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Recent Marine Wood Preservation Research in Australia

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ABSTRACT

Marine wood preservation research over the last 15 years in Australia has tackled two main problems for the industry. The first was to demonstrate that existing commercial treatments could give reliable performance in the sea, despite earlier erratic performance and inadequate specifications. The key solution was to study the biology of marine borers. Collating and identifying marine borers from different areas around Australia, and examining their preservative tolerances, enabled the Australian coastline to be divided into seven major hazard zones. Piling options can now be specified that will give more than 20 years service life in each zone. More recent difficulties for the industry are questions concerning the fate of copper-chromium-arsenic (CCA) and creosote, preservatives commonly used to protect wood in the sea. Current research focuses on the CCA levels found in barnacles growing on treated piles. Alternative chemicals and methods of protection that seem intrinsically more appealing environmentally are also being examined. These include new generation wood preservatives that are arsenic and chromium free, alternative oil and silica treatments, and potentially active agents extracted from marine organisms.

INTRODUCTION

Timber is a material naturally abundant in the sea, as at least 130 described species of marine borer have evolved to make it home. Those marine borers are a diverse group derived from several families that vary in their modes of attack and timber substrate preferences. Without an understanding of these differences, unexpected failures of timber structures can occur. Some timbers such as *Syncarpia glomulifera* (Sm.) Niedenzu (turpentine) are naturally resistant to marine borers (Barnacle, 1976), but most are susceptible and can be completely riddled within several years. Despite this, the qualities of wood; its strength, resilience, corrosion resistance, ease of handling and association with sustainable forest management practices, make it an ideal building material for the sea.

Engineers and researchers in Australia have long searched for the most reliable timber for use as piles. The most important early works were by Iredale *et al.* (1932) for the Maritime Services Board of Sydney Harbour, and Watson *et al.* (1936) for the Port of Brisbane, both of whom combined the expertise of wood technology, engineering and taxonomy. These and other studies mainly examined the natural durability of timber in the sea (Maiden & De Coque, 1895; Armstrong, 1916; Mackenzie, 1927; Wilson, 1941; Shillinglaw & Moore, 1945; Johnson & Moore, 1950; Moore, 1961). The application of toxins by surface coating and the floating collar technique were also practised but gave temporary protection. Long term protection of non-durable timbers was achieved with physical barriers such as Muntz metal (Anon., 1907), pipes filled with sand, and concrete jacketing (Watson *et al.*, 1936). Modern physical barriers are generally plastic wraps (Steiger & Horeczko, 1982; Eaton, 1996), although concrete jacketing continues to be used.

The first commercial pressure treatment plants in Australia were built in the late 1950s. The first marine borer trial of pressure treated wood was installed by CSIRO in 1960 (Barnacle, 1960), but the marine wood preservation industry got off to a difficult start. In 1969 and the early 1970s, there were several disasters in the sea with the CCA (copper chromium arsenic) preservative that had proved so successful on land. CCA treated *Corymbia maculata* (Hook.) K.D. Hill & L.A.S. Johnson (spotted gum) mooring piles failed after three years during a storm in Bowen Queensland, taking several boats with them (Cokley, 1969). CCA-treated *Pinus radiata* D. Don (radiata pine) oyster posts in Port Stephens NSW broke, dumping valuable crops in the mud. Creosote-treated *P. radiata* in marine trials was being heavily attacked by *Limnoria* (Beesley, 1969). Even the double treatment being promoted in the USA (CCA followed by creosote) was found in 1970 to be severely attacked by *Limnoria* in our small specimen test (Barnacle & Cookson, 1995), although this was concluded to be due to the use of low temperature rather than high temperature creosote (Cookson & Barnacle, 1987a). These early failures spurred the first comprehensive survey of marine borers around Australia in 1970-1972 to generate more fundamental knowledge. Beesley (1971) distributed panels to 42 ports in Australia and PNG, and invited Dr Ruth Turner, a mollusc specialist, and students Jeanette (Marshall) Ibrahim and Suzanne Rayner to collect and identify the molluscs found during the survey. Unfortunately, the details of much of this work remained unpublished (Marshall, 1973), but a checklist of known Australian teredinid species is provided here (Table 1). Later work by Harrison & Holdich (1984) and Cookson (1991; 1994; 1996a) concentrated on the crustacean borers.

MARINE BORERS AND SUBSTRATE TOLERANCES

Limnoriidae

The Limnoriidae contains three genera, the *Paralimnoria* (wood borers), *Limnoria* (wood, algal and seagrass borers) and *Lynseia* (seagrass borers). *Paralimnoria* has the most plesiomorphic features in the family (Cookson, 1990), whereas *Lynseia* are apomorphic (Cookson & Poore, 1994). The group probably evolved in the tropics from species boring into dead wood, later moving into live plant material (Cookson, 1990). There are two known species of *Paralimnoria* and 28 species of *Limnoria* found in wood (Menzies, 1957; Cookson, 1990), of which seven of the latter genus have been found in commercial timber piling in Australia. Some of the substrate preferences have been noted (Menzies, 1951; Barnacle *et al.*, 1983; Cookson & Barnacle, 1987b; Cookson, 1990; Karande *et al.*, 1993). The most important species in Australia are *L. tripunctata* Menzies (found often in softwoods, less so hardwoods, treated with creosote, process oil, chlorothalonil etc.), *L. quadripunctata* Holthuis (found often in dense hardwoods, including those treated with CCA), and both *L. saseboensis* Menzies and *L. indica* Becker and Kampf (often in dense hardwoods and turpentine). Minor species are *L. unicornis* Menzies (found often in CCA-treated hardwoods), *L. platycauda* Menzies and *L. insulae* Menzies.

