood blocks resulted in lower mortalities, which were all less than 26 % after the leaching treatment (Tables 3, 4).

In the resistance test, NaF-treated blocks induced different eating responses of termites compared to controls (Fig. 3). The blocks were eaten by termites along their full length in the controls. Tunnels and cavities were observed in the control blocks as a result of termite feeding. Termites were observed foraging on the surface of the NaF treated blocks and the blocks suffered from localized feeding. This finding was similar to that by Johanson and Howick (1975) wherein blocks treated with NaF easily suffered from localized feeding, mostly at the ends which were embedded in the matrix. Feeding behavior of termites to NaF-treated wood suggested that fluoride could be able to be developed as an anti-feedant to prevent termite damage in the future.

4 Conclusion

This study evaluates two important aspects of NaF as a wood preservative, viz. toxicity to termites and

Table 3 Wood mass losses and termite mortalities. The termites were exposed to wood blocks (prior to leaching) for 2 months

NaF concentration (%)	Treatment in choice-test	Wood mass loss (g)	Termite mortality (%)
Control (not NaF treated and no termites added)	Not treated	0.0350 ± 0.0080 a	ND
Control (not NaF treated and termites added)	Not treated	0.1700 ± 0.0116 bc	8.17 ± 6.36 a
0.1	Not treated	0.1862 ± 0.0111 c	8.67 ± 4.51 a
	Treated	0.0374 ± 0.0077 a	
0.25	Not treated	0.1754 ± 0.0075 bc	22.00 ± 3.61 b
	Treated	0.0209 ± 0.0084 a	
0.5	Not treated	0.1661 ± 0.0092 b	29.67 ± 8.96 b
	Treated	0.0267 ± 0.0052 a	
1	Not treated	0.1582 ± 0.0100 b	26.67 ± 11.06 b
	Treated	0.0207 ± 0.0049 a	
2	Not treated	0.1589 ± 0.0169 b	47.00 ± 3.61 c
	Treated	0.0220 ± 0.0102 a	

Seven blocks were used for each treatment. Each value represents the mean ± standard deviation. The same letters indicate that there is no statistical difference according to Duncan's Multiple Range Test ($p \leq 0.05$)

ND not determined

Table 4 Wood mass losses and termite mortalities. The termites were exposed to wood blocks (after leaching) for 2 months

NaF concentration (%)	Treatment in choice-test	Wood mass loss (g)	Termite mortality (%)
Control (not NaF treated and no termites added)	Not treated	0.0299 ± 0.0078 a	ND
Control (not NaF treated and termites added)	Not treated	0.1633 ± 0.0139 bc	6.67 ± 3.73 a
0.1	Not treated	0.1792 ± 0.0173 c	8.33 ± 2.52 a
	Treated	0.0345 ± 0.0062 a	
0.25	Not treated	0.1645 ± 0.0193 bc	15.00 ± 4.58 ab
	Treated	0.0219 ± 0.0048 a	
0.5	Not treated	0.1612 ± 0.0051 bc	14.00 ± 3.61 ab
	Treated	0.0259 ± 0.0101 a	
1	Not treated	0.1550 ± 0.0090 b	19.67 ± 4.16 bc
	Treated	0.0226 ± 0.0074 a	
2	Not treated	0.1579 ± 0.0044 b	25.33 ± 8.50 c
	Treated	0.0199 ± 0.0070 a	

Seven blocks were used for each treatment. Each value represents the mean ± standard deviation. The same letters indicate that there is no statistical difference according to Duncan's Multiple Range Test ($p \leq 0.05$)

ND not determined

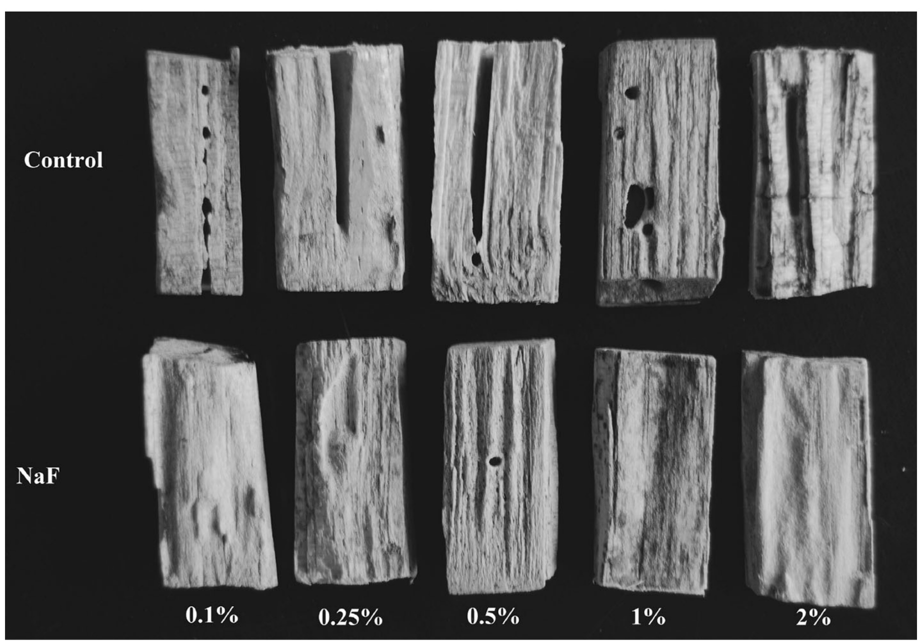

Fig. 3 Sapwood specimens. Seven specimens were used for each treatment. The specimens were leached and exposed to termites for 2 months

leachability. Although the toxicity to termites using no-choice test in filter paper was relatively high, low retention of fluoride could significantly inhibit termites even at retention of 0.057 % (wt/wt) in a choice test. This demonstrated that NaF has anti-feedant effects against termites. In addition, after non-soil contact field leaching for 4 weeks, retention levels of NaF in the wood blocks at a concentration of 0.1 % could be sufficient against fungi and termite. This study also indicated that NaF, when used as a wood preservative and exposed to the weather, does not leach easily. NaF is a potential wood preservative to protect timber from termite and fungal decay.

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