

Fuel Consumption Pattern by the Mechanized Fishing Sector in Kerala

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Results of the study on the fuel utilization pattern in the mechanized fishing sector in Kerala are presented. Stratified random sampling revealed the fuel consumption of 97204 kl. by 3823 crafts, with an expenditure of Rs. 204 crores at the price level of 2002, during which only 55% of the fishing capacity was found utilized. The substantial fuel expenditure calls for optimum fuel utilization measures and appropriate management of fishing operations.

Keywords: Fuel consumption, mechanized fishing craft

The spread of mechanized fishing technology has completely transformed the fishing sector in India and the consumption of fuel has gone up as the number and size of mechanized crafts steadily increased over the years. Along with mechanized fishing the traditional sector also has been converting to motorization on a large scale where outboard engines of 8.00 hp to 40 hp are extensively used. Over 90% of the marine fish catch is presently accounted under mechanized and motorized fishing (Anon, 2000). The mechanized fishing boats of 28' to 40' LOA introduced in the sixties have mostly been replaced by larger boats of sizes upto 60' LOA fitted with 126 hp marine engines. The large boats are designed for longer sea endurance and also for deep-sea fishing. The fishing industry in India is supported by 53684 mechanized and 44578 motorized crafts, of which Kerala's share is 8% and 39% respectively (Anon, 2001).

An earlier study conducted by CIFT

(Unnithan *et al.*, 2004) has revealed that 77% of the operating cost of fishing goes towards fuel, affecting the profitability of fishing itself. Presently, no reliable estimate on the quantity of fuel used and the pattern of fuel consumption by the fishing industry is available. In this background, it is imperative that current status of fuel consumption in the fishing industry is ascertained in detail for economic evaluation of fishing vessels and also to evolve suitable policy formulations.

The present study attempts to bring out the fuel utilization pattern by different class of mechanized fishing vessels and estimate the total quantity consumed by the fishing industry in Kerala state.

Materials & Methods

The study was carried out during 2002 in Kerala. For making a sampling frame for the study, the number of mechanised crafts based on size viz., small (below 40' LOA), medium (40-48' LOA) and large (above 48' LOA), number of fishing days and trips per

craft per annum were collected. As the available data was not found up to date and reliable, a complete enumeration of the fishing crafts was carried out in the state level. For collecting the above information the trawl ban period of 15th June to 31st July was chosen so that actual counting of crafts could be possible when they are safely berthed at their respective jetties, adjacent water bodies or repair yards. For enumeration the coastal area of Kerala was divided into three zones viz. Kollam (Thiruvananthapuram and Kollam districts), Kochi (Alappuzha, Ernakulam and Thrissur) and Calicut (Malappuram, Kozhikode, Kannur and Kasargod). The physical counting of crafts (sick units excluded) was undertaken after careful planning and execution so that figures were available in time for each of the three regions. Information on the number of fishing days and trips by crafts of sizes of small, medium and large were collected simultaneously from the boat operators. Based on this preliminary data the distribution pattern of the fishing trips undertaken by different classes of crafts was arrived at. However the actual number of fishing trips made by the vessels during the year under study was collected in Cochin region as per secondary data available with the port authorities and officials in the mechanized craft landing centers including the Cochin and Munambam fisheries harbours. The fuel consumption data for each category of fishing vessels was collected from Ernakulam district of Kerala where about 30% of the fishing activity of the state is concentrated (Anon, 2003).

As the rate of fuel consumption was observed to vary considerably between boats of various sizes, the stratified random sampling techniques (Sukhatme and Sukhatme, 1970) was adopted for making the estimates. The boats were stratified into 3 strata of small (below 40'), medium (40-48') and large (above 48') based on vessel size. Data was randomly collected from each stratum by trained field staff based on a structured proforma to include fuel utilization, hp of the engine, average speed and rpm, area of operation, fishing time, duration, and trip cycle. Collection of data was performed from each stratum on every fifth day for a period of 10 months excluding the two months trawl ban period. A total of 4414 trips were covered for the study of which sampling ratio was 1% for the small class, 8% for the medium and 6% for the large class of vessels based on the population size. The actual quantity of fuel utilized per trip was taken as the fuel utilized for reaching the fishing ground and returning, and the fuel spent for fishing.

The formula used for the estimation was:

$$\sum^h \hat{Q}_h = \sum^h \left(\frac{N_h}{n_h} \times \sum_{i=1}^{n_h} q_{hi} \right) \text{ where } Q_h \text{ is the}$$

estimated fuel consumption; n_h is the number of trips sampled and the N_h is the total number of trips in the h^{th} stratum, q_{hi} is the fuel consumption of the i^{th} observation in the h^{th} stratum. The summation is taken over h strata for pooling the fuel consumption to obtain estimate at the district and state levels. The variance of estimates was worked out by calculating

$$v(\hat{Q}_h) = \frac{N_h(N_h - n_h)}{n_h} \times \frac{1}{n_h - 1} \left[\sum_{i=1}^{n_h} q_{hi}^2 - \frac{\left(\sum q_{hi}\right)^2}{n_h} \right]$$

The percentage error of pooled estimate is

$$SE = \frac{\sqrt{\sum^h v(\hat{Q}_h)}}{\sum \hat{Q}_h} \times 100$$

summation running over all strata at the respective levels.

The estimates of the fuel consumption made for each stratum were pooled for making the final estimates. This was also followed by the corresponding standard errors.

Results and Discussion

The first stage stratification of the vessels was based on the vessel size. The size wise information was collected through the enumeration of the boats and is furnished in Table 1 for Ernakulam district and Kerala state. The area of operation of the vessels were found to be on the West coast. As revealed by the table it may be observed that there has been an appreciable increase in the

number of larger boats which operate for multi-day fishing spanning a period of 2 to 10 days per trip and totaling about 280 fishing days a year. The small class of vessels are generally fitted with ALM 370 engine with a maximum of 70 hp. The medium size vessels are fitted with engines of about 100 hp (ALM 400 and 402) whereas the large vessels use engines mostly of 126 hp (ALM 412). The small crafts of below 40' were observed to be slowly vanishing from the fishing activities as a result of poor economic returns. Data compiled also indicated that about 15 h of fishing operations is conducted daily on an average and night trawling operation is generally not practiced.