When designing structures it is important to attach bracing above the tidal zone, as *Limnoria* have a tendency to settle and bore within crevices. This behaviour is due mainly to their negative reaction to light and to their tendency to seek contact with surfaces (thigmotactic behaviour) (Eltringham, 1971). This behaviour is also noticed in aquaria bioassays where *Limnoria* generally align on test blocks beside rubber bands used to hold the test blocks in place (Cookson & Woods, 1995). The effect can be quite pronounced over time. In a recent inspection of 70 year old turpentine piles at Station Pier, Melbourne, most piles were in excellent condition, with just 5-30 mm radius lost from the heartwood (sapwood entirely lost). However, those piles which at various times had bearers fixed for work platforms in the tidal zone had mostly failed or were in poor condition due to erosion by *L. quadripunctata* (unpublished data).

While this review is about Australian research, much has been written recently on the biology and mode of attack of *Limnoria* by researchers from the Buckinghamshire College and Portsmouth University, UK (Pitman *et al.*, 1995; Henderson *et al.*, 1995; Wykes *et al.*, 1997; Praël *et al.*, 1999).

Table 1 Checklist of Teredinidae found in Australia and Papua New Guinea. Compiled from Watson et al. (1936), Marshall (1973), Turner & McKoy (1979), Ibrahim (1981), and Rayner (1983).

Teredinid species	Distribution in Australia (Fig. 1) and PNG
Bactronophorus thoracites (Gould)	5, PNG
Dicyathifer manni (Wright)	5, PNG. 4 (=Ballina, NSW)
Teredothyra dominicensis (Bartsch)	PNG
Teredothyra matocotana (Bartsch)	5, PNG
Teredothyra excavata (Jeffreys)	5 (=Townsville), PNG
Teredothyra smithi (Bartsch)	PNG
Teredora princesae (Sivickis)	5, PNG
Lyrodus bipartita (Jeffreys)	2-5, PNG
Lyrodus massa (Lamy)	5, PNG
Lyrodus medilobata (Edmonson)	3-5, PNG
Lyrodus tristi (Iredale)	4,5 (east coast), PNG
Lyrodus pedicellatus (Quatrefages)	1-5, PNG
Teredo fragilis Tate	1-5 (northern limit = Townsville)
Teredo clappi Bartsch	1, 3-5, PNG
Teredo furcifera von Martens	1-5, PNG
Teredo fulleri Clapp	PNG
Teredo johnsoni Clapp	PNG
Teredo poculifer Iredale	4-5 (southern limit = Brisbane), PNG
Teredo navalis Linnaeus	1-4
Teredo mindanensis Bartsch	5, PNG
Teredo somersi Clapp	PNG
Teredo triangularis Edmonson	5 (Wyndham)
Spathoteredo obtusa (Sivickis)	PNG
Nototeredo edax (Hedley)	3-5, PNG
Nausitora dunlopei Wright	4 (east coast),5, PNG
Nausitora globosa Sivickis	5 (east coast), PNG
Nausitora hedleyi Schepman	PNG
Bankia barthelowi Bartsch	PNG
Bankia australis (Calman)	1-5, PNG
Bankia bipalmulata (Lamarck)	5 (east coast), PNG
Bankia bipennata (Turton)	5 (Cairns), PNG
Bankia campanellata Moll & Roch	1,5, PNG
Bankia carinata (Gray)	1-5, PNG
Bankia gracilis Moll	5, PNG
Bankia johnsoni Bartsch	PNG
Bankia neztalia Turner & McKoy	1,2,4 (east coast)
Bankia nordi Moll	PNG
Bankia philippinensis Bartsch	PNG
Bankia rochi Moll	3,5, PNG
Uperotus rehderi (Nair)	PNG
Uperotus clavus (Gmelin)	5 (Green Island, Qld), PNG

Sphaeromatidae

The two important wood boring species of *Sphaeroma* in Australia are *S. quoyanum* Milne Edwards and *S. terebrans* Bate (Harrison & Holdich, 1984). *S. triste* Heller is sometimes found in untreated turpentine piles in Queensland, and *Ptyosphaera alata* (Baker) can be found at low salinity locations such as the Yarra River in Victoria and the Brisbane River in Queensland. *P. alata* causes shallow etches or small holes in decaying wood. In New South Wales (NSW) and Queensland, *Sphaeroma* generally causes more damage than other marine borers to the commercially available piling options listed in Table 2. Cragg (1988) provides a list of piling timbers that are susceptible to *Sphaeroma*. On the coast of West Australia the extent of the *Sphaeroma* hazard to marine timbers is less clear. *S. quoyanum* occurs in the Swan River (Serventy, 1955) and *S. terebrans* occurs at Exmouth Gulf (Harrison & Holdich, 1984). Generally, the presence of *Sphaeroma* limits the use of CCA-treated softwoods, and they are usually the first marine borers to attack older double treated eucalypt piles. Some of this tolerance derives from the ability to immobilise and store copper in the hepatopancreatic caeca (Cragg & Icely, 1982). Also, *Sphaeroma* is a filter feeder rather than a wood feeder (Rotramel, 1975), and so can avoid some of the toxic effects of wood preservatives.

