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# BASIC COPPER WOOD PRESERVATIVES

# PRESERVATIVE DEPLETION – FACTORS WHICH INFLUENCE LOSS

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# Preservative depletion – Factors which influence loss

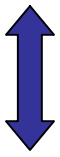
- Solvent characteristics
- Complex formation
- Test methodology
- Solvent type
- Solvent to copper ratio
- Copper concentration
- Effects of heat
- Laboratory vs Field

# Solvent characteristics

| Solvent | B.pt (°C) | $pK_b$ | |
|---|---|---|---|
| $NH_3$ | -33.3 | 4.75 | |
| $HO(CH_2)_2NH_2$ | 171 | 4.17 | MH |
| $NH_2(CH_2)_2NH_2$ | 117 | ~ 4.3 | en |

# Ammoniacal copper preservatives - fixation

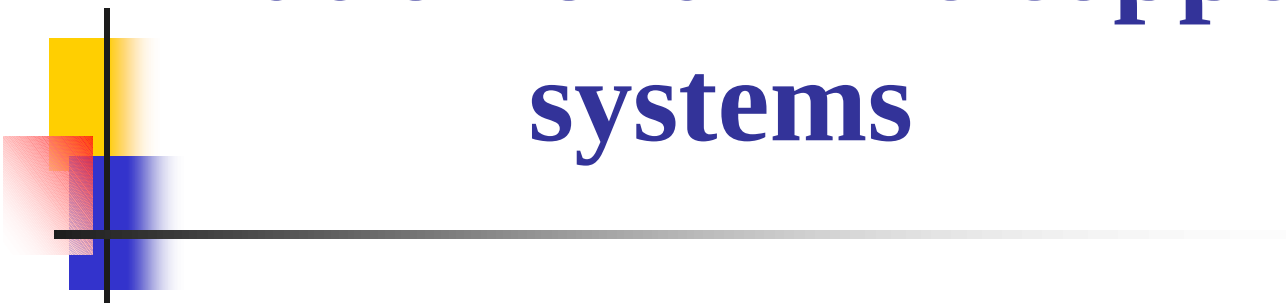
$$[Cu(NH_3)_4(H_2O)_2]^{2+}$$



$$[Cu(NH_3)_{4-n}(H_2O)_{2+n}]^{2+} + nNH_3\uparrow$$

**Fixation is driven by loss of ammonia leading to breakdown of tetramminocopper ion**

# Fixation of amine copper systems



$$\text{Wood-OH} + \text{R-NH}_2 \Leftrightarrow \text{Wood-O}^- + \text{R-NH}_3^+$$

$$2\text{Wood-O}^- + \text{Cu}^{2+} \Leftrightarrow (\text{Wood-O})_2\text{Cu}$$

- pH of solution decreases
- Fixation is not driven by loss of solvent by evaporation

# Fixation of monoethanolamine copper

$[Cu(MH)_2]^{2+} \Leftrightarrow [Cu(MH)(M)]^{+} \Leftrightarrow [Cu(M)_2]$

pH 5-7 7-10 >10

Solution pH is >10

Treated wood pH is <7

**Fixation is driven by changes in pH causing changes in aminocopper complexes**

# Fixation of amine copper

## Possible reactions

**At pH 7 to 10**

$[Cu(MH)M]^{+} + Wood\text{-}O^{-} \Leftrightarrow [Cu(MH.M)(O\text{-}wood)]$

$[Cu(MH)M]^{+} + Wood\text{-}O^{-} \Leftrightarrow [Cu(M)(O\text{-}wood)]$

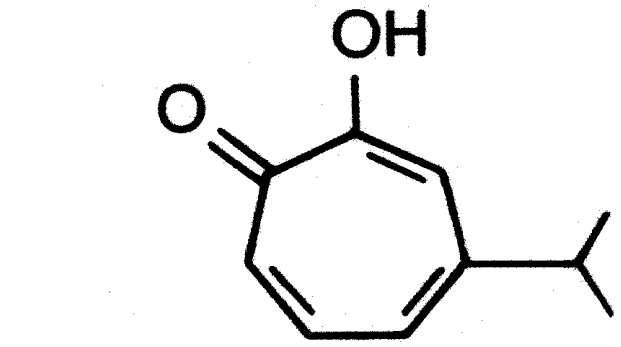
**At pH <7**

$[Cu(MH)_2]^{2+} + 2Wood\text{-}O^{-} \Leftrightarrow [Cu(MH)_2(O\text{-}wood)_2]$

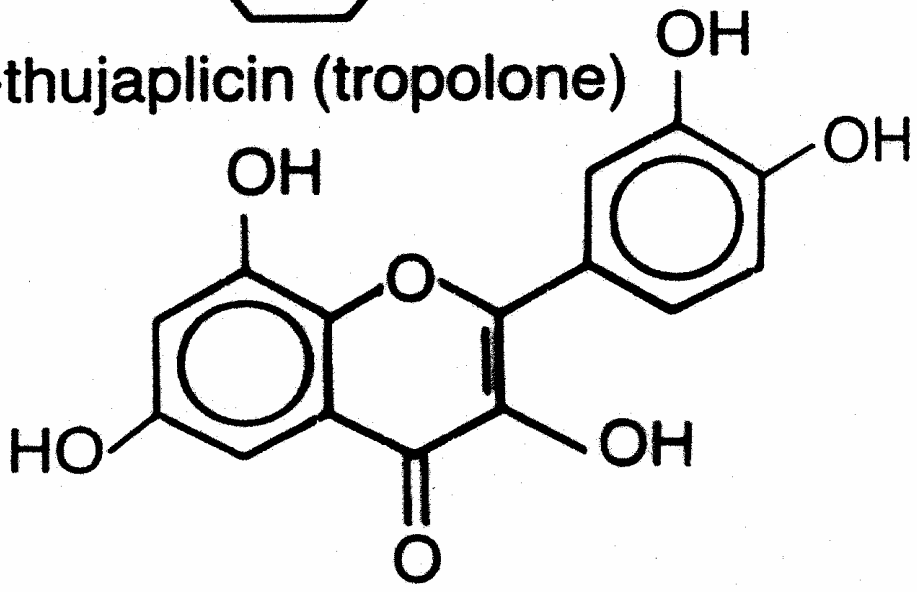
$[Cu(MH)_2]^{2+} + 2Wood\text{-}O^{-} \Leftrightarrow [Cu(O\text{-}Wood)_2] + 2MH$

