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Monitoring losses of copper based wood preservatives in the Thames estuary

J.A. Hingston [a,*], R.J. Murphy [b], J.N. Lester [c]

[a] Environmental Processes and Water Technology Research Group, Department of Environmental Science and Technology, Faculty of Life Sciences, Imperial College, London SW7 2AZ, UK
[b] Department of Biology, Imperial College, London SW7 2AZ, UK
[c] School of Water Sciences, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK

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Wood preservative field trials in the UK indicate that standard laboratory tests overestimate losses compared to those resulting from real environmental exposures.

Abstract

Field trials were conducted at two sites in the Thames estuary to monitor losses of copper, chromium and arsenic from wood preservative treated timbers of varying sizes and treatment regimes. Results indicated that leaching tests conducted under standard laboratory conditions might overestimate losses compared to losses resulting from real environmental exposures. Amine copper treated wood was noted to leach higher levels of copper compared to chromated copper arsenate treated wood, and was therefore considered an inappropriate replacement biocide for fresh and marine construction purposes on this basis. Increases in copper concentrations in the outer sections of amine copper treated posts may have represented re-distribution of this component in this timber. No accumulation of metals was found in sediments surrounding field trial posts.

Keywords: Wood preservation; Copper; Chromium; Arsenic

1. Introduction

Leaching of wood preservatives under laboratory conditions can be investigated by following a number of standard protocols (AWPA, 1983; ANS, 1986; BS EN, 1997; ENV, 1994). These protocols are relatively simple and easily repeatable. However, results do not necessarily give an accurate estimation of losses in the field. A number of field trials have been performed to try and better quantify the losses of wood preservatives under more realistic environmental conditions. In long term marine field trials, CCA treated pine leached as much as 25% of total active ingredients within 6 months, with total losses rising to 52% after 85 months (Archer and Preston, 1994). Hayes et al. (1994) also observed that losses of Cu from pine submerged in coastal waters occurred most within the first 12 weeks of a 72-week leaching trial. Field trials testing the durability of different CCA treated timbers indicated that the average leaching rates of CCA were 1.8–17.3%, and that those with the highest leaching rates had the minimum lifespan (Cherian et al., 1979).

There are a number of possible explanations for why standard laboratory protocols may not be appropriate for accurately assessing losses in the field. Timber in the field may be exposed to a more severe leaching environment than that in the laboratory due to increased physical stresses leading to abrasion and cracking, and borer attack may also increase the surface area available for leaching (Merkle et al., 1993). Periodic wetting and drying of CCA treated wood in seawater, as in tidal flux, have been shown to result in surface separation

* Corresponding author. Present address: Pesticides Safety Directorate, Mallard House, Kings Pool, 3 Peasholme Green, York YO1 7PX, UK.
E-mail address: james.hingston@psd.defra.gsi.gov.uk (J.A. Hingston).

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of tracheid cells, possibly due to the formation of salt crystals as water evaporates (Johnson et al., 1992) and may result in increased losses of preservative. Conversely, the growth of fouling organisms on the surface of wood in the field has been considered a possible cause of reduced leaching rates (Hayes et al., 1994). Due to the effect of pH on leaching rates, it has been postulated that high concentrations of humic acids in surface waters may increase leaching (Cooper, 1994).

The current study was instigated as part of a series of investigations into the leaching of copper based wood preservatives in the laboratory and in the field (Hingston et al., 2001, 2002a,b), to better understand the mechanisms of leaching and to quantify losses under representative environmental conditions.

2. Materials and methods

Professionally treated blocks and posts of Southern yellow pine (SYP) (*Pinus* spp.) were obtained from the industrial sponsors of the project, Laporte Inc., Charlotte, USA. All timber were subjected to an initial vacuum of −85 kPa for 30 min, followed by a 30-min pressure cycle at 1034 kPa (150 PSI). Loading was based on measurement of pre- and post-treatment weights. Dimensions and mean loadings of treated timbers are shown in Table 1. All treatments were representative of typical marine (high) or freshwater (low) loading ranges. To achieve the target loadings, blocks were treated with solutions ranging from 2.20 to 7.94% CCA oxides, and from 1.53 to 5.26% amine copper (calculated as CuO equivalent; the amine in the formulation was mono-ethanolamine at a concentration of 2.75 (±0.25) times the weight of CuO equivalent).

Atomic absorption spectrometer model Analyst 800 (Perkin Elmer Ltd, Beaconsfield, UK) was employed for all metal analysis in either Flame Atomic Absorption Spectroscopy (FAAS) or Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) mode. Conditions for analysis were based on well defined standard operating conditions (Perkin Elmer, 1996). For As analysis by FAAS, the 197.2-nm wavelength was selected over the recommended 193.7-nm line, since the 193.7-nm line can produce non-specific absorption in samples with high salt content (Perkin Elmer, 1996).