In marine localities *Sphaeroma* damage is virtually restricted to the tidal zone (see, for example, Barnacle *et al.*, 1986). However, in estuarine water a lower percentage of the *S. terebrans* and *S. quoyanum* population will attack timber below the low water mark (Cheriyan, 1973; Cookson, 1994). Because *Sphaeroma* activity is mostly concentrated in the tidal zone, remedial treatments and protection can often be applied economically. The floating collar technique was once a standard maintenance procedure in Sydney Harbour (Iredale *et al.*, 1932), but is no longer applied because of creosote loss to the environment. In Townsville Port, PVC tape is often applied to untreated turpentine piles at the predicted tidal zone depth before being driven; this prevents attack unless boats damage the tape. In NSW and Queensland, merely placing and maintaining physical barriers on piles in the tidal zone would double the life of double treated piles, CCA-treated softwood piles and untreated turpentine piles. The average life of turpentine piles in Sydney Harbour was 34 years, whereas those protected by the floating collar method had average service lives of 70 years (Moore, 1961).

There are many questions to answer about the environmental cues that cause *Sphaeroma* to bore. For example, *S. quoyanum* is very destructive and able to bore holes as readily as *S. terebrans* in central and northern NSW, but in Victoria, while still common, *S. quoyanum* only occasionally bores shallow etches into softened timber. Presumably the difference in hazard intensity is related to temperature, or a differing geographical population, but this remains to be demonstrated. In Victoria, *S. quoyanum* seems most responsible (with other wood grazers) for an unusual pattern of attack found in old hardwood piles. *S. quoyanum* can excavate longicorn beetle emergence holes, common in some untreated hardwood piles, to give scalloped indentations throughout the tidal zone region of the pile. Neither is it known what drives *Sphaeroma* to live mainly in the tidal zone, be it predation, planktonic food levels, substrate weathering that makes wood easier to bore, salinity, temperature, or competition from

Martesia. At Townsville, *S. terebrans* has a minor preference to bore on the shady side of fender piles (Cookson, 1994). In estuaries it has an increased tendency to bore upwards, perhaps to reduce the amount of silt that might clog the burrow (Cookson, 1994).

Table 2. List of marine borer hazards and appropriate piling options that should provide service lives of at least 20 years (modified from Cookson, 1987).

			Hazard Zone						
			1	2	3	4	5	6	7
Salinity ppt			30-36	30-36	30-36	30-36	30-36	10-30	1-10
Approximate location			Tas	Vic	SA	Sth WA NSW	Nth WA Qld, NT	Port Stephens	Brisbane River
Marine borer:									
Limnoria tripunctata			-	low	mod	ext	mod	high	-
L. quadripunctata			mod	mod	mod	high	-	-	-
L. indica/saseboensis			-	-	-	high	high	-	-
L. unicornis			-	-	-	-	mod	-	-
L. insulae			-	-	-	-	low	-	-
L. platycauda			-	-	-	-	low	-	-
Sphaeroma terebrans[A]			-	-	-	high	ext	ext	mod
S. quoyanum[A]			low	low	mod	high	low	ext	-
S. triste			-	-	-	-	low	-	-
Ptyosphaera alata			-	-	-	-	-	low	low
High salinity teredinids			mod	mod	mod	high	ext	high	-
Nausitora spp.			low	low	low	low	low	mod	ext
Martesia striata			-	-	-	mod	ext[B]	low	-
			mod = moderate, ext = extreme						
Marine Pile	Min. retention kg/m³		Piles should last at least 20 years						
	CCA	HTC							
S. glomulifera	none	None	✓	✓	✓	✓[C]	✓[C]	✓[C]	x
E. marginata	none	None	✓	✓	✓	x	x	x	x
E. camaldulensis	none	None	✓	✓	✓	x	x	x	x
E. muellerana	none	None	✓	✓	x	x	x	x	x
Hardwood	32	None	✓	✓	✓	x	x	x	x
Softwood	32	None	✓	✓	✓	✓[D]	✓[D]	x	?[E]
Hardwood	none	220	✓	✓	✓	✓	✓	✓	?
Softwood	none	220	✓	✓	✓	x	?	x	?
Hardwood	32	150	✓	✓	✓	✓	✓	✓	✓
Softwood	32	220	✓	✓	✓	✓[C]	✓[C]	✓[C]	?[E]
Any listed & full length barrier			✓	✓	✓	✓	✓	✓	✓

A = *Sphaeroma* hazard in WA to be determined.
B = *Martesia* hazard extreme, especially in estuaries with variable salinity (often below 30 parts per thousand).
C = May require a barrier in the tidal zone.
D = Will require a barrier in the tidal zone. May also require knot protection.
E = *P. radiata* given this treatment were in good condition after ten years in the Brisbane River, but were then washed away by floods.

Teredinidae

Turner (1966) made a major contribution to the taxonomy of this group, and produced a useful key to the species (Turner, 1971a). In Australia and Papua New Guinea (Table 1), 33 species were collected in the 1970-1972 survey, with the major species found listed by Turner (1971b). *Uperotus clavus* (syn *Glumebra elegans*) can also be found in Australia in drifting coconuts and other seed pods (Watson *et al.*, 1936). Ibrahim (1981) examined the settlement of 17 species, while Rayner (1983) examined teredinids in Papua New Guinea. Rimmer *et al.* (1983) examined the distribution of *Bankia australis* in a mangrove creek. Brackish water species of *Nausitora* appear to be particularly destructive, as demonstrated in the Brisbane River (Watson *et al.*, 1936). Some taxonomic difficulties have arisen in that differences in breeding habits and rate of larval release suggest the division of some species. Calloway and Turner (1983), working with material from Florida, separated *L. pedicellatus* and *L. floridanus* (Bartsch), but did not determine the wider species distribution. Turner & Calloway (1987) indicated that some other species that were identical by external morphology could be separated by life cycle and histology, but unfortunately did not give details.

