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Influence of Leaching Protocol Regimes on Losses of Wood Preservative Biocides

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Current international pesticide substance legislation, such as the Plant Protection Products Directive (91/414/EC) and the Biocidal Products Directive (98/8/EC) in the E.U. and the Federal Insecticide, Fungicide and Rodenticide Act in the U.S. requires the utilisation of laboratory based data to inform decisions on the environmental acceptability of chemical products. The need for standardised laboratory protocols has been well recognised if a consistent approach to the decision making process is to be achieved. An area that has received considerable interest is that of standardised leaching tests. Numerous leaching protocols exist in different fields, primarily to protect soil and groundwater from contamination as a result of leaching from, for example, waste in landfill or from construction materials during their service life. One specific area of leach test considered worthy of review and further development is that covering leaching of wood preservative biocides. There are currently a number of recognised standards specific to wood preservatives which are in common use and accepted for regulatory purposes (AWPA 1983; BSENV84 1989; ENV1250:2 1994). Individual parameters of leaching tests vary. For example, timber ranging from standard block sizes of 15 x 25 x 50 mm, up to piles 250 mm in diameter and 1200 mm in length have been used. However the basic principal of all protocols is fairly similar i.e. treated blocks are submerged in aqueous solutions and subjected to set leaching periods, with solutions generally completely renewed at each sampling point and retained for analysis of leached components.

Conflicting data concerning the bioaccumulation and toxicity of wood preservative leachates has been published (Weis, et al. 1991; Albuquerque and Cragg 1995). Increasingly stringent environmental legislation is likely to make it extremely important that testing is capable of producing an accurate and realistic assessment of preservative leaching, and may also force the unification of the existing standards into a single internationally recognised protocol. Against this back drop of developing legislation and increasing environmental concern, it was decided to investigate more closely some of the aspects of these leaching protocols to assess how good a measure they are of leaching, and how important individual parameters are in determining the end result.

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MATERIALS AND METHODS

Fifty sapwood blocks of Scots pine (*Pinus sylvestris*) were cut from straight-grained timber to dimensions of 15 x 25 x 50 mm. Specimens were treated with a 1.95% CCA oxides w/v solution using a laboratory vacuum dessicator. The treatment solution contained approximately 9% elemental Cu, 16% Cr and 11% As. Treated blocks were maintained in a sealed bag in the absence of light for five days, then allowed to air-dry naturally at room temperature for 4 weeks prior to the initiation of the study. The mass of each block was recorded before and after treatment to allow calculation of preservative uptake, and indicated that mean retentions were approximately 20 kg m^{-3}. A generic leaching protocol was developed drawing closely on aspects of existing agreed protocols. In this way it was hoped that the findings of the study would be generally applicable, and not specific to a single protocol. The first trial consisted of leaching three replicate blocks for 7 d in glass beakers. All glassware was washed with 1M HNO_3 and triple rinsed with deionised water prior to use. Blocks were submerged for 18 hrs and removed for 6 hrs every day to simulate estuarine conditions. The three blocks were leached simultaneously in 1.125 l of water. Leaching solutions consisted of either ultrapure water (UPW) produced by a Maxima Ultrapure water generator or artificial seawater (ASW) made up according to ENV1250:2 (1994) (Table 1). Tests were conducted at either 7 or 21 ± 1°C, and under either static or dynamic conditions. Water was sampled after 24, 48, 96 and 168 hrs, and on each occasion water was replaced with a fresh volume of leaching solution. By altering a single parameter at each step across a spectrum of conditions, it was possible to assess the influence of temperature, stirring, test duration and solution origin on leaching rates. Analysis was by ICP-AES for Cu and Cr, and by HG-AES for As. Control studies were conducted with untreated blocks, and indicated that no leaching of metals occurred. Statistical comparisons were undertaken using the paired student t-test, with $p = 0.05$ selected as the level of significance.

Following initial studies, a second set of leaching experiments were conducted using Southern yellow pine blocks (15 x 25 x 63mm) treated with a 6.9% CCA oxides solution by Chemical Specialities Inc, Charlotte, U.S. to a mean retention of 35 kg m^{-3}. Although these blocks were slightly longer than those used in the first phase of experiments, this was not considered to effect results significantly. Leaching experiments were conducted in ASW and natural seawater (NSW) collected from the River Thames estuary, at Swanscombe, U.K. in July, 2000. Tests were conducted at 21 ± 1°C under constant stirring conditions. Three replicate blocks were each leached separately in 180 ml of water, completely submerged, with an increased sampling regime where waters were completely replaced after 1, 3, 6, 11, 27, 51, 147, 315 and 507 hrs. Analysis was by flame AAS (Cu) or graphite furnace AAS (Cr and As). Statistical comparisons were undertaken using ANOVA, with $p = 0.05$ selected as the level of significance.