Based on the analysis of the data collected, on an average one litre of fuel can generate the power of 5 hp in medium and larger vessels. In the vessels with turbo charged engines the Sfc (Specific fuel consumption) is reported to be low owing to its efficiency. It was observed that the present trend was to go for large vessels, as vessels of higher hp have more sea endurance. The medium class of vessels are observed to make a trip of average 5 days whereas the larger class of vessels generally make a trip of 7 fishing days.

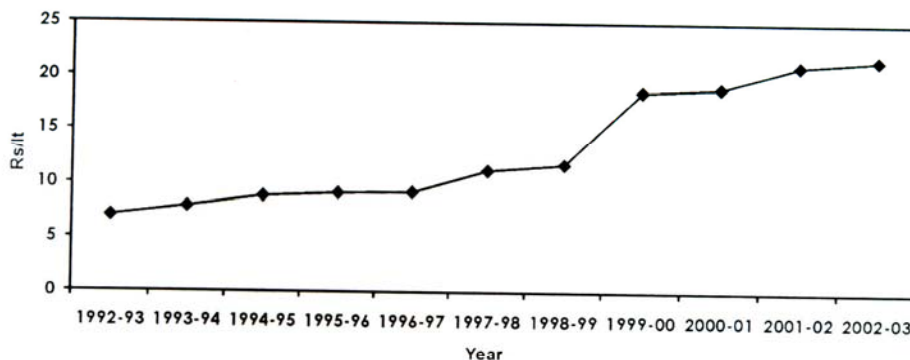


Fig. 1. Price of fuel (1992-2003)

Table 1. Number of craft and ideal number of trips for each category of craft

Vessel class (LOA)	Number of craft- Ernakulam	Number of craft- Kerala	Ideal number of trips per annum
Below 40'	484	1498	180
40-48'	265	912	80
Above 48'	736	1413	40
Total	1485	3823	

According to information collected from boat operators the small class of boats perform 180 days of operation whereas the larger types of boats engage in fishing operation for 280 days per annum in an ideal fishing season. In terms of trips this is equivalent to 180 (1 day trip), 80 (3 - 5 trip days) and 40 (5 - 7 trip days) trips for small, medium and large vessels respectively (Table 1).

However it has been observed that the maximum fishing capacity of the boats are not expended in some seasons owing to fluctuations in catch and poor returns. On the basis of the actual number of trips performed by vessels during 2002, the number of trips by small, medium and large vessels for Ernakulam was worked out to be 47966, 12182 and 15989 and for Kerala 148458, 41924 and 30696 respectively (Table 2).

As given in the table, an average of 195 L of fuel per day is utilized by small type of vessels. The medium class of vessels

consume 766 L per trip of 3 to 5 days and larger vessels consume 1200 L per trip of 5 to 7 days.

The estimate gives the consumption pattern of 9394 kL, 9336 kL and 18752 kL for small, medium and large vessels respectively, in Ernakulam district. The consumption in Kerala state was 29074 kL by small, 32129 kL by medium and 36001 kL by large vessels. Thus the consumption of fuel by the mechanised fishing industry in Ernakulam was estimated at 37482 kL and the corresponding figure in Kerala state as a whole was 97204 kL during the year 2002. The standard errors worked out are within the reasonable limits indicating the reliability of the estimates.

Attempt was made to estimate the consumption of fuel based on two stage stratification, the second strata being the duration of trip days. The estimate was thus made based on class of vessels as well as on trip days. The compilation of data on the basis of the second stage units based on trip days for medium and large vessels (40-48' and above 48') revealed the following distribution pattern (Table 4). However, the pooled estimate showed similar pattern as indicated in the single stage stratification and hence the second stage stratification was not considered. Hence the result of the first stage sampling is only provided in the paper.

Table 2. Ideal and actual number of trips for each category of craft

Vessel Class (LOA)	Ideal number of trips - Ernakulam	Actual number of trips - Ernakulam	Ideal number of trips - Kerala	Actual number of trips - Kerala
Below 40'	87120	47966	269640	148458
40-48'	21200	12182	72960	41924
Above 48'	29440	15989	56520	30696

Table 3. Estimated fuel consumption for different classes of mechanized craft in Ernakulam district & Kerala state

	below 40	40-48	Above 48	Pooled
Estimate of fuel used (kL)- Ernakulam district	9394	9336	18752	37482
SE (%)	0.13	0.94	0.98	0.54
Estimate of fuel used (kL)- Kerala state	29074	32129	36001	97204
SE (%)	0.13	0.94	0.98	0.54

As already indicated, the study has revealed that only 55% of the fishing capacity was actually utilized during the year under study. It has been noted that the vessels remain only for a few days at sea in lean fishing season or remain idle in jetties during certain other times due to uneconomic fishing and hence the reduction in the utilized fishing capacity. The demand of fuel by the industry at 100 % fishing capacity utilization will be 68148 kL for Ernakulam district and 1767735 kL for Kerala state.

The domestic fuel price for the past ten years is furnished in Fig. 1 indicating a price rise of 209% during the past decade and an annual price rise of 18.5% during the past five years ending 2002-03. At price levels of 2002 the total expenditure on fuel by the mechanized fishing industry in the works

Table 4. Percentage distribution pattern of fishing trips based on number of days by medium and large class of vessels

Vessel Class (LOA)	1-2 days	3-5 days	Above 5 days
40-48'	20.39	74.24	5.37
Above 48'	8.37	55.95	35.68

out to Rs 204.13 crores which is highly substantial. Considering the fact that the fuel cost is the major component in the operational cost of the mechanized vessels a substantial rise in the fuel cost will adversely affect the economic viability of the fishing vessels and hence there is an urgency of attaining fuel efficiency by suitable means.