Preservative tolerances within the teredinid species are not as well known as for the crustacean borers. Johnson & Lebow (1996) showed that adult *Bankia gouldi* are much more tolerant of CCA in softwoods than larvae, so that if larvae can establish in untreated or poorly treated heartwood sections of timber, treated timber is more at risk. This may partly explain the susceptibility of CCA-treated eucalypt sapwood to teredinids, as this tissue has less uniform preservative distribution on a microscopic scale by comparison with pine sapwood (Greaves, 1974). A number of other species are also able to bore into CCA-treated timbers. CCA-treated *C. maculata* at Bowen failed in three years (Cookson, 1987), mainly because of *Dicyathifer manni*, a borer normally more common in nearby mangroves. *L. bipartitus*, *B. australis* and *T. fragilis* were found in CCA- and CCB (copper chromium boron)-treated eucalypts (Cookson and Barnacle, 1985). *L. pedicellatus* is another species common in failing treated timber (unpublished data). While teredinids can destroy timber faster than other marine borers, they are generally more sensitive to oil-borne preservatives such as creosote and chlorothalonil.

Pholadidae

A number of *Martesia*, *Lignopholas, Pholas, Barnea*, and *Xylophaga* species within the molluscan family Pholadidae are able to bore into soft timber (Turner, 1971a). The wood boring Pholadidae are well represented by deep water species (Turner, 1972; Santhakumaran, 1982). Of most concern to coastal structures are the *Martesia*, with four known species, *M. fragilis* Verrill and Bush, *M. nairi* Turner and Santhakumaran, *M. cuneiformis* (Say), and *M. striata* (Linnaeus). *M. fragilis* occurs in tropical and warm temperate locations, mainly in driftwood and pelagic plant material (Turner, 1971a). *M. nairi* was found in the Northern Territory and on the east coast at several locations from Cairns (Queensland) to Wallis Lake (NSW) (Turner & Santhakumaran, 1989). It was collected mainly from mangroves, although at Cairns it was found in wooden test panels. *M. cuneiformis* occurs in the western Atlantic ocean (Turner, 1971a).

M. striata is the dominant wood-boring species in Australia, and is found widely along the tropical coastline of Australia. This range may extend occasionally as far south as Sydney, where it was reported attacking creosote-treated wood and untreated turpentine (Moore, 1947). *M. striata* is common in tropical estuaries. On untreated turpentine piles in rivers in Cairns, Port Douglas and Townsville, most severe attack occurs near low tide, below but overlapping with the heaviest band of *Sphaeroma* attack at mid tide. It also produces a more scattered distribution of holes below the tidal zone through to mud line. In the Burnett River at Bundaberg, however, most severe attack was recorded by under-water video just above mud line in turpentine piles in three metres of water (presumably by *M. striata*, although specimens were not collected). Attack in the tidal zone by *M. striata* was sparse. For Townsville the *Martesia* hazard is severe in the Ross River estuary, but virtually absent about four kilometres away in the full salinity location of Townsville Harbour. *Martesia* juveniles actively bore into wood or soft substrates, but cease boring upon the formation of the callum in the adult (Boyle & Turner, 1976). CCA inhibits the settlement of *M. striata* more than creosote (Barnacle & Ampong, 1983). The deterrent effect of CCA was noticed in experimental piles at Port Douglas, where untreated turpentine piles had severe *M. striata* attack near low tide and similar CCA-treated piles had very limited attack (Cookson *et al.*, 1989). *S. terebrans,* however, could severely attack either pile.

MARINE BORER HAZARD MAP

A better understanding of marine borer species, in particular their distribution and tolerances, has led to the division of the Australian coastline into seven major hazard zones (Figure 1). Table 2 provides a list of piling options that should give a minimum service life of 20 years in each zone. Cookson (1987) provides an in-depth explanation for this table. This work was incorporated into the Australian Standard (AS 1604-1997), where in order to ensure treatment compliance the hazard was simplified into just two zones, southern and northern. Today in Australia the problem for timber marine piling is no longer the risk of premature failure. There are enough timber piling options available to ensure that a pile correctly specified and placed anywhere along the Australian coastline will have a service life of at least 20-30 years (Cookson, 1987; AS 1604-1997), a time sufficient to satisfy many coastal development needs. Longer service lives can be achieved using some of the treatments listed or when used in conjunction with physical barriers. The main task now is to address concerns that the wood preservative treatments being used can cause problems to non-target organisms and the environment. Our approach is to both quantify the risk (Scown & Cookson, 2001) and search for preservatives or systems that might be intrinsically safer.