$[Cu(MH)_2]^{2+} + 2Wood\text{-}O^{-} \Leftrightarrow [Cu(M)(O\text{-}wood)]$

# Complex formation - Extractives




β-thujaplicin (tropolone)




Quercetin (flavonoid)

# Ammonical coppper complexes with taxifolin

$$[Taxifolin]_2.Cu_3(NH_3)_4.2H_2O$$

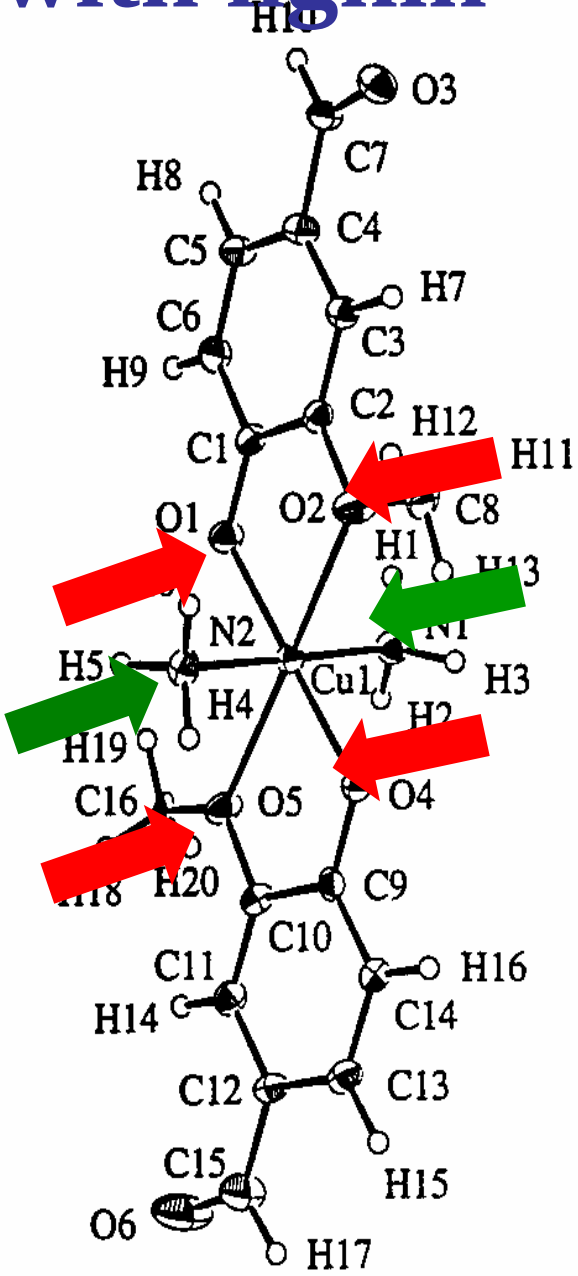
**Calc.** **C: 38.96; H: 3.35; N: 6.26; Cu: 21.12**