The cost of fuel has been rising steadily and the decrease in fishing capacity utilization that was observed during the study can be attributed to the increasing fuel cost coupled with low returns, especially during the lean season. In this scenario the future of the industry will depend on appropriate technological and managerial interventions like development of new-generation, fuel efficient fishing vessels, fuel saving fishing techniques and optimization of the mechanized fishing fleet.

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Leaching of Chromated Copper Arsenate (CCA) Wood Preservative into the Aquatic Environment – a Review

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The scarcity of timber and its rising costs necessitates the use of chemical preservative treated wood for aquatic use. Preservative treated wood contains components that may be harmful to the environment. The wood treated with the most common preservative, Chromated Copper Arsenate (CCA), may form a significant source of metals in the aquatic environment. The studies on the factors affecting the leaching rates like pH, salinity, and temperature of the leaching media, the block size and the preservative treatment conditions are reviewed. Recent studies have generated conflicting data in this regard and Field studies in this direction are also found to be few. This communication highlights the need for further research in this field.

Key words : Wood preservative, Chromated Copper Arsenate (CCA), leaching, aquatic environment, speciation

The structural, economic, environmental and aesthetic benefits of wood make it the preferred material for a wide variety of construction applications. Its major weakness is susceptibility to attack by natural enemies- wood borers, insects and fungi. Over the past century a variety of wood preserving treatments have been developed that introduce a small controlled amount of protective preservative into the wood cells. Preservatives that are widely used for pressure treatment of wood can be classified as oil borne, water borne and solvent type. The water borne preservatives have largely replaced the oil borne preservatives for aquatic use, on environmental and human health considerations. The water borne preservatives include chromated copper arsenate (CCA), chromated copper boron (CCB), ammoniacal copper arsenate (ACA), acid copper chromate (ACC), ammoniacal copper zinc arsenate (ACZA) and ammoniacal copper quat (ACQ). Solvent type preservatives include pentachlorophenol and copper naphthanate. Out of the 16.7 million m³ of wood preserved in USA in 1996, 13.2 million m³ i.e., 79.1% were treated with water

borne preservatives amounting to 1.9 million kg. The most widely used wood preservative for timbers exposed in aquatic environments is CCA. Nearly 5.8 million board m of preserved timber were prepared for marine construction, of which 95% was treated with CCA (AWPI, 1997). The treated wood is extensively used to build structures such as decks, fences, poles, pilings, playgrounds, and picnic tables. CCA-treated wood represents approximately 90 % of the treated wood market by volume in Korea (KFRI, 2002). Minimum life spans in fresh and marine water for CCA treated panels are considered to be 30 and 15 years respectively (AWPA, 1994). In India about 150 treatment plants are there using 1000 tonnes of water borne preservatives to treat 0.4million m³ of wood annually and it is estimated that it would increase to a maximum of 10000 tonnes over the next decade (Kumar, 1990).

The components of CCA, chromium, copper and arsenic all have important roles in preservative efficacy. The primary role of chromium in CCA is fixation of its components with reduction of chromium from

hexavalent to trivalent state. These reactions result in the insolubilization of CCA components in the wood so that they resist leaching and provide lengthy service. Copper and arsenic are vital to the preservative efficacy of CCA because of their toxicity to fungi and insects. Copper is an excellent fungicide and arsenic is especially effective against insects and helps to provide protection against some copper tolerant fungi. Recent toxicity studies have suggested that leaching of preservative components from wood used in aquatic media may be harmful to the environment. The focus of much of the early work concerning leaching of CCA has been on monitoring leaching in terms of durability of wood and the ability of treated timbers to withstand biological decay, rather than quantifying its release to the environment and its after effects (Fahlstorm *et al.*, 1967; Hager, 1969; Cherian *et al.*, 1979; Johnson, 1982; Eaton, 1989; Green *et al.*, 1989). Only few among the previously conducted leaching experiments have examined the rate of release and the factors which may affect the leachability of Cu, Cr and As from CCA treated wood specimens (Johnson, 1977). Conflicting evidence exists about the extent of leaching of Cu, Cr and As from CCA treated wood. Examination of CCA treated products following prolonged terrestrial and marine weathering showed that CCA-C treated wood effectively retained Cu, Cr and As (Arsenault, 1975; Johnson, 1977). In contrast, Hegarty and Curran, (1986) showed that CCA treated beech and Scots pine specimens weathered in seawater for one-year period showed measurable losses of Cu, Cr and As. Recent studies have also shown a similar pattern of leaching of Cu, Cr and As from CCA treated wood submerged in coastal water for one to four years (Archer & Preston, 1994; Hayes *et al.*, 1994). However the immersion conditions can affect the results obtained. In some situations, the leached preservative in the water may reach concentrations that inhibit further leaching (Brooks, 2002).

The efficacy of CCA against biodeterioration of wood exposed to the sea, soil and atmospheric condition have been studied in India. Retention levels of 16 kgm^{-3} have been found to be very effective in resisting borer attack in seawater (Kumar, 1985). Catamarans made of CCA treated logs of *Bombax ceiba* used for 15 years service at the Lawson's Bay fishing village, Visakhapatnam in India were studied for the efficacy of the preservative. Only 2/3rd of the preservative was found leached and the catamarans were still in usable condition (Kuppusamy *et al.*, 2002). The efficacy of CCA and the effect of its treatment in the physical and mechanical properties of boat building timbers have been studied at the Central Institute of Fisheries Technology, Cochin (Edwin *et al.*, 2005). The studies on the secondary species of timber have led to the adoption of preservative concentration of 7.5% for marine purposes. The strength of wood was not found to be affected when lesser concentrations of CCA were used along with creosote (Edwin *et al.*, 1993; Thomas *et al.*, 1998). The dual preservative treatment technology involving the pressure impregnation of CCA followed by creosote, with a drying period in between was used in the study on the resistance of preservative treated rubber wood to marine borers. After an exposure of 33 months in sea, the dual treated wood showed excellent performance without biodeterioration (Edwin & Pillai, 2004).