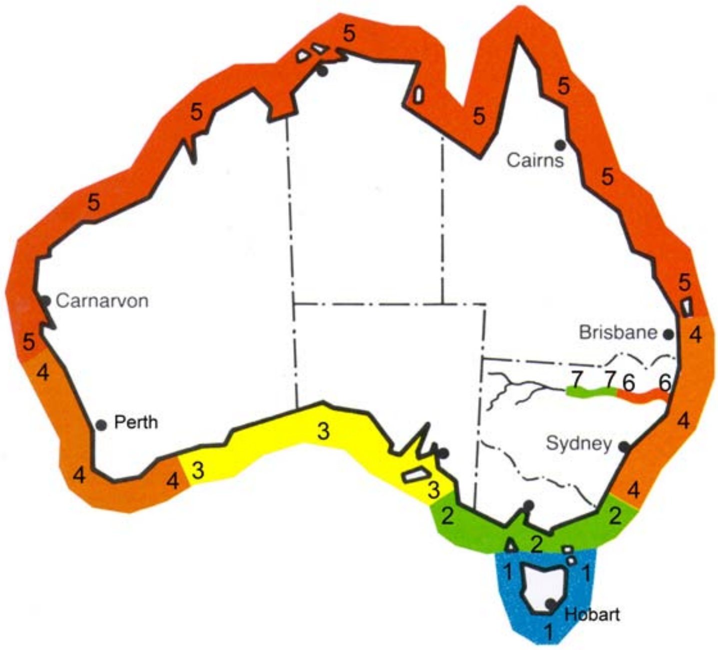

Figure 1 Marine borer hazard zones of Australia. Generalised estuarine river (zones 6 & 7) not to scale (after Cookson, 1987).

ALTERNATIVE MARINE WOOD PRESERVATIVES

Marine wood preservatives such as CCA and creosote that are used on their own as single treatments will often be successful in cool temperate waters. However, for most applications in warm temperate or tropical waters, a double treatment or preservative combination will be needed to protect timber from the variety of marine borers found. Often a wood preservative will be effective against a particular marine borer but less efficient against others. Alternative marine wood preservatives will probably need to be used in conjunction with other preservatives, either as a double treatment where the preservatives are applied in separate stages, or as a mixed formulation within one treatment (fortified creosote for example). Another factor to consider is that the marine wood preservation industry in most countries is relatively small, so it is unlikely that a treatment plant will be developed for preservatives that solely target marine borers. To be successful commercially, a marine preservative should also be effective against either termites or decay fungi and as such, will become an adjunct to more routine treatments. The other possibility is preservative fortification, where specific marine borer biocides are mixed with standard preservatives currently in use at a treatment plant when a call for marine timbers is made. A variation sometimes attempted is protection of timbers by brush or dip treatment, which could allow specific marine borer biocides to be applied over a standard treatment. However, such applications do not normally allow deep preservative penetration, and service life might only be extended by 1-3 years due to leaching of the surface chemical.

The process found most successful to date for double treatment is to combine a fixed water-borne preservative such as CCA (mainly for *Limnoria* and *Martesia*) with an oil-borne preservative such as creosote (mainly for teredinids and *Sphaeroma*). Whereas the components of a CCA solution react chemically with wood to become fixed, the creosote remains an insoluble liquid trapped by surface tension within the wood's cellular structure. The following discussion will be divided into water-borne and oil-borne alternatives.

ALTERNATIVE WATER-BORNE PRESERVATIVES

Copper chromate

Copper chromate is not being sold commercially in Australia. CCA is the preferred water-borne preservative because the inclusion of arsenic is said to improve performance against termites and marine borers (Richardson, 1993). The arsenic also improves performance against some copper-tolerant fungi in laboratory bioassays (Da Costa & Kerruish, 1964). However, our results suggest that arsenic contributes little towards the control of marine borers and is an unnecessary inclusion for that purpose. Copper chromate performed as well or better than CCA over 25 years in marine trials near both Sydney and Perth (Barnacle & Cookson, 1995). Good performance of copper chromate was also shown by Preston & Chittenden (1980) after 2.5 years in New Zealand waters, and by Bergman & Lundberg (1990) after 16 years in Sweden. In-ground field tests in Australia showed that copper chromate performed as well as CCA preservatives against decay fungi and termites after 25 years (Johnson & Thornton, 1991). It should be noted that the copper chromate in the Australian trials included 5% chromium acetate in the formulation.

Other evidence suggesting no need for arsenic in marine exposure was derived from an international marine trial of CCA and copper chromium boron (CCB). There was no apparent difference in performance against marine borers between the two preservatives after up to eight years (Eaton, 1989), even though most boron had leached from the CCB-treated samples within a short time (Leightley, 1987). When these stakes were examined again after 17 years at the Australian test site in Sydney Harbour (Table 3), CCA and CCB were still performing similarly in the timber species remaining in test. An interesting observation was that the CCB-treated specimens were more eroded than those with the corresponding CCA treatment (Table 3), suggesting that the treated wood was softer due to adverse preservative effects or microbial action. Such a slight difference might not be noticeable in structural-sized timbers. Similarly, the performance of creosote did not improve significantly with added arsenic after ten years (Cookson & Barnacle, 1987a) and twenty years (unpublished data).

Arsenic is often naturally high in some marine organisms, which have adapted so they can metabolise and excrete any excess (Ünlü & Fowler, 1979). Chromium leaching should be of more concern than arsenic, although chromium is the component in CCA with greatest leach resistance (Leightley, 1987).

Table 3 Final results of marine trial comparing CCA and CCB treated stakes (150 x 20 x 20 mm) in Sydney Harbour after 17 years. Mean (standard deviation) of three replicates. Marine borer rating from 4 to 0, where 4 = sound and 0 = destroyed. Volume (cm^3) determined by water-displacement on air dried blocks returned to laboratory. Original volume was 59.7 cm^3.