RESULTS AND DISCUSSION

Leaching is represented as either a flux (μg cm^{-2} hr^{-1}), or as total metal lost per block (μg) (Table 2). Somewhat unusually, the greatest leaching rates from the Scots pine treated blocks were observed for Cr, with initial leaching rates sometimes a factor of 10 higher than those of Cu. Arsenic was observed to be the most leach resistant metal. This differs from most other observations on modern CCA formulations, where the hierarchy of leaching is generally agreed to be Cu>As>Cr (Table 3). The elevated leaching of Cr in these experiments suggests that there may have been an excess of this element in the initial treatment solutions, or insufficient fixation of Cr prior to test initiation. Although no specific measure of fixation was undertaken, such as the diphenyl carbazide test, wood was stored in excess of the period recommended by the British Wood Preserving and Damp-proofing Association and in accordance with conditions of approval under COPR (1986) to allow complete fixation. Leaching rates of Cu and As agreed reasonably well with those of previous studies, which would indicate these elements were adequately fixed.

Leaching rates of all metals showed rapid reductions during the first few sampling periods, and the rate of As leaching in ASW at two temperatures is shown in Figure 1. Although both As and Cu loss was elevated at the higher temperature, rates of Cr loss were lower at 21°C. Although it has been shown that leaching of Cu, Cr and As may be reduced at lower temperatures (Van Eetvelde, et al. 1995), other work has indicated decreased flux of As at 20°C compared with leaching at 4°C (Breslin and Adler-Ivanbrook 1998), therefore these results may not be surprising. Changes in leaching of Cr and As were not significant ($p > 0.05$), although the increase in Cu at 21°C was significant ($p = 0.03$).

The reductions in the leaching rates of all three metals from Scots pine can be observed in Figure 2. It is clear that while the rate of Cr leaching declines rapidly, the As rate falls more slowly. Most protocols suggest durations of only 7 d maximum, and estimates of leaching rates based on these studies may not be sufficient to quantify the long term loss rate of As. The relatively slow reductions in As leaching rates has also been observed in other studies, although no hypothesis was suggested for why As behaves so differently to Cr (Breslin and

Table 1. Physico-chemical properties of leaching solutions.

	pH	Salinity (ppt)	DOC (mg l^{-1})
Ultrapure water	6.38	0	<0.005
Artificial seawater	7.46	24.5	<0.005
Natural seawater	8.12	17.2	9.86

Table 2. Summary of initial flux rates and total losses over 7 d for Cr, Cu and As from Scots pine treated blocks (n=3) under various experimental conditions.

Experimental conditions	24 hr flux ($\mu g\ cm^{-2}\ hr^{-1}$)			Cumulative loss after 7 d (μg)		
	Cr	Cu	As	Cr	Cu	As
21°C unstirred UPW	0.84	0.20	0.030	1397	1159	69.6
21°C unstirred ASW	1.31	0.14	0.018	2260	479	58.7
7°C unstirred ASW	1.28	0.08	0.014	2580	241	37.2
7°C stirred ASW	1.54	0.12	0.023	2906	291	44.1

Adler-Ivanbrook 1998). Arsenic fixation in wood is thought to be almost exclusively due to complex formation with the Cr and Cu (Pizzi 1982). Since leaching rates reduce over time, there may be less free Cr ions available to react with free As ions, resulting in less precipitation of As as, for example, $CrAsO_4$, as time proceeds.

Cumulative losses for Cu and As from Scots pine from four different experimental conditions are shown in Figure 3. Comparison of the studies conducted with ASW at 7°C under static and stirred conditions indicated that the simulation of aquatic motion significantly increased leaching of both metals (Cu, $p = 0.02$; As, $p = 0.0003$). Stirring may simply prevent the build up of a saturation layer of leached preservative around the wood, which would affect diffusion gradients of further preservative leaching out of treated wood (Van Eetvelde, et al. 1995). It is unlikely that in field conditions the build up of such saturated zones would occur. The use of UPW was also found to significantly elevate leaching of Cu and As compared to ASW at 21°C under static conditions (Cu, $p = 0.01$; As, $p = 0.001$). The lower pH of UPW may have enabled greater concentrations of H^+ ions to partake in ion-exchange reactions with Cu. In addition, the presence of NaCl in the ASW may have had a coagulating effect on Cu fixation complexes which at low salinities (0-24‰) is suggested to increase surface area of these complexes, and so reduce solubility (Irvine and Dahlgren 1976).