Leaching rates from preservative treated wood are dependent on several factors, especially the amount and kind of drying the wood is allowed to do (Hingston *et al.*, 2000). According to Hingston and Moore, wood dried for a longer time period at natural ambient temperatures, will fix more CCA preservative, leaving less to leach out (Hingston *et al.*, 2000). To enable a more realistic assessment of the possible environmental effects of CCA treated timber accurate quantification of component leaching rates is required. The aims of this review are

- To evaluate the process of fixation of the preservative
- To identify the principal factors of the medium that effect leaching rates.
- To assess the effect of sheathing/coating on leaching.
- To assess various leaching protocols.
- To evaluate the role of field trials in leaching studies.
- To evaluate the speciation of the leachate.

FIXATION OF PRESERVATIVE

Although the term fixation is routinely used, the actual meaning of this term in the context of preservative treatment has not been precisely defined. In general, fixation refers to the series of chemical reactions that render the preservative non leachable during service. Fixation can otherwise be defined as the process that minimizes the leaching of the chemical components of the preservative and wood or other substrate when all chemical reactions are complete (Cooper *et al.*, 1993). The fixation reactions are highly dependent on treating factors, such as preservative formulation, preservative retention, processing techniques and post treatment conditioning factors such as temperature, humidity and air-flow (Lebow, 1996). The effect of wood species on the fixation and efficacy of treated wood and fixation reaction of CCA with lignin, cellulose and their model compounds have been extensively investigated (Greaves, 1972; Greaves, 1973; Greaves, 1974). The reactions that take place in the wood during the fixation of CCA have a great influence on the metal species that are emitted from the wood, and the subsequent toxicity of the leachate.

Formulation

The ratio of components in CCA formulations is crucial to allow rapid and complete fixation. Differing commercial formulations have been produced that meet AWPA standards for types A, B and C

(AWPA, 1994). Fahlstrom, (1967) found a clear relationship between the Cr:As ratio and total metal leachability and proposed a ratio of Cr: As of 1:1.3 as optimum. Smith and Williams (1973) studied a range of CCA formulation and suggested a Cr:As ratio of 1:1.9 or greater for maximum arsenic fixation. As a result of this variation in fixation of different formulations, the leaching studies conducted earlier generated variable results, with arsenic always proving to be the most leached element, probably due to insufficient Cr available for complexation (Fahlstrom *et al.*, 1967; Henshaw, 1979).

Preservative treatment

Physical parameters of the preservative treatment process such as magnitude and duration of vacuum and pressure cycles may influence penetration and retention of preservatives. In order to ensure prevention of leaching adequate time should be allowed for fixation before placing the wood in service. The time required for fixation varies with wood species, specimen size and retention, but the most important parameter is temperature. Temperature is very important in obtaining adequate and timely fixation. Much work has been done to develop methods of high temperature fixation such as kiln drying, steam baths or water baths. Peek and Willeitner pioneered earlier works in the field of accelerated fixation (Peek Willeitner, 1981). Rapid drying may cause redistribution of chemicals between lignin and cellulose leading to higher proportions of CCA products in the cell lumens, where again they may be more accessible to leaching (Lee *et al.*, 1993; Cooper *et al.*, 1997).

Loading / retention

The exact relationship between preservative loading or retention and leaching is not understood, even though preservative loading is known to affect the absolute concentration of elements leached (Cooper, 1994; Albuquerque & Cragg, 1995a; 1995b; 1996). Fahlstrom *et al.* (1967) suggested the

effect of retention on leaching was dependent on preservative composition with percentage leaching decreasing with increasing retention in As rich formulations. In Cr rich formulations, leaching increased with retention. Proportional losses have been found to decrease at increased loadings (Archer & Preston, 1994; Hayes *et al.*, 1994). Following 85 months exposure in the marine environment, percentage losses were 52 and 44 from pine treated to retentions of 24 and 48 kg/m³ respectively. The reduced leaching was supposed to be due to increased total Cr concentrations in the system available to fix the remaining metal elements (Archer & Preston, 1994). At the same time other workers have shown increased leaching with increasing retentions (Albuquerque *et al.*, 1996; Irvine *et al.*, 1972). Long term copper and chromium leaching rates were highest in CCA treated wood with retention levels >35kg.m⁻³, whereas long term As leaching rates were increased in wood with retention levels <35kg.m⁻³ (Breslin & Alder-Ivanbrook, 1998).

CHARACTERISTICS OF THE LEACHING MEDIUM

Many features of the leaching media are important in determining leaching rates, particularly salinity, pH, wood: water volume, rate of water movement around the specimen, temperature, orientation of wood grain etc. Leaching medium is an important factor affecting release of preservative components from treated wood because physical and chemical characteristics of medium increase or decrease the solubility of fixed preservative components (Kartal *et al.*, 2004).

Salinity

Standard leaching test methods for preservative leaching from treated wood usually requires distilled or de-ionized water (Kartal *et al.*, 2004; Kartal & Imamura, 2005). Water is a key factor for release of preservative components from treated wood. A study by Kartal *et al.* (2004) showed that

sea water and tap water containing higher ion concentrations than distilled water resulted in less leaching of wood preserving and calcium precipitating agent, N,N-hydroxynaphthalimide (NHA) from treated wood specimens. Scots pine and beech sap wood blocks treated with CCA were exposed in cooling towers receiving water from fresh water, sewage effluent and marine sources with results indicating increased loss of copper and chromium with increasing conductivity of the surrounding waters (Irvine *et al.*, 1972). It has been suggested that at low salinities NaCl has a coagulating effect on the crystalline Cu fixation complexes increasing surface area and decreasing solubility, and at salinities above 24ppt the increased formation of complexes between chloride and copper may explain the increased leaching (Irvine & Dalgren, 1976). The characteristics of the leaching water can also influence leaching of preservatives. The presence of some types of inorganic ions in water has been reported to increase leaching from CCA treated wood (Irvine *et al.*, 1972; Ruddick *et al.*, 1993).