**Found** **C: 38.29; H: 3.48; N: 6.74; Cu: 21.04**

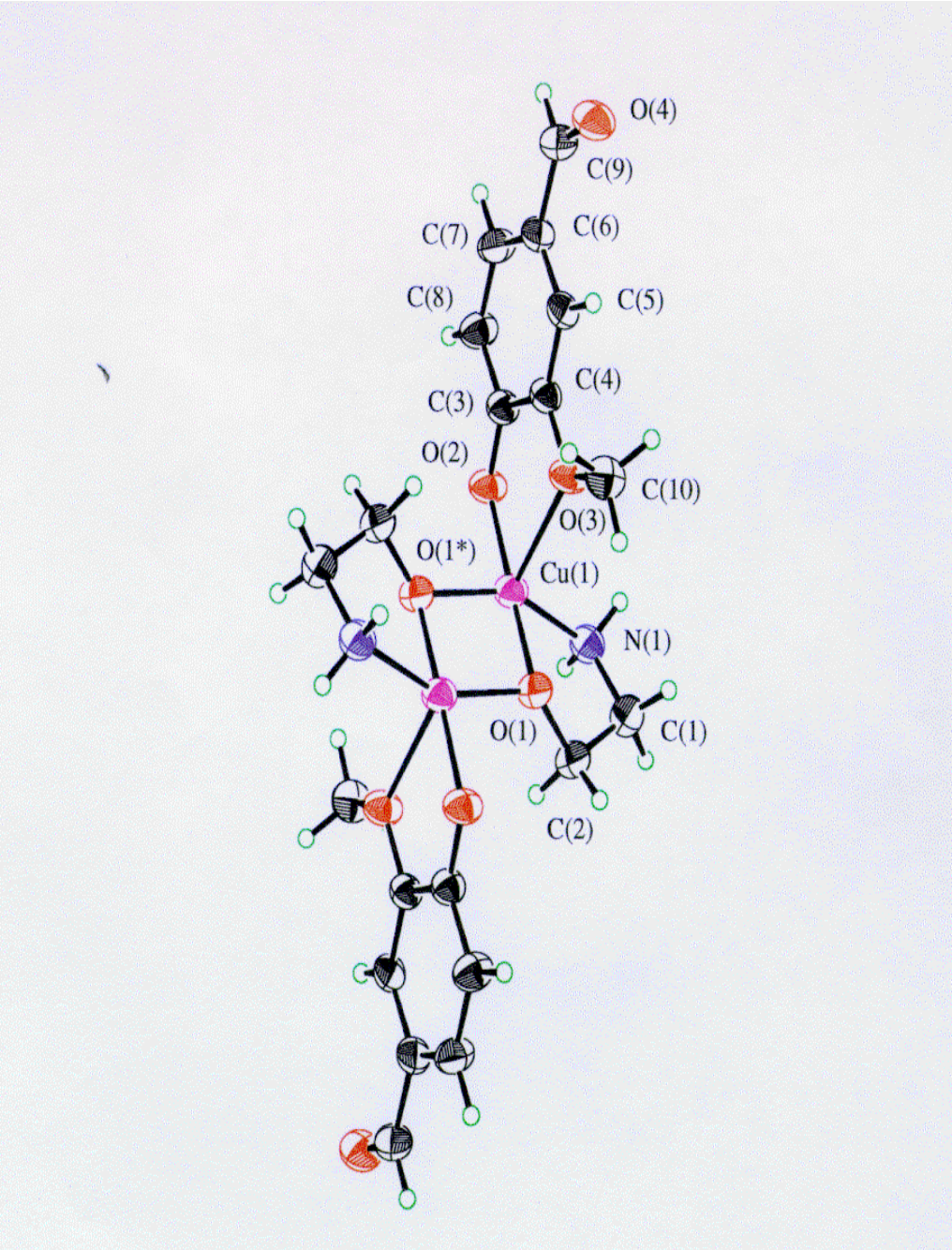
**This is the ammonia copper complex that makes ammoniacal copper treated wood almost black in colour**

# Ammonical coppper complexes with lignin

**Crystal structure of di(amine). bis(vanillato). copper(II)**



# Amine copper complexes with lignin

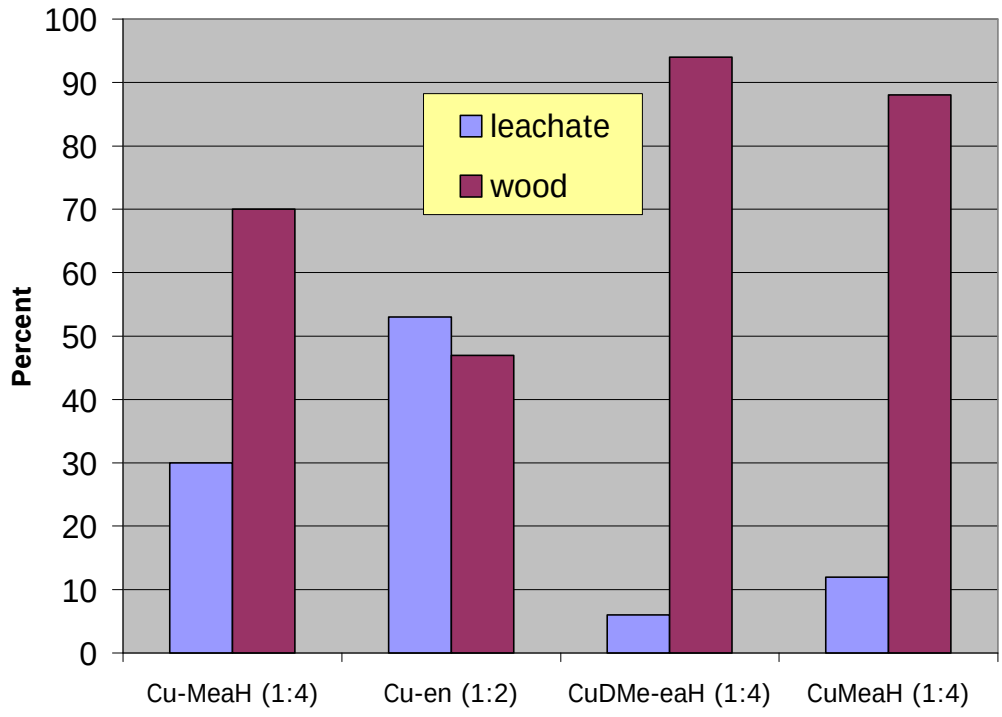


# Leaching rate - Laboratory

Will depend on

- Block size, leaching regime, chemical loading, chemical complex formation, heartwood vs sapwood, etc.
- Will generally be higher than that observed for wood in service because of the above factors
- For chemicals like copper which undergo ion-exchange, this approach will not account for redistribution onto available fixation sites

