Adsorption of ACQ Components in Wood

Myung Jae Lee & Paul Cooper

Faculty of Forestry

University of Toronto

Introduction

- Worldwide use of Alkaline Copper Quat (ACQ)
- Difficulty for high retention application
- Different fixation mechanism with CCA

Preservative Retentions by use category			
Use category		Service condition	Retention(kg/m^3)
UC 1,2		Interior construction	CCA: 4 ACQ: 4
UC 3		Exterior construction above ground	CCA: 4 ACQ: 4
UC 4		Ground contact or fresh water	CCA: 6.4-9.6 ACQ: 6.4-9.6
UC 5		Salt or brackish water	**CCA: 40** **ACQ: N.A**

(AWPA 2006)

Canada pest management regulatory agency (PRMA)
: Ground contact 6.4 kg/m^3

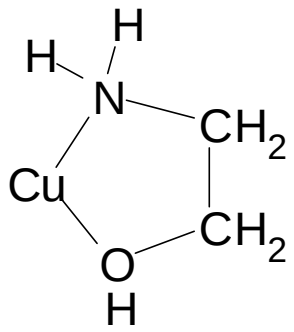
Background : ACQ & Cu-Mea

❖ ACQ

Composition (ACQ-D)		Weight ratio (%)
Ingredient	CuO	66.7
	Quat	33.3
Co-Solvent	Ethanolamine	183

(AWPA 2006)

❖ Cu-Mea complexes in solution



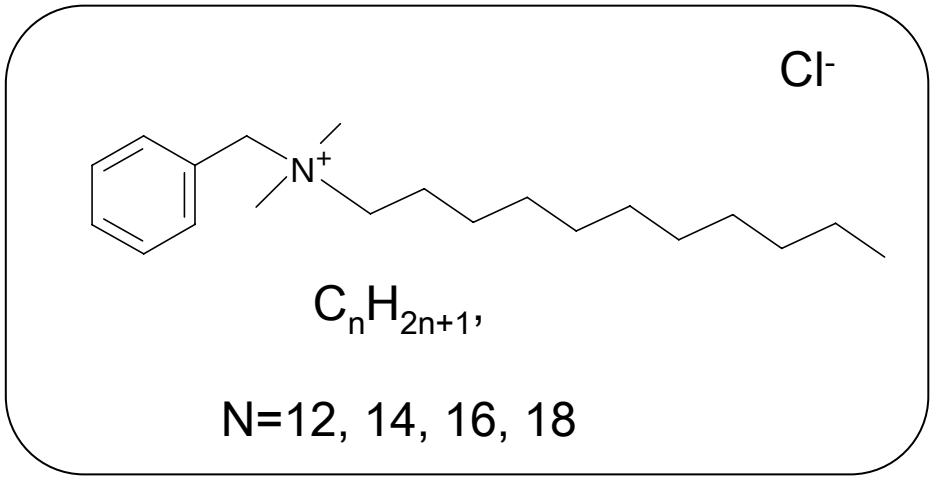
$[CuMea]^{2+}$

Cu complexes	Optimum pH	Formation %
Cu^{2+}	<4.0	100
$[CuMea]^{2+}$	5.5	24
$[Cu(Mea)_2]^{2+}$	6.8	24
$[Cu(Mea)_3]^{2+}$	8.2	1
$[Cu(Mea)_2]^{+}$	8.8	84
$[Cu(Mea)_2]^{0}$	>11.0	95

(Zhang and Kamdem 2000)

(Pankras and Cooper 2009)

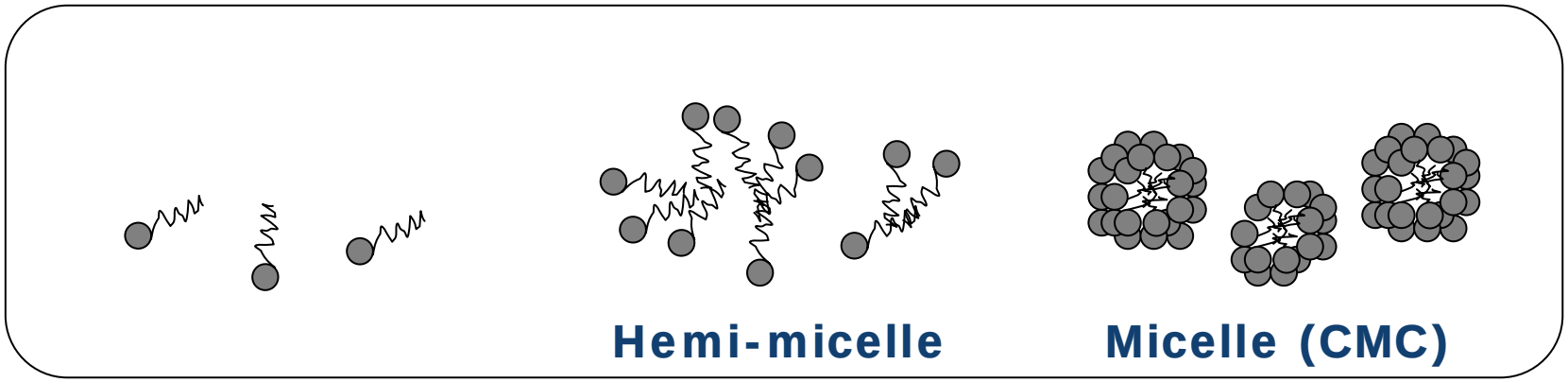
❖ ADBAC (alkyl dimethyl benzyl ammonium chloride)



Hydrophilic

vs.

Hydrophobic



Purpose

❖ Copper

- Cu adsorption capacity of wood
- Effective Cu-Mea complex for adsorption
- Cu adsorption mechanism in wood

❖ Quat

- Effect of micelle formation on quat adsorption
- Leaching resistance of micelle form adsorption
- Quat adsorption mechanism in wood

Experimental Method

❖ Copper