The results of the studies conducted by Lebow *et al.* (2000), comparing leaching in de-ionized water and seawater are worth noting. The effect of salinity on the rate of copper release changed with time. For the first month, the rate of release of copper in deionized water was greater than or equal to that in seawater. However in the remaining months, copper release in the seawater was significantly greater than the release in deionized water. When leaching rates stabilized after 10 to 15 months, the rate of copper release in seawater was 8 to 25 times greater than that in deionized water. In comparison to copper, chromium release rates were much lower and relatively insensitive to the seawater concentration of the leaching solutions. Arsenic release tended to be greater in the deionized water than seawater solution. Unlike chromium, the greater release in deionized water did not appear to decrease over time.

pH

The effects of the pH of solution on preservative loss were investigated by conducting studies using water buffered with NaOH and Citric acid. This study indicated very high leaching rates at low pHs, with losses of Cu up to 100% at pH 4.5 (Warner & Solomon, 1990). Leaching in dilute sulphuric acid solutions was reduced by up to a factor of 5 and later demonstrated that the high losses were due to the use of the citric acid buffer (Cooper, 1991).

In a study, sulphuric acid/nitric acid buffers were used to investigate the effect of pH on CCA leaching from western hemlock blocks (Kim & Kim, 1993). The study showed that the leaching of copper was between 16 and 25% at pH 3, but decreased to about 1% at pH 4. Leaching of arsenic was found less affected by pH, but was generally around 2-3% at pH 4 and above. Leaching of CCA is greatly increased when the pH of the leaching water is lowered to below 3, and the wood itself also begins to degrade (Cooper, 1991; Kim & Kim, 1993). Water pH ranges are less likely to have significant effect on leaching, although the presence of organic acids may influence leaching at moderate pH levels (Murphy & Dickinson, 1990).

Wood: water volume

The volume of leaching water used is an important aspect, where a high wood: water volume ratio allowed toxic concentrations of metals to build up (Weis *et al.*, 1991; Albuquerque & Cragg, 1995a). Studies have been conducted exposing marine organisms to CCA treated wood or leachate waters and deleterious effects have been shown against a range of aquatic organisms (Weis *et al.*, 1991; Weis *et al.*, 1992). Criticism of this work focused on the unrealistically high ratio between wood and water volume, which allowed metal concentrations to build up to toxic levels (Albuquerque & Cragg, 1995a; Breslin & Alder-Ivanbrook, 1998). During

laboratory leaching trials, the size and dimensions of wooden blocks used were found to have major influence on the percentage of preservative leached from the wood. The relatively large surface area to volume ratio of the typical small sample blocks used in most studies allows proportionately more wood available for leaching (Cooper, 1994). Significant reductions in leaching rates of all CCA elements were observed with a decrease in surface area to volume ratio (Cooper, 1994).

Rate of water movement

The rate of water movements around the test specimens can also influence leaching, although this effect has not well quantified. Van Eetvelde *et al.*, (1995) reported that leaching of CCA was greater when using stirred leaching water than with static leaching trials. The AWPA standard leaching test specifies the use of a low stirring speed (eg. a tip speed of 25 – 50 cm per second). With adequate care for the method of stirring or agitation used, the mechanical abrasion of the surface of the wood can be avoided.

Temperature

Leaching of Cu, Cr and As has been shown to be reduced at lower temperatures and leaching of Cr at 20°C N is reported to be 0.119 $\mu\text{g m}^{-2} \text{s}^{-1}$ compared with 0.079 $\mu\text{g m}^{-2} \text{s}^{-1}$ at 8°C (Van Eetvelde, 1995). Cu, Cr and As leaching were approximately 1.4, 1.6 and 1.5 times greater, respectively from wood leached at 20°C than that at 8°C. Brooks (2002) also concluded that leaching of Cu from CCA treated wood could be substantially increased as water temperatures increased from 8°C to 20°C. A similar temperature effect was noted in study of release of creosote components from treated wood (Xiao *et al.*, 2002). However, temperature may not be a deciding factor in the leaching of CCA in the tropical waters because fluctuation in temperatures is not so pronounced in these regions.

Orientation of wood grain

The rate of movement of liquids along the grain of wood is several orders of magnitude greater than that across the grain, and samples with a high proportion of exposed end grains will exhibit exaggerated rates of preservative leaching. Losses within 24 hours have been shown to be greatest from the radial and tangential surface, although long term leaching was greatest from end grain (Osler & Holland, 1993). End grain penetration has been shown to be 40 times greater than lateral penetration and may greatly influence leaching rates (Morgan & Purslow, 1973). In commodity size timber, end-grain may represent only a small percentage of exposed surfaces, but may form a significant portion of the standard test blocks. This leads to laboratory studies grossly over estimating leaching rates (Archer, & Preston, 1994; Cooper, 1994; Albuquerque, & Cragg, 1995a). The shape, size, volume and proportion of end grain in the wood are of prime importance in determining the potential for leaching (Cooper, 1994). Hayes *et al.* (1994) found a considerable reduction in the amount of metal lost with increasing block size.