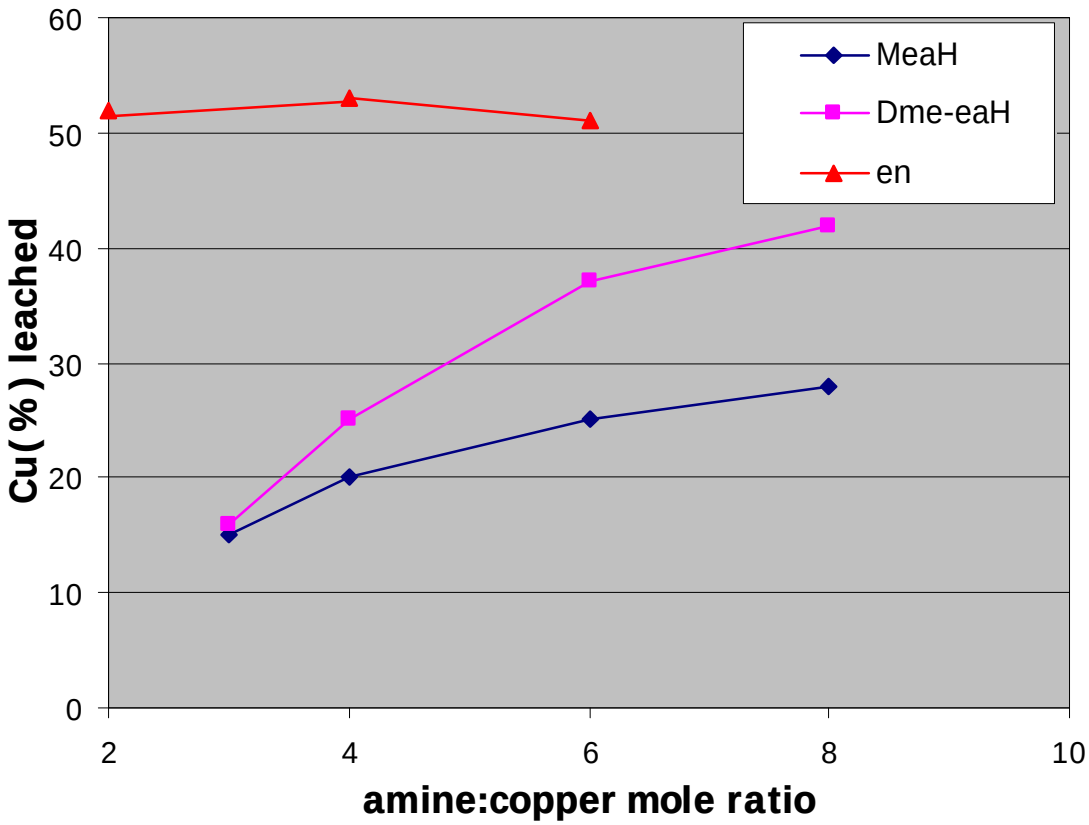
# Influence of amine type on copper leaching



# Influence of amine type on copper leaching

- **Monoethanolamine (MeaH) is superior to diamines (en) in fixing copper in wood**
- **This is due to the formation of σ Cu-O bonding to the ligand during fixation, which diamines can not undergo**
- **Conversely, one might expect reactions with co-biocides will be enhanced by diamines compared to MeaH**

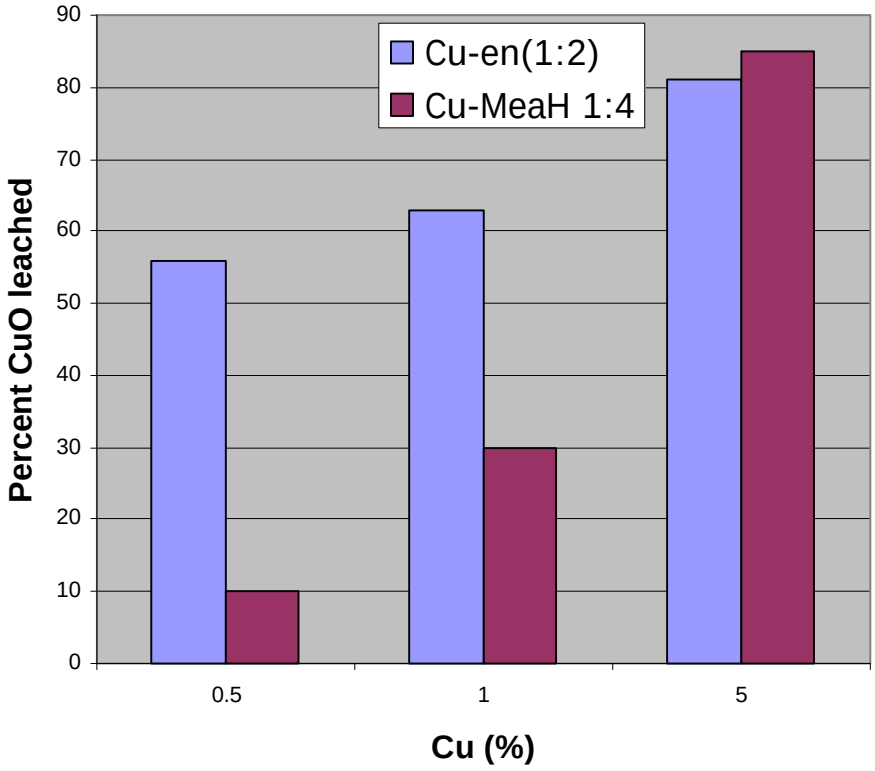
# Influence of amine to copper ratio on copper leaching