Since temperature, stirring and water type clearly had an influence on leaching, repeat experiments were conducted with ASW and NSW. Given the concerns over the fixation of chromium in the Scots pine blocks used in the first phase of experiments, the second set of leaching experiments were conducted with Southern yellow pine blocks treated professionally and stored for in excess of 6 months to ensure complete fixation. An increased sampling regime was employed to better characterise losses in the early stages of the leaching experiments. In addition, studies were run for an extended period of 3 weeks. Results are shown in Table 4.

Table 3. Leaching of Cu, Cr and As (after Breslin and Adler-Ivanbrook (1998))

Source	Calculated 12 h flux ($\mu g\ cm^{-2}\ day^{-1}$) Cr	Cu	As
Our data,			
Scots pine[a]	31.4	3.36	0.43
Southern yellow pine[b]	0.2-0.6	6.0-6.4	0.6-1.3
Breslin and Adler-Ivanbrook (1998)	0.2-1.0	5.7-17.8	0.1-3.9
Putt (1993)	1.5	7.6	6.9
Weis, et al. (1991)	0.08	41.3	0.4
Merkle, et al. (1993)	0.03-0.1	4.3-5.6	3.3-8.2

[a]based on 18hrs leaching in ASW at 21°C
[b]based on 11hrs leaching in ASW at 21°C

For the Southern yellow pine leaching experiments, results are more in line with previous observations in the literature (Table 3). It is also noticeable that initially some Cr leaching rates were higher than As, though after 51 hrs Cr rates reduced to below those of As. This observation is in agreement with results of leaching from Scots pine blocks, where reduction in Cr leaching rates were the greatest of all three metals. This view is also supported when one considers the cumulative metal leaching generated by these leaching rates, where loss in the first 24 hrs equated to around 50% of total Cr loss, but only around 25% of total Cu and As loss. Since blocks were leached individually, the level of replication is effectively improved, and statistical analysis by ANOVA was possible to determine the effect of the different leaching solutions on metal loss. It is important to note that no statistically significant differences were observed for different blocks leached in the same water (p>0.05 for all metals). Copper and Cr were shown to leach to

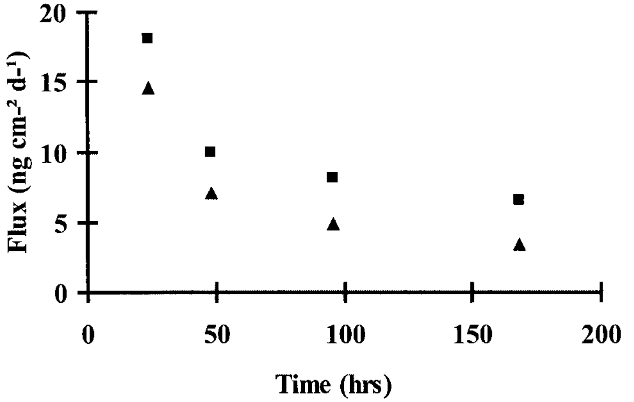

Figure 1. Comparison of As flux at 7 (▲) and 21°C (■) from Scots pine treated wood blocks (n=3) leached in ASW.

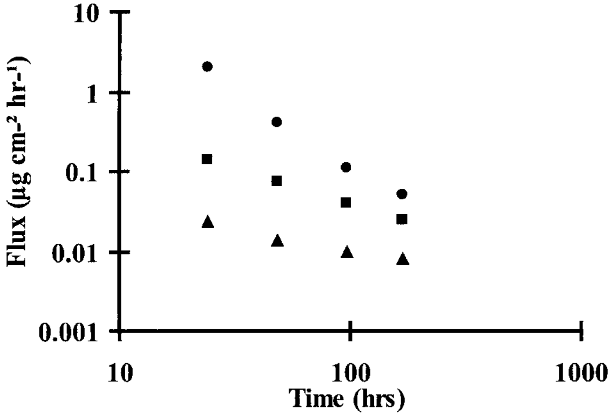

Figure 2. Log plot of flux declines for Cr (●), Cu (■) and As (▲) at 7°C from Scots pine treated wood blocks (n=3) leached in ASW.

a greater degree in ASW compared with NSW (Cu $p<0.01$, Cr $p<0.01$) while As loss was not significantly different in different waters ($p = 0.22$). The increased rate of leaching of Cu may have been due to an increased coagulating effect of NaCl in the less saline NSW compared with ASW. The presence of organic material, such as humic acids which are known to bind freely with Cu ions, may have been expected to increase leaching in NSW, however this is clearly not the case here. It is possible that organic and particulate matter present in the NSW may have actually inhibited loss by forming a layer on the wood surface. This phenomenon may be of even greater significance in the natural environment, where viable populations of fouling species may be present and able to colonise timbers. The reduced loss of Cr and Cu in NSW may have been due to increased