EFFECT OF SHEATHING/COATING ON LEACHING

The manufactures of CCA wood have recommended the use of surface coatings to reduce cracking of wood resulting from effects of weather such as rain, temperature, humidity, solar radiation etc. (USEPA, 2001). Boards with polyurethane, latex/acrylic, oil stain and spar varnish coatings were evaluated by Stilwell, Scientific Certification Systems and California Department of Health Services. The results indicate that these remained very effective in reducing dislodgeable CCA chemicals for at least one year after they are applied. The Scientific Certificate Systems study evaluated the impacts of two post treatment coatings, (Superdec stain and 3M clear sealer/polyurethane) and one coating incorporated into the CCA treatment process (Osmose water

repellent). The results indicated that only 3M polyurethane sealant was effective at reducing dislodgeable arsenic whereas the superdec stain and osmose water repellent were not effective. The California Department of Health Services evaluated Structures that were in current use and therefore effects of wear and tear on the efficacy of the coatings were included. This study suggests that coatings provide a considerable reduction in the amount of dislodgeable arsenic especially in the case of polyurethane, which is sufficient for two years after post treatment. Since the decrease in dislodgeable arsenic was very large, the data are considered to be meaningful even in the absence of an uncoated control.

The ability of coatings to reduce the leachability of arsenic from CCA treated wood was studied by Cooper *et al.* (1997). The results showed that Thomson's water seal (applied after CCA treatment) significantly reduced the quantity of arsenic leaching for a period of two years after its application. The water repellents applied as a part of CCA treatment were not effective at reducing leachable arsenic concentrations.

Lebow & Evans (1999) evaluated the use of a water-soluble acrylic polymer with an iron oxide, which was applied prior to treatment with CCA. Results from this study found that the pre stain was able to reduce the leaching of arsenic by 25 to 30% that simulated natural rainfall over a 17-week period. Application of coating/sheathing in field structures also found to reduce leaching. One report indicated that a clear water repellent finish greatly decreased CCA release from fencing (Cooper *et al.*, 1997). Even after two years, arsenic concentration in rainwater collected off the finished specimens was approximately five times lower than that from the unfinished specimens. A laboratory study has also indicated that latex paint, oil-based paint and semi-transparent penetrating stains are all effective in decreasing leaching from horizontal surfaces (Lebow *et al.*, 2002). Results of these

studies as a whole support that surface coatings applied after CCA treatment are effective at reducing the quantities of arsenic leaching. Reductions of 70 to 90% in dislodgeable arsenic were observed as CCA treated wood was subjected to natural weathering. It is suggested that future experiments should evaluate the efficacy of different types of coatings on the quantity of toxins leached.

LEACHING PROTOCOLS

A number of standard protocols that have been used for short-term (<24 h) leaching tests for CCA-treated wood include the toxicity characteristic leaching procedure (TCLP, SW-846 method 1311) and the synthetic precipitation leaching procedure (SPLP, SW-846 method 1312) (USEPA, 1996) and British Standard EN.84 (BSI, 1997). Results of these short-term leaching tests have often been used for regulatory decisions on management of CCA-treated wood in-service or discarded. For example, in the United States TCLP results of CCA-treated wood have created growing concerns for environmental communities and regulatory agencies in regard to the exclusion of CCA-treated wood from the definition of hazardous waste. Although many short-term leaching tests have been routinely used for regulatory purposes and in risk assessments at a fixed solid-to-liquid ratio, most tests do not provide the rate of long-term release of arsenic, chromium, and copper from CCA-treated wood in the environment. Studies have shown that CCA-treated wood leaches preservative compounds at greater rate when first exposed to leaching solution as compared to prolonged exposure period of time. Thus, extrapolating short-term data may lead to an over estimation of losses of metals expected during the long service life or disposal period of CCA-treated wood (Hyunmyung *et al.*, 2005).

The existing standard leaching protocols for conducting laboratory leaching studies (AWPA, 1997; ANS, 1986; BSI, 1994

& 1997). ENV.1250:2 of British standards recommends immersing five end sealed test blocks (50 x 25 x 15 mm) in 500 ml of water or artificial sea water, stirring at 20°C, for six leaching periods of increasing duration up to 48 hours. ENV. 1250:2 also recommends an intermediate drying period of 16hour during the test to simulate natural drying of wood exposed to tidal regimes (BSI, 1994).

According to AWWA, E-11, six blocks should be selected from panels having selected retentions. The six blocks should then be immersed in 300 ml of de-ionized water for 30 minutes. Then the panels should be leached in accelerated condition using magnetic stirrers (at a stirring speed of 25-50 cms⁻¹) with the same type of magnetic stir bar for each leaching flask. Samples of leachates should be then collected and the whole solution should be replaced with fresh de-ionized water after 6, 24, 48, 96, 144, 192, 240, 288 and 336h. Willeitner and Peek (1998) briefly reviewed standard test methods for measuring environmental inputs of waste and other material by leaching and proposed general requirements necessary for leaching studies with wood preservatives.

B.S. EN.84 represent the most severe leaching test of all available protocols because of the incorporation of a water impregnation stage, where test blocks are immersed in water and maintained in a vacuum desiccator for two hours prior to leaching. Potential drawbacks of this approach are the inability to end seal test blocks, the use of static water conditions and lack of a rigid sampling regime. American Nuclear Society suggests a leaching pattern for tank leaching studies. The temperature and salinity should be varied to determine the effect of these variables in the rate of Cu, Cr and As leaching from CCA-C pressure treated wood. Filtered seawater (0.40 µm) prepared using Type 1 reagent grade water having salinities 3‰, 13‰ and 26‰ should be used. The temperature of the leaching water should be varied by conducting the experiments at room temperature (20°C) or

in a refrigerator (4°C). Leachate samples should be collected following 12, 24, 48, 96, 168, 336, 504, 840, 1176 and 2160 h for half the number of samples and following 12, 24, 120, 168, 312, 504 and 1440 h for the rest of the samples. The samples should be analyzed for metals.

Adopting a single recognized protocol for all leaching studies would certainly aid comparisons of laboratory-based data. An important aspect of any leaching protocol is that sampling should be conducted at sufficiently regular intervals to allow quantification of the decline in leaching rates during the early periods of exposure.