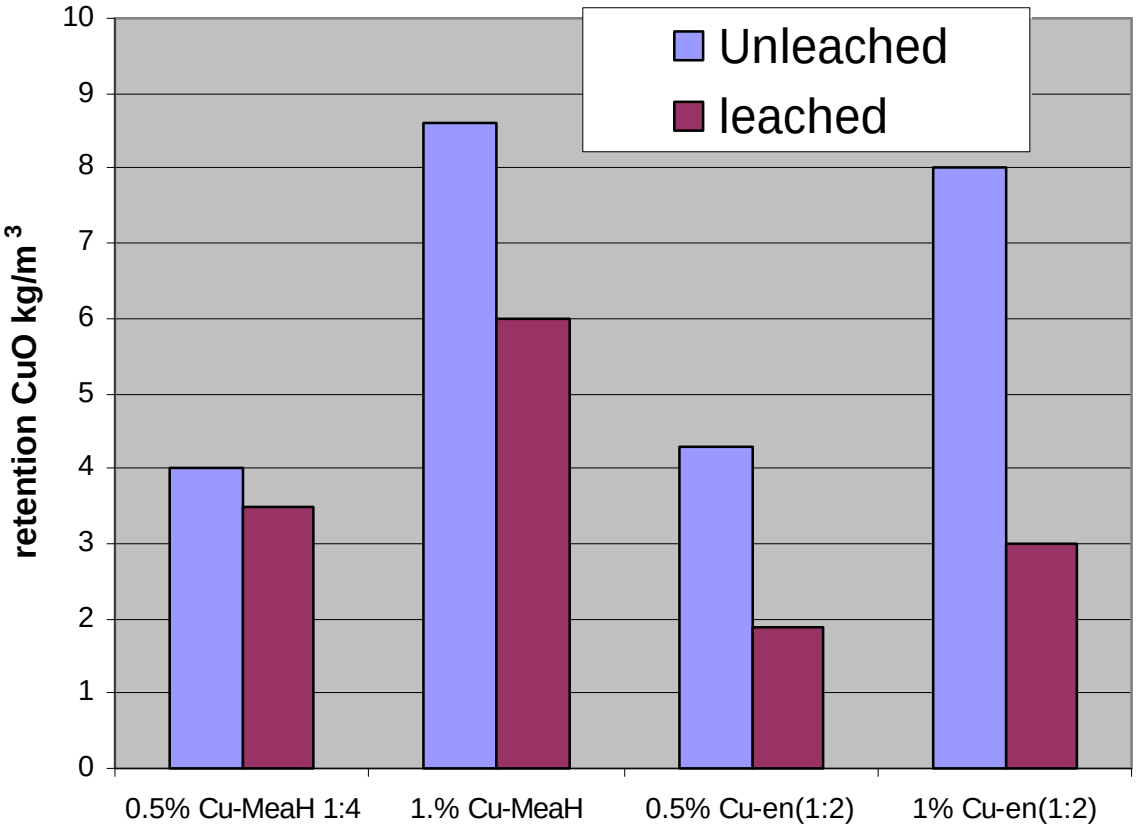
# Influence of amine to copper ratio on copper leaching

- With higher amine to copper ratios the leaching of copper increases
- This may be due to a retarding of the neutralization reaction by wood protons, slowing the reduction of the pH to <7, which is needed to enhance the wood amine copper reaction
- The extra amine may also retard the release of amine from amine copper complexes during the reaction with wood

# Influence of copper concentration on copper leaching



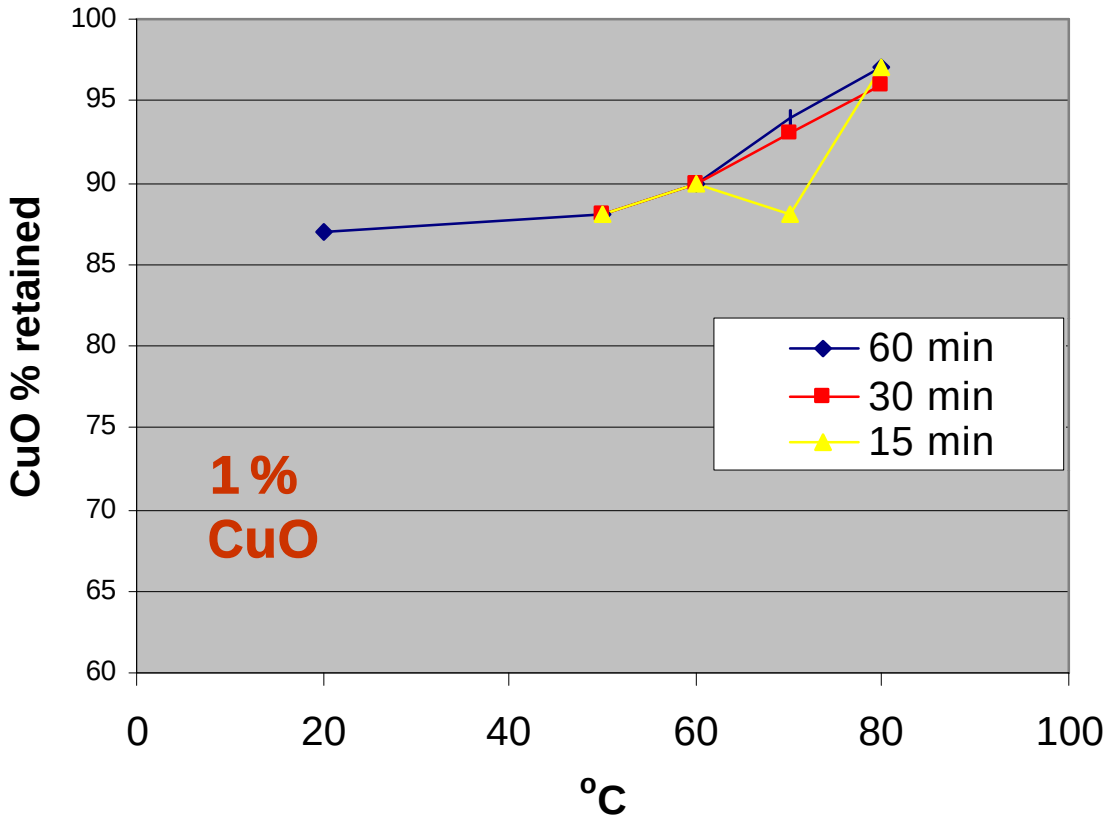
# Retention of copper in amine copper treated wood