Treatment solution	Factor	*Alstonia scholaris*	*Fagus sylvatica*	*Pinus sylvestris*
6% CCA	Rating	3.8 (0.3)	0.0 (missing)	3.5 (0.0)
	Volume	39.3 (1.0)		37.6 (1.8)
6% CCB	Rating	3.8 (0.3)	0.0 (missing)	3.5 (0.5)
	Volume	28.9 (4.4)		23.4 (0.2)
10% CCA	Rating	4.0 (0.0)	3.5 (0.0)	3.5 (0.0)
	Volume	50.1 (1.4)	30.6 (0.6)	50.3 (1.7)
10% CCB	Rating	3.8 (0.3)	3.8 (0.3)	3.7 (0.3)
	Volume	40.7 (0.8)	26.3 (0.8)	31.3 (1.0)

Copper dimethyldithiocarbamate

There has been a great deal of research on copper-based preservatives, as alternatives to CCA, that are chromium and arsenic free. Some of these have been examined in Australia for marine borer control. Copper dimethyldithiocarbamate (CDDC) is being developed as a CCA alternative. The treated timber has a chocolate brown appearance. It was compared with CCA in a 1.5 year laboratory aquaria trial for the sapwood of *P. radiata*, southern yellow pine (a mixture of probably three species) and *E. regnans* F. Muell. (Cookson *et al.*, 1998a). CDDC performed similarly to CCA against *Limnoria*, but was much more effective against teredinids than CCA as it prevented larval settlement. This preservative contains a higher proportion of copper than CCA, but in a limited five day trial leached less copper than CCA. Therefore, the reason for its improved performance in inhibiting teredinid settlement is still unclear (suspected copper leaching or the presence of dimethyldithiocarbamate). However, CDDC requires a two-step application procedure, making it a more expensive treatment than CCA. Commercialisation of this product is currently focusing upon the home decking market in North Carolina.

Ammoniacal copper quaternary

Ammoniacal copper quaternary compound (ACQ) is being evaluated by the Timber Research Division of the Queensland Department of Primary Industries at a marine test site in Mourilyan Harbour, North Queensland. After three years exposure, ACQ is performing as well as CCA (K. Archer, personal communication, 1996).

Table 4 Six year inspection results for a marine trial of small specimens of *P. radiata* (250 x 50 x 40 mm) and *E. obliqua* (natural rounds 40-80 mm diameter and 250 mm long) exposed below low tide at Townsville. Mean rating (standard deviation) of six replicates. Marine borer rating from 4 to 0, where 4 = sound and 0 = destroyed.

	P. radiata			*E. obliqua*		
Treatment	Mean retention kg/m^3	Teredinid	Limnoria	Mean retention kg/m^3	Teredinid	Limnoria
Water	427	0 (0.0)	0 (0.0)	506	0 (0.0)	0 (0.0)
P9 Oil	429	4 (0.0)	1.4 (1.2)	346	3.3 (0.5)	3.6 (0.3)
CCA	32 (salt)	2.4 (1.3)	3.9 (0.2)	32 (salt)	0.4 (0.7)	4 (0.0)
PROCCA	32 (salt)	3.9 (0.2)	4 (0.0)	33 (salt)	1.4 (0.7)	4 (0.0)
Basic zinc chloride	59 el. Zn	4 (0.0)	3.8 (0.3)	Not tested		
HTC	304	4 (0.0)	3.5 (0.0)	210	3.9 (0.2)	3.7 (0.3)
PEC	274 (as HTC)	4 (0.0)	3.9 (0.2)	205 (as HTC)	3.9 (0.2)	4 (0.0)
Chlorothalonil in oil	29	4 (0.0)	3.4 (0.2)	23	4 (0.0)	3.9 (0.2)
CCA + PEC	32 + 279	4 (0.0)	4 (0.0)	33 + 191	4 (0.0)	3.9 (0.2)
CCA + chlorothalonil	33 + 29	4 (0.0)	3.9 (0.2)	32 + 22	4 (0.0)	3.9 (0.2)

Zinc hydroxide

Pendleton & O'Neill (1986) reported that Douglas fir piles treated with basic zinc sulphate were still in excellent condition after 19 years in Hawaii. The treatment is based on the formation of insoluble zinc hydroxide within wood. We investigated basic zinc chloride, where six *P. radiata* blocks were treated with zinc chloride to a mean retention of 58 kg/m^3 zinc, and then re-treated with a solution of ammonia and sodium hydroxide to precipitate the zinc. After six years exposure below the tidal zone in Townsville, those specimens are still in excellent condition, as four blocks are without attack and two blocks have only superficial attack by *Limnoria* (Table 4). However, the zinc-treated timber was softer than comparative CCA-treated specimens due to the acidic effects of unreacted zinc chloride. A marine preservative based on the formation of zinc hydroxide could lead to a relatively safer environmental option for water-borne preservatives.

ALTERNATIVE OIL-BORNE PRESERVATIVES

Pigment emulsified creosote

A major improvement in the environmental credentials of creosote was the development of pigment emulsified creosote (PEC) (Greaves *et al.*, 1986). This preservative combines 65% high temperature creosote (HTC) as an emulsion with 35% water containing pigment, emulsifiers and stabilisers. Virtually all hardwood marine piles in Australia are now treated with PEC rather than HTC. The benefits are cleaner wood surfaces, reduction of crud and vapour emissions, and improved performance. This creosote is particularly suited to eucalypts, in which the pigment blocks vessels and pathways to reduce crud formation. Laboratory work with an earlier formulation of PEC showed less leaching of fungitoxic components than from HTC (Cookson & Greaves, 1986). More recent comparison in a marine trial at Townsville showed that

PEC is performing better than HTC, either because of reduced leaching or (less likely) the presence of additives such as pigment (Table 4).