FIELD STUDIES

Many factors that can influence leaching in service are difficult to arrange in a laboratory. Even if experimental conditions are more difficult to control in field or service leaching studies, the results tend to be more useful indicators of actual leaching amounts. In long term marine field trials, CCA treated pine leached as much as 25% of total active ingredients within six months, with total losses rising to 52% after 85 months (Hegarty & Curran, 1986). Hayes *et al.* 1994 also observed 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 highest leaching rates had the minimum life span (Cherian *et al.*, 1979). Chemical and anatomical differences between wood species result in different rates of leaching. The chemical nature of wood affects the mode and quality of fixation (Cooper, 1994). Wood anatomy determines depth of penetration, but may also facilitate leaching. Cherian *et al.* (1979) found considerable differences in leaching rate between different species of Indian timbers exposed in Cochin Harbour, India. Marked differences in rate of seawater leaching were noted between European

beech (*Fagus sylvatica*) and Scots pine (*Pinus sylvestris*) (Lightly, 1987).

Results of the study by Breslin and Alder Ivanbrook show that preservative retention and the leaching of elements from CCA-C treated lumber was highly variable. A 90 day leaching rates for Cu and Cr increased as CCA retention increased whereas arsenic flux decreased with increased CCA retention. There has been a recent increase in evaluation of preservative release from in-service structures that are generally observational (not controlled) studies. An evaluation of in-service structures provides valuable information in leaching and environmental accumulation in actual applications. The disadvantage of these types of studies is that they are specific to the conditions at that specific site and difficult to tolerate other exposures. The original treatment may be unknown, and there may be little historical data to indicate whether the site was previously exposed to contamination from construction debris or other non-leaching sources. The type of exposure or application also greatly influences in-service leaching. Regardless of whether the treated wood is exposed to precipitation, freshwater, seawater, sediments or soil, the movement and composition of water is the key to leaching of the preservative components from the wood (Hayes *et al.*, 1994; Albuquerque *et al.*, 1996).

For a field study, the specific parameters or hypothesis of interest relevant to the inference populations such as a 95% confidence interval for median amount of copper within 152 mm of a structure, need to be identified before the study. Subsequently, these best sampling strategy and analysis methodologies to address these information needs can be selected. Selection and number of sampling locations for removal of environmental samples can also influence levels of preservative components detected. Common preservative components such as copper, chromium and arsenic are reactive with soil constituents (Lebow, 1996) and are not freely

mobile in soil. Thus environmental concentrations tend to be concentrated in areas immediately adjacent to treated wood or water drips off treated wood into soil. Even when soil samples are removed from directly under the drip line of a deck, environmental concentrations of leached preservative components can vary greatly (Lebow *et al.*, 2000).

Sediment analysis

The impacts due to the release of elements from CCA-C pressure treated lumber depend on many factors: the amount of treated wood present, treatment level, age of the wood and the movement of water surrounding the structure. The accumulation of these elements in the sediments, water column and biota would be expected to be highest for recently constructed large structures built in poorly flushed systems and less for smaller structures built in well flushed systems. Brooks (1996) developed a model based on the Putt (1993) leaching data to estimate the impacts of Cu leaching on the water column and sediments surrounding CCA-C pressure treated bulkheads and pilings. The initial (<7day) Cu leaching rates found in the Brooks model and those measured in a study conducted by Breslin and Alder-Ivanbrook (1998) are similar. The model is highly dependent on input parameters, including wood age, initial CCA-C retention, water depth, bulkhead length and tidal velocity. The Brooks model does demonstrate that initial (<3 weeks) water column copper concentration may be high (>2.5µg/l) near structures placed in poorly flushed areas or where the surface area of the bulk head is a significant portion of the water body surface area (marine water area/CCA surface area <259). However, water column copper concentrations are predicted to be low near CCA-C treated wood structures placed in well-flushed bodies of water.

The summary of the detailed study recently conducted (Brooks, 2002) on the environmental suitability of CCA-treated

marine piling is as follows. The results are against any suggestions that treated piling is harmful to sediment-dwelling life. Measured amounts of copper, chromium and arsenic in naturally occurring water, sediment, leachate and treated sediments established that some variability occurred between measured amounts due to the behavior of the three metals in natural environmental conditions (e.g., seawater, sediment and wood). Although this variability was observed and was consistent with expectations of naturally occurring environmental conditions, reliable and useful trends were established which can be used to understand the general leaching and adsorptive properties associated with the CCA-C treated wood and subsequent exposure in natural marine environments. Analyses for arsenic demonstrated that approximately 59.5 mg arsenic/m² of treated wood surface area leached from the treated pilings. Arsenic did not appear to adsorb onto sediment of either type and, in almost all cases, was not observed in interstitial or overlying water.

SPECIATION OF THE LEACHATE

The degree of toxicity of leachate depends upon the chemical speciation of the components of CCA that are released when treated wood is placed in seawater. Although considerable information exists on speciation of the individual elements in CCA, there is little research specific to CCA leachates (Albuquerque, 1995a). It is not clear if metals are leached as individual elements, as Cu or Cr arsenates, as inorganic complexes or possibly even as organo-metallic complexes bound to water-soluble extractives (Lebow, 1996). Baldwin *et al.* (1996) studied partitioning of metals to sediment during laboratory leaching trials with marine piles, and found that Cu bound to both low and high organic carbon sediment to the same degree and did not desorb to the overlying waters. Cr exhibited minimal adsorption to a high organic carbon sediment only and arsenic was found in all cases in the interstitial or overlying waters. Speciation into oxidation

states was not possible due to low concentrations. The toxicity of Cu, Cr and As is highly dependent on the specific form in which it is present. Cr in the +6 oxidation state is known to be carcinogenic and mutagenic, but if reduced to Cr (III), as during the CCA fixation process, it may be significantly less harmful (Sanders & Reidel, 1987). Arsenic may also be carcinogenic and mutagenic as well as teratogenic and, of the predominant oxidation states, As (V) is thought to be the more prevalent and less toxic form than As (III). Inorganic arsenic and hexavalent chromium Cr (VI) originates from leached CCA chemicals causes health problems in human (Townsend *et al.*, 2001; Hingston *et al.*, 2000).

Many analytical procedures can only measure the total metal concentration, some times with the ability to distinguish between oxidation states. Few techniques are able to provide information concerning complexation. In seawater, metals can exist as free metal ion, or combine with anionic or naturally derived organic ligands to form complexes. A relatively low equilibrium percentage of free metal ions are usually present in total dissolved metal in seawater (Bruland, 1983). The percentage of free metal ions is known to vary depending on pH, but the buffering capacity of the seawater is assumed to resist major pH changes (Langston, 1990). Becher *et al.*, (1983) found that copper forms complexes with humic acids found in seawater. Fractions of organically associated copper exceeding 98% have been reported in Atlantic waters (Buckley, 1986; Kramer, 1986). The presence of organic ligands in seawater suggests that a high proportion could become bound to organic material and thus less toxic to biota. The possible species that may be subject to leaching from treated wood are Cu hydroxide ions, CrO_3 , HCrO_4^- or CrAsO_4 (Hayes *et al.*, 1994). Pizzi suggested that of the forms of Cu present in CCA treated wood, CuSO_4 physically adsorbed by the various wood constituents was the likely leachate component (Pizzi, 1982). Lebow *et al.* (1999)

compared the release of copper, chromium and arsenic into seawater and deionized water from CCA treated wood and the following results were observed. In the initial stage of leaching, when the release of copper is high in solution, a variety of forms of copper are being removed from the wood. These might include copper bound to water-soluble extractives, copper adsorbed to particulate matter and copper precipitated within the wood structure. Leaching of more conventionally fixed copper, such as that fixed by ion exchange reactions with wood would become a greater proportion of the copper release. It is known that seawater cations such as Ca^{2+} and Mg^{2+} compete with metals for ion exchange sites on organic matter (Salomons & Forstner, 1984). Although copper may form stronger complexes with organics than does Ca^{2+} or Mg^{2+} , the high concentrations of these ions in seawater can decrease copper complexation with organic ligands (Bodek *et al.*, 1988). The relatively low initial release rate in seawater may have been caused by precipitation of chromium in colloidal form. Chromium is likely to form complexes with polyflavanoid tannin extractives and these complexes may have been precipitated by seawater metals but remained soluble in deionized water leachate (Ryan, & Plackatt, 1987). It has also been reported that the presence of metal cations (such as Na^+ , Mg^{2+} , K^+ , and Ca^{2+} in seawater) could result in the immobilization of soluble arsenic through the precipitation of metal arsenates (Bodek *et al.*, 1988). Cr is present in seawater as the more toxic Cr (VI) form rather than Cr (III). This is because of the high pH of seawater (Ahrland, 1975). It is readily taken by phytoplankton as the soluble chromate ion, CrO_4^{2-} (Baldwin *et al.*, 1996). This is comparable in size and charge to the sulphate ion (Ahrland, 1975). The chromate ion does not form complexes with anions but acts as a potential metal coordinating ligand itself. Arsenic has two main oxidation states, As (V) and As (III), the former is less toxic form and is predominant in seawater (Sanders & Windom, 1980). As (V) occurs almost entirely as HASO_4^- ions in

the arsenate form, it bears a similarity to phosphate hence is readily taken up by phytoplankton (Sanders & Windom, 1980). As (III) occurs mainly (87%) as $\text{As}(\text{OH})_3$.

Conclusion

A number of interesting conclusions may be drawn from this review. The period between treatment and immersion in water greatly influences the magnitude of initial CCA release. Significant differences were observed in leaching of Cr and As between wood dried for one or four weeks. Increased time allows greater reaction between preservative and wood components to occur, reducing the leachable component. CCA treated timber intended for marine use should be treated with the most leach resistant formulation available provided that such a formulation also provides adequate protection from borers. Particular care should be taken to ensure that post-treatment fixation is properly conducted.

Better understanding of the importance of water selected for leaching studies, potential underestimation of losses in artificial seawater solutions and the effect of organic acids is required if the usefulness of existing laboratory data is to be determined. Both the environmental conditions and the preservative treatment of wood may affect its leachability. Factors such as preservative formulation, fixation, temperature, post-treatment handling, timber dimensions and pH, salinity and temperature of leaching media have been shown to affect leaching rates. More rigorous examination of these factors is required if accurate prediction of in-service leaching rates is to be made based solely on results of laboratory studies.

Although the fixation reaction greatly reduce leaching, measurable quantities of Cu, Cr and As can be found in leaching solutions from properly leached wood. On examining the existing information it was found that a number of other areas are worthy of further research in order to gain a more realistic assessment of preservative

treated timber in aquatic environments. The review suggests that

- The experiments should be of sufficient duration in order that the longer-term leaching rates are accurately quantified.
- End sealing of test blocks will help to minimize the effects of high leaching rates from timber end grains, which may form a significant proportion of standard test blocks.
- Simulation of water motion and tidal movements by incorporation of stirring devices and daily drying periods may also be important parameters in any leaching protocol.
- The effects of surface area: volume ratio and total sample size on leaching rates in order that models may be developed to allow extra-protection of leaching rate data generated from standard laboratory protocols to wood with commercial use dimensions.
- Field trials in both saline and fresh water environments to evaluate losses in-service to allow further refinement of laboratory based data to losses expected from real environmental exposures.
- Speciation analysis of leached components to determine if metals are lost as individual elements, metal complexes, or bound to inorganic or organic ligands; this will allow further refinement of risk assessments since the toxicities of CCA components, particularly Cr and As are greatly influenced by valence state.

The studies regarding the impact of leaching are found to be very less in the tropical waters. Hence further studies need to be taken up in this direction.

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