# Influence of copper concentration on copper leaching

- Lower concentrations <1% have reduced loss of copper
- When the available copper increases above the sites available, excess copper remains leachable
- This amount of copper ion exchanged can vary as the availability of protons in wood is also pH driven.
- This would suggest at high retentions (marine and high pole retentions) copper will be leached unless other strategies are undertaken to improve its immobility

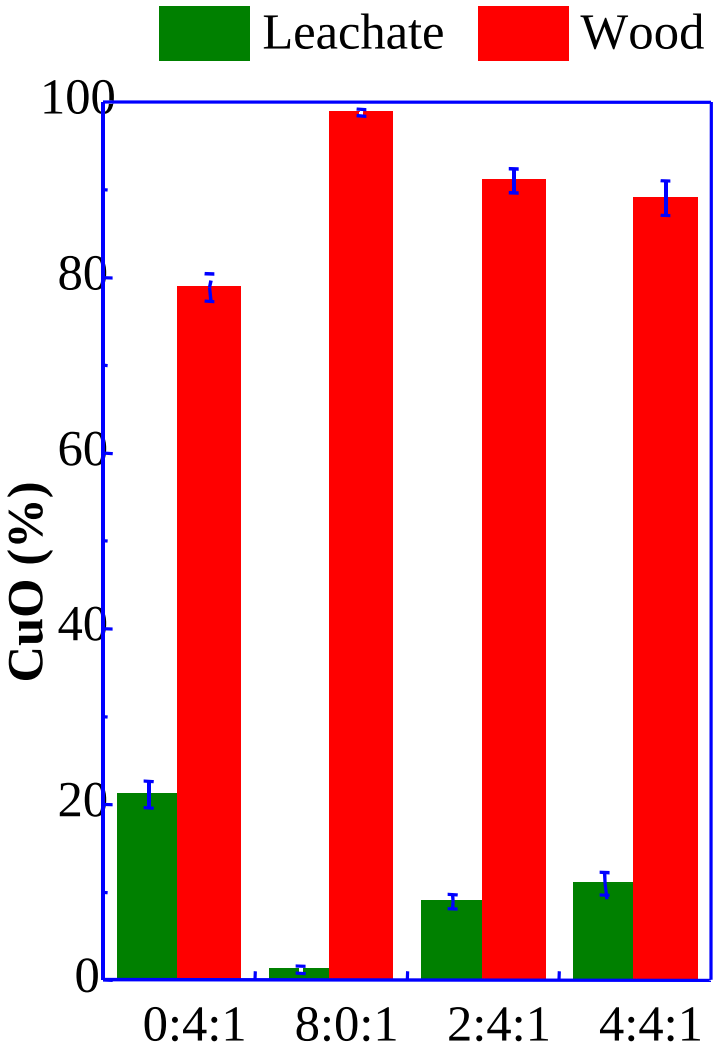
# Effect of heat on fixation of copper in Cu-MeaH



# Effect of heat on fixation of copper

- Heat seemed to slightly improve fixation
- The improvement in fixation has been reported to be higher in wood not wrapped
- This may indicate that loss of amine might be a factor or that longer heating times than 60 min. are required
- Examination by x-ray diffraction confirmed the increasing presence of Cu (I) above 50 °C
- $Cu_2O$ is insoluble, but is not a biocide