Creosote in the marine environment is biodegradable. There are a number of marine microorganisms such as *Pseudomonas creosotensis* O'Neill, Drisko & Hochman that are capable of degrading creosote (Drisko & O'Neill, 1966). These bacteria grow on pile surfaces and possibly adjust to the slow release of creosote from the pile. Any long term leaching must be slow. In a marine trial of low temperature creosotes (Barnacle & Cookson, 1990), which contain more water soluble fractions than modern creosotes, 70% of the creosotes remained in the wood after 25 years (Cookson *et al.*, 1996). Other studies in the USA found up to 75% creosote remaining in piles after 40 years service (Bramhall & Cooper, 1972). The main environmental problem for creosote-treated piles occurs shortly after installation when a combination of hitting the pile with a driving hammer and the swelling of wood with water forces some creosote from the pile. Leaking sometimes endures for several weeks after installation until the pile 'equilibrates'. There is also some volatilisation of creosote from surface fibres above the tidal zone. With age, brown-grey coloured double treated eucalypt piles usually turn light green above the tidal zone when CCA dominates surface colour after creosote loss. Creosote contains a number of compounds that are suspected carcinogens (Bestari *et al.*, 1998), so appropriate safety equipment should be worn during pile installation.

Chlorothalonil

Chlorothalonil is a fungicide widely used in agriculture for the control of various plant diseases (Davis *et al.*, 1997). Although chlorothalonil is an organochlorine it is readily metabolised by mammals and so has a very low oral toxicity (Woods & Bell, 1990). It is nearly insoluble in water, but highly toxic to fish. However, any chlorothalonil that leaches from treated wood should rapidly degrade as its half life is only about 48 h in estuarine water containing unsterile sediment (Walker *et al.*, 1988). Chlorothalonil is also effective against decay fungi and termites (Preston, 1986; Creffield & Chew, 1993). In an aquaria trial (Cookson & Woods, 1995) and a six year old sea trial in Townsville (Table 4), oil-borne formulations of chlorothalonil provided timber with good resistance to teredinids, but in softwoods was attacked by *L. tripunctata*. Chlorothalonil therefore follows a similar pattern of performance to creosote. Performance against *L. tripunctata* was improved by fortification with chlorpyrifos (Cookson & Woods, 1995). Chlorothalonil is also proving to be effective as a double treatment with CCA (Table 4).

Oil

The oil-type preservatives have both toxic (or repellent) and physical (bulking) effects on teredinids. The relative importance of the bulking effect where wood cells are filled with oil is not yet determined. However, simply treating wood with process oil such as P9 oil from the USA will protect *P. radiata* from teredinids for more than six years, although the specimens will rapidly decline due to *L. tripunctata* (Table 4). The treatment is also useful in *E. obliqua* L'Herit. (Table 4). A similar effect was noticed in a comparison of CCA with a CCA-oil emulsion called PROCCA (see Cookson *et al.*, 1998b). The PROCCA formulation contains just 5% oil, but still slightly increased *E. obliqua* service life at our severe Townsville test site by one year by comparison with CCA. PROCCA has also improved performance in *P. radiata* over that achieved by CCA (Table 4). A double treatment of CCA and 100% oil is not likely to provide the protection gained by CCA and creosote; however, treatment with oil should markedly improve the performance of eucalypt piles treated with CCA alone. Just which oils would be best is not known.

Table 5 Performance of supplementary treatments of biocides dissolved in creosote against marine borers after 21.3 years in Sydney Harbour. Mean (standard deviation) rating for 4-6 specimens. Rating scale of 4-0 where 4 = sound and 0 = destroyed.

Conventional timber/treatment	% Biocide dissolved in a suppl. creosote treatment	Main biocidal action	Mean rating (sd)
160 kg creosote/m^3 *P. radiata*	3.0% Lindane	insects	2.9 (1.6)
	2.8% Tributyl lead acetate	fungi	0.6 (1.3)
	2.8% Captan	fungi	0.0 (0.0)
	3.0% Fenitrothion	insects	0.0 (0.0)
	1.1% Endrin	insects	3.7 (0.3)
12 kg CCA/m^3 *P. radiata*	1.7% Aminocarb	insects, molluscs	0.0 (0.0)
	3.0% Tributyl tin oxide	fungi	1.5 (1.6)
	1.5% Azinphos-ethyl	insects	3.5 (0.6)
	1.5% Thiram	fungi	0.0 (0.0)
	1.9% Toxaphene	insects	0.7 (1.1)
120 kg creosote/m^3 *E. obliqua*	3.0% Malathion	insects	2.3 (1.3)
	3.0% Tributyl tin oxide	fungi	2.1 (1.3)
	0.3% Methiocarb	insects, molluscs	1.8 (1.4)
	1.9% Niclosamide	molluscs	0.7 (0.8)
16 kg CCA/m^3 *E. obliqua*	3.0% Aldrin	insects	2.3 (1.6)
	3.0% Tributyl lead acetate	fungi	0.0 (0.0)
	0.5% Tetrachlorvinphos	insects	0.0 (0.0)
	2.9% Fenthion	insects	2.6 (1.8)

Fortification of creosote or oil

The performance of creosote (and probably oil) can be improved by fortification with other biocides that dissolve in the oil-based preservatives. The aim of such an approach could be several: to improve creosote performance, to lower the level of creosote needed in a treatment, or to avoid the need for double treatment with CCA.