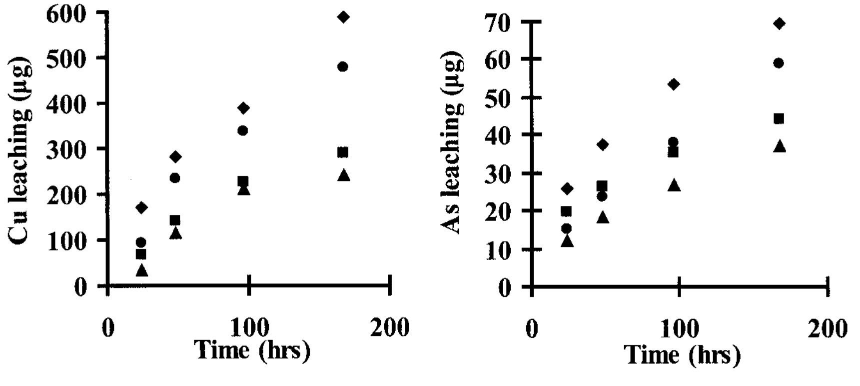

Figure 3. Comparison of cumulative leaching from Scots pine treated blocks (n=3) of Cu and As under four varying experimental conditions (21°C static UPW (◆); 21°C static ASW (●); 7°C static ASW (▲); 7°C stirred ASW (■))

Table 4. Summary of flux rates for Cr, Cu and As from Southern yellow pine blocks (n=3) leached in either ASW or NSW.

Sample time (hrs)	ASW Cr	ASW Cu	ASW As	NSW Cr	NSW Cu	NSW As
	Mean (S.E) $\mu g\ cm^{-2}\ d^{-1}$			Mean (S.E) $\mu g\ cm^{-2}\ d^{-1}$		
1	3.22 (0.73)	30.42 (2.11)	2.76 (0.50)	1.98 (0.09)	20.77 (1.66)	3.51 (0.44)
3	0.94 (0.13)	12.99 (0.72)	1.47 (0.42)	0.69 (0.08)	8.13 (0.88)	2.04 (0.56)
6	0.63 (0.11)	9.13 (0.45)	1.09 (0.29)	0.44 (0.08)	5.63 (0.68)	1.91 (0.74)
11	0.37 (0.10)	6.19 (0.09)	0.96 (0.20)	0.22 (0.03)	3.52 (0.34)	1.35 (0.50)
27	0.14 (0.04)	3.04 (0.15)	0.66 (0.09)	0.10 (0.01)	1.58 (0.15)	0.72 (0.20)
51	0.09 (0.01)	2.06 (0.15)	0.55 (0.09)	0.06 (0.01)	1.04 (0.07)	0.57 (0.17)
147	0.03 (0.01)	1.31 (0.12)	0.21 (0.03)	0.03 (0.001)	0.64 (0.09)	0.27 (0.06)
316	0.01 (0.003)	0.84 (0.08)	0.13 (0.02)	0.01 (0.001)	0.30 (0.04)	0.18 (0.04)
507	0.009 (0.003)	0.64 (0.11)	0.12 (0.01)	0.006 (0.001)	0.20 (0.04)	0.16 (0.02)

competition for suitable binding ions in the more complex natural mixture, compared with the relatively simple ASW solution. It is possible that the use of ASW in laboratory tests may overestimate the losses of Cr and Cu. This may have consequences regarding the decisions made on the environmental acceptability of such preservative products if decisions are based solely on such data.

It is clear that factors such as water movement and temperature can have a significant effect on leaching rates of all metals from CCA treated wood. This work also demonstrates that the choice of ultrapure, artificial or natural seawater as leaching medium will have an impact on results of such experiments. Given that NSW clearly has an effect on leaching rates, this may be seen to be the most suitable and realistic leaching medium for timbers exposed in marine areas. However, given the need for ease of replication in any standard developed for international legislation, NSW may not be considered appropriate where differences in local water characteristics may affect results. Care must be taken when evaluating leaching data produced in ASW, since Cu and Cr rates may be overestimated. The results also suggest a number of areas where additional research would improve the further development of leaching protocols. The precise effect of temperature remains to be fully characterised, and the choice of controlled temperature is unclear. Although stirring has been shown to be of importance in laboratory tests, the extent that rapid stirring may create an artificially aggressive leaching environment should be investigated. Better replication of samples, through leaching of blocks individually, may allow more rigorous analysis of data. In addition, investigation of the effects of varying timber block size, leaching from end-grains, and alteration of water:wood volume ratios are proposed to be of potential importance. A robust protocol will therefore have to establish well justified guidelines for each parameter.

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