# Leaching of copper from mixed amine-ammonia copper treated wood

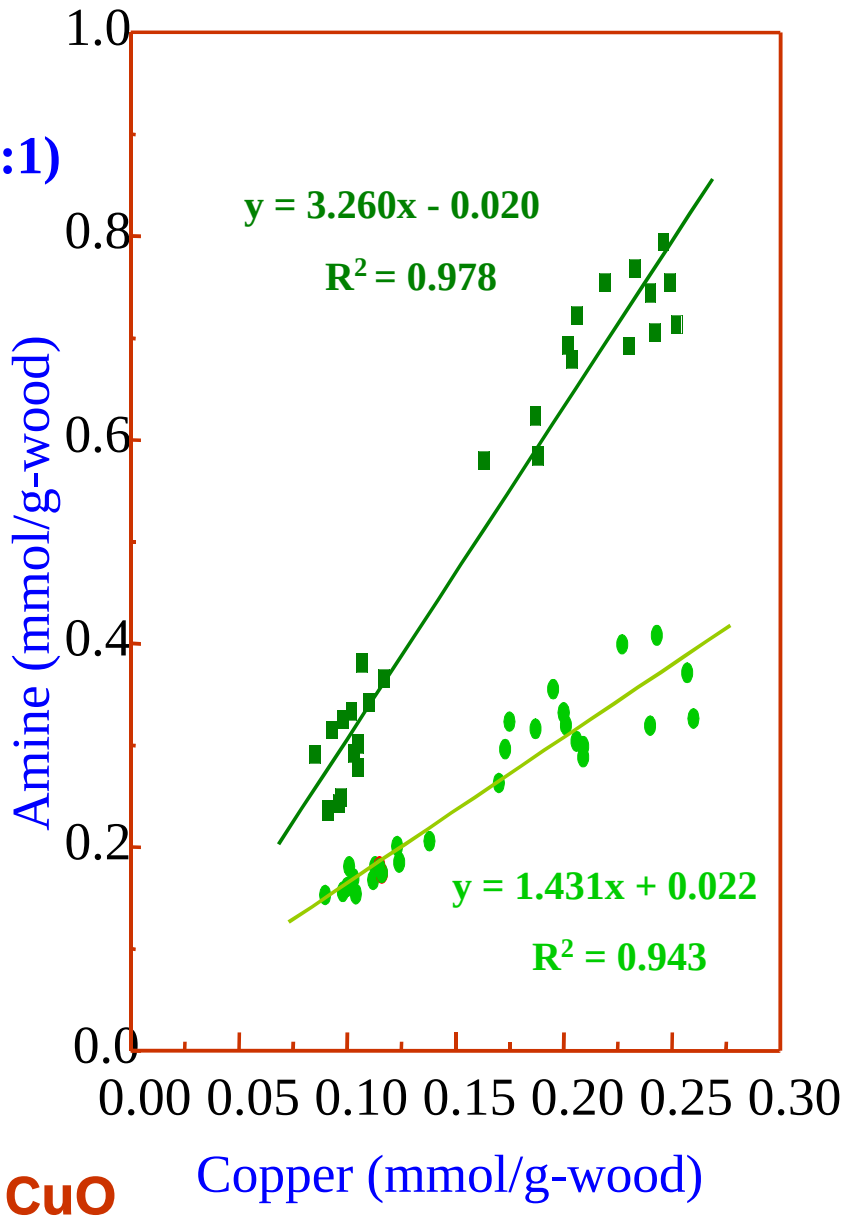


# Effect of ammonia on amine copper treatments

- **Addition of ammonia to MeaH-Cu treatments reduces the loss of copper**

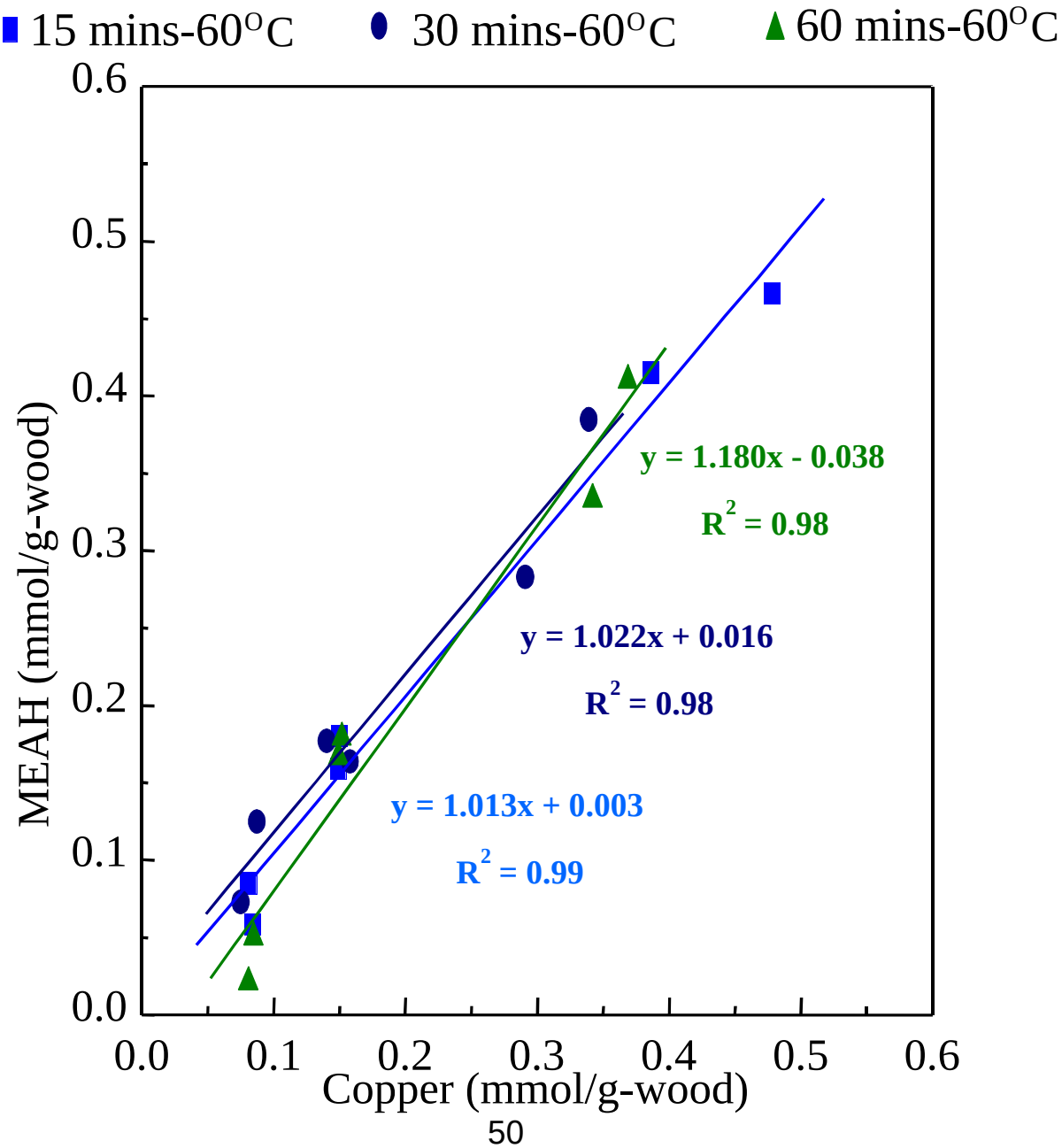
# Amine to copper ratio before leaching

- Cu-MEAH (4:1)
- Cu-en (2:1)