This approach was explored in a study where 16 different organic biocides were added to creosote (Table 5). After 13.5 years the results showed that insecticides were generally more effective additives than fungicides or molluscicides (Cookson *et al.* 1991). This test was continued in Sydney, where after 21 years the best supplementary treatments were the insecticides lindane, endrin, azinphos-ethyl, and fenthion (Table 5). As the organochlorines lindane and endrin have no real future in Australian wood preservation, the best biocide worthy of further study is azinphos-ethyl. Chlorpyrifos is another insecticide that improves the performance of oil-type preservatives such as creosote (Johnson & Gutzmer, 1990) and chlorothalonil (Cookson & Woods, 1995).

A more recently installed trial of supplementary treatments in Australia was described by Eaton & Cragg (1995) and Cragg & Eaton (1997). They examined the performance of synthetic pyrethroids (permethrin, cypermethrin and deltamethrin) as single or supplementary treatments for *Pinus sylvestris* L. Specimens were exposed for 59 months at Mourilyan Harbour, Queensland. Those treated with the pyrethroids dissolved in white spirit were severely attacked, whereas all creosote containing samples were only slightly or moderately attacked. Fortification of creosote with deltamethrin generally gave better results than the other two pyrethroids (Eaton & Cragg, 1995).

UTILISING THE PROTECTIVE MECHANISMS FOUND IN PLANTS

The natural durability of a range of timber species against decay fungi and termites has been examined extensively (Johnson *et al.*, 1996), but performance against marine borers is poorly known. Barnacle (1976) noted that natural durabilities on land do not necessarily apply in the sea. Some comparative marine studies were undertaken by Watson *et al.* (1936) for eight timber species in Brisbane waters, and Johnson & Moore (1950) compared seven West Australian timbers in Sydney Harbour. Cookson (1996b) conducted a one-year aquaria trial to compare the relative durability of 22 timber species available in Australia. Results from a parallel sea trial will be reported at a later date.

The chemicals causing marine borer resistance in some plants could be extracted and used to treat other less durable timbers. For example, an obtusaquinone isolated from the central American timber *Dalbergia retusa* Hemsley (cocobolo) was found to be effective against teredinids, although not against *Limnoria* (Bultman & Parrish, 1979).

It has long been recognised that many of the timbers that are naturally durable in the marine environment have high silica content (Amos, 1952). The theory proposed was that hard siliceous granules within the timber blunt the boring organs of marine borers, thereby preventing attack (van Iterson, 1933). Additional support for this theory came from the fact that saws tend to blunt more quickly when used on siliceous timbers. However, attempts to replicate this natural means of preservation by impregnation with silicon-containing compounds have been generally unsuccessful (Edmondson, 1953; Roe *et al.*, 1957; Serpa, 1980). This inability to duplicate marine natural durability by silicon impregnation has led some researchers to doubt the role of silica in natural durability (de Silva & Hillis, 1980).

Recent work, however, has shown that timber can be impregnated with certain ethyl silicate formulations in a way that will mimic the pattern of resistance found in some naturally durable and siliceous timbers such as turpentine. This silica treatment, described in a provisional patent (Cookson *et al.*, 1999), has protected *P. radiata* blocks from teredinids for 2.5 years in the extreme hazard found at Townsville, though the treatment fails for *Limnoria*. The silica could therefore be used as an alternative to creosote in a double treatment with CCA or one of the water-borne alternatives mentioned previously. Action by silica may occur in the gut of borers rather than by affecting wood boring organs such as the mandibles or shell. Teredinids must swallow all that they chew, while *Limnoria* may be able to avoid consuming silica granules.

In searching for pesticides that are environmentally benign to non-target organisms in the sea, another useful approach might be to obtain active ingredients that are already produced naturally by certain marine organisms (Holmström & Kjelleberg, 1994). The presumption is that those chemicals will also be biodegradable in the sea. Possible candidates are derivatives of secondary metabolites obtained from marine red algae that are being examined for antifouling activity (de Nys *et al.*, 1995). One of these compounds looked promising in a laboratory bioassay against *L. quadripunctata* (Scown *et al.*, 1999). It also provided moderate protection to treated *P. radiata* blocks exposed for 13 months at Williamstown (Scown *et al.*, 1999). While analogues of this product might not provide the long term protection normally required in wood preservation, it might be useful in aquaculture where timbers can be recoated on a more regular basis.

CONCLUSIONS

Marine wood preservation research in Australia has reached the stage where treated timber marine piles can now be specified to provide long service life. Knowledge of marine borer species, distributions and substrate preferences has led to the development of a marine borer hazard map that can be used to aid in the selection of the correct timber pile. Further research is driven by the need to evaluate the environmental impact of using treated timber in the sea, and an interest in the development of alternative preservatives. New formulations are likely to be preservative combinations due to the need to protect timber from the wide range of marine borers found, especially in warmer waters.

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Additional Papers

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ABSTRACT

This volume contains nineteen papers from the 10th International Congress on Marine Corrosion and Fouling, held at the University of Melbourne in Melbourne, Australia, in February 1999. The scope of the congress was to enhance scientific understanding of the processes and prevention of chemical and biological degradation of materials in the sea. Papers in this volume range across the themes of marine biofilms and bioadhesion, macrofouling processes and effects, methods for prevention of marine fouling, biocides in the marine environment, biodeterioration of wood in the sea, and marine corrosion.

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