During digestion and analysis of field sediments, a 0.5-g sample of the marine reference sediment material PACS1 (National Research Council, Ottawa, Canada) was included in each batch. Concentrations of Cu, Cr and As in the reference material were observed to be within 10% of the published values, and were therefore considered acceptable.

For analysis of treated timbers, no standard reference material was commercially available with concentrations in the same range as found in the material analysed. Therefore, reference materials were developed specifically for this work to monitor extraction and analytical sensitivity. During the digestion of each batch of wood, a reference sample was included consisting of 0.5 g of untreated SYP sawdust and 5 ml of each metal standard at a concentration of 1000 mg l^{-1}. This produced expected concentrations of 100 mg l^{-1} in the final sample, which was in the middle of the calibration range and conveniently allowed percentage recovery to be monitored. Mean percentage recoveries for Cu, Cr and As were observed to be around 99, 92 and 95%, respectively, and no further amendment of data was undertaken to take into account any slight differences in recovery efficiency.

Table 1
Dimension and mean loading of treated Southern yellow pine blocks

Dimensions	CCA loading (kg m^{-3})	CuO loading (kg m^{-3})
5 × 10 × 76 mm	49.2; 14.45	30.1; 7.82
15 × 25 × 125 mm	35.5; 11.50	27.2; 6.52
38 × 38 × 228 mm	42.8; 13.0	27.6; 9.8
9 × 9 × 243.8 cm	43.9; 13.6	8.7

Field trials were initiated during the last week of July 2000. Following consultation with the Environment Agency and the Port of London Authority, two sites were selected along the River Thames. The first site was on the northern side of Chiswick Ait, West London (OS Grid TQ521815 177946). The second was approximately 33 miles east at Swanscombe, Kent (OS Grid TQ55990 176140).

Posts measuring 9 × 9 × 243.8 cm, treated by Laporte Inc., were used for the field trial. A section approximately 5 cm was cut from the middle of each post and retained for analysis of background concentration levels. By dividing the posts thus, it was possible to place one length at the Chiswick site, and the matching section at the Swanscombe site. The use of such end-matched sections to analyse preservative concentrations has been recommended by several authors (Rak and Clarke, 1974; Albuquerque et al., 1996). In theory the variation between adjacent sections of timber should be less than that between unrelated samples, and analysis will provide a much more accurate measure of preservative loading than simply using weight increases post-treatment.

Timber treated with CCA to mean loadings of 13.6 and 43.9 kg m^{-3} and treated with amine copper to a mean loading of 8.7 kg m^{-3} were used. Each treatment was applied to 15 posts, and following bisection resulted in 30 posts of each treatment measuring approximately 9 × 9 × 120 cm. Fifteen posts of each treatment were placed at each site in a 5 × 3 grid pattern along the shore line leaving approximately 60 cm exposed. In addition, five untreated posts were placed at each site as a control.

Posts were sampled after total exposure durations of 1, 3, 6, 9 and 12 months. At each sampling period three replicate posts from each treatment group were removed completely. In addition a single untreated post was removed at each period. The posts removed at each sampling period from one site matched the posts removed at the other i.e. each post formed matching halves of a single post that was originally treated. At each sampling period replicate sediment samples were again taken and bulked to form single composite samples of approximately 250 ml from each position. Water temperature, pH and sediment Redox were also measured and results are shown in Table 2.

2.1. Analysis of field timbers

Timbers were stored for a minimum of 2 weeks to allow partial drying. Sub-samples were then removed from each post for analysis. Sampling resulted in four replicate surface samples (outer 2 cm), four replicate subsurface samples (inner 2 cm), and a single replicate centre sample (1 cm) from each sampling point. Samples were taken from two positions along each post. The first position was 30.48 cm from the top of each post. This represented the middle of the exposed portion. The second set of samples was taken from a distance of 91.44 cm from the top of the post i.e. 30.48 cm below the top of the sediment and therefore in the middle of the sediment bound portion.

Timber samples were taken using a JCB-CD18C cordless hammer drill with a 10-mm stainless steel drill bit, dried overnight at 105 °C and approximately 0.5 g was weighed into Teflon digestion vessels. To each sample was added 2 ml of 30% H_2O_2 and 5 ml of 69% HNO_3. The vessels were allowed to react for a minimum of 30 min and then subjected to microwave digestion in a Milestone MLS Mega 1200 High Performance microwave digestion unit using recommended manufacturer's digestion conditions. On completion of the microwave digestion cycle, vessels were allowed to cool completely and the digested sample was transferred to a 50-ml volumetric flask and made up to volume with Ultrapure water ready for analysis by FAAS.

Table 2
Environmental conditions of field trial sites

Parameter	Chiswick	Swanscombe
Water temperature (°C)	5.0–16.8	10.7–15.6[a]
pH	7.67–7.83	7.92–8.22
Sediment Redox (mV)	182–261	218–284
Salinity (‰)	11	17

[a] Water sample not collected at the 6-month sampling period at this site.