**0.5 and 1 % CuO**

# Amine to copper ratio after leaching



# Amine to copper ratio after leaching

- The amine to copper ratio of unleached 1% Cu-MeaH (ratio 1:4) treated wood blocks was about 3.2:1, so an increase in amine in the treating solution may be anticipated
- The amine to copper ratio of these blocks after leaching stabilized at about 1:1
- This is consistent with the lignin model prediction of a 1:1:1 complex with copper:amine:wood

# Field testing of treated decking

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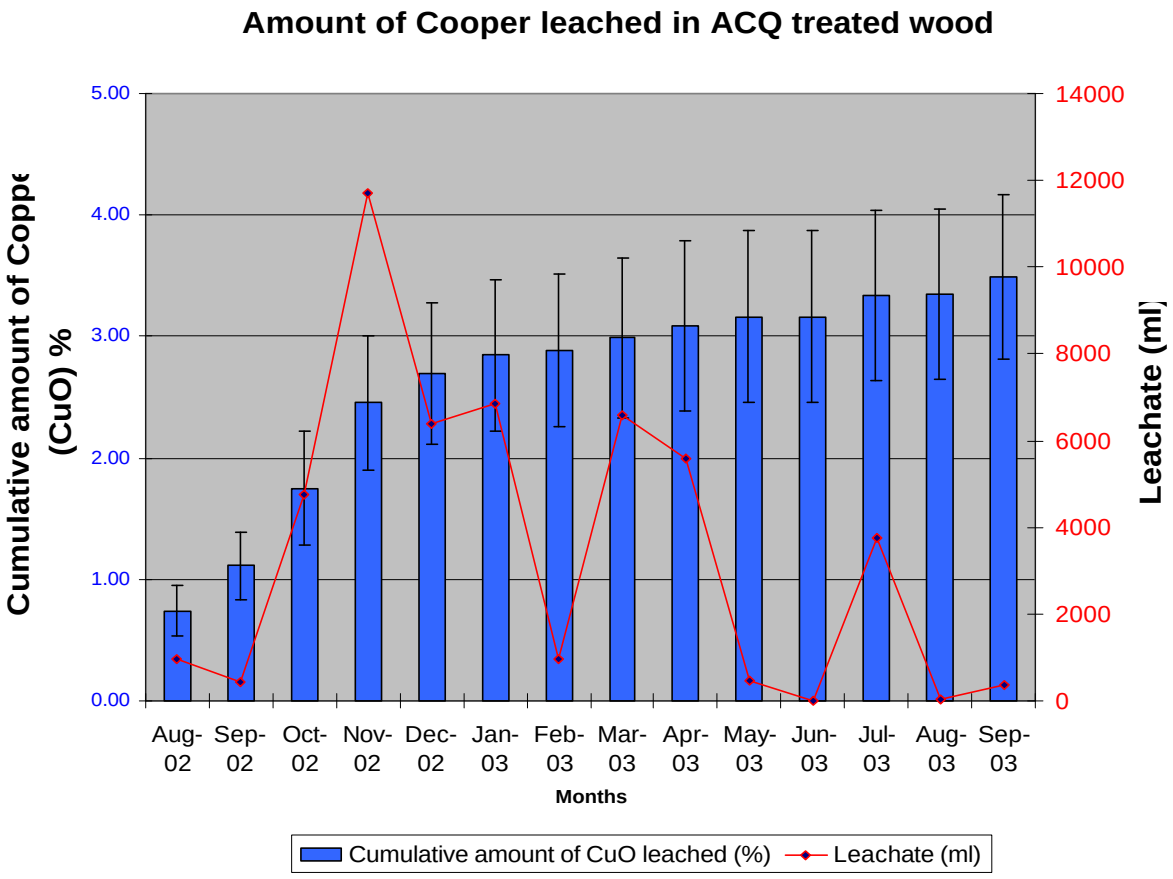
- **Preliminary results for ACQ for over 1 year and CB-A for almost five months suggest losses of copper are significantly below that found in laboratory tests**

# Field testing of treated decking



# Summary

- Amine copper fixation has different chemistry from ammonium hydroxide
- The copper retention influences the amount of leaching
- Higher amine to copper ratios result in increased copper losses
- Post treatment heating may reduce the leaching of copper.

# Summary

- Because of the corrosion and environmental impact of heating amine copper treated wood, the use of heat to accelerate fixation is unlikely to be practical for amine copper treated wood
- The addition of ammonia can also reduce the loss of copper

# Summary

- **Post treatment pressure washes of amine copper treated wood (to remove excess amine and some mobile copper) coupled with water repellant treatment, offers the best solution to maximizing fixation, while minimising corrosion and mold growth on treated wood**

# Summary

- The ratio of amine to copper in treated wood is lower than in treating solutions
- After leaching, wood treated with 1% copper solution with an MeaH:Cu ratio of 4:1, the amine to copper ratio reduces to about unity
- Field leaching of amine copper treated wood is typically less than 4% after one year, with most of that being lost in the first three to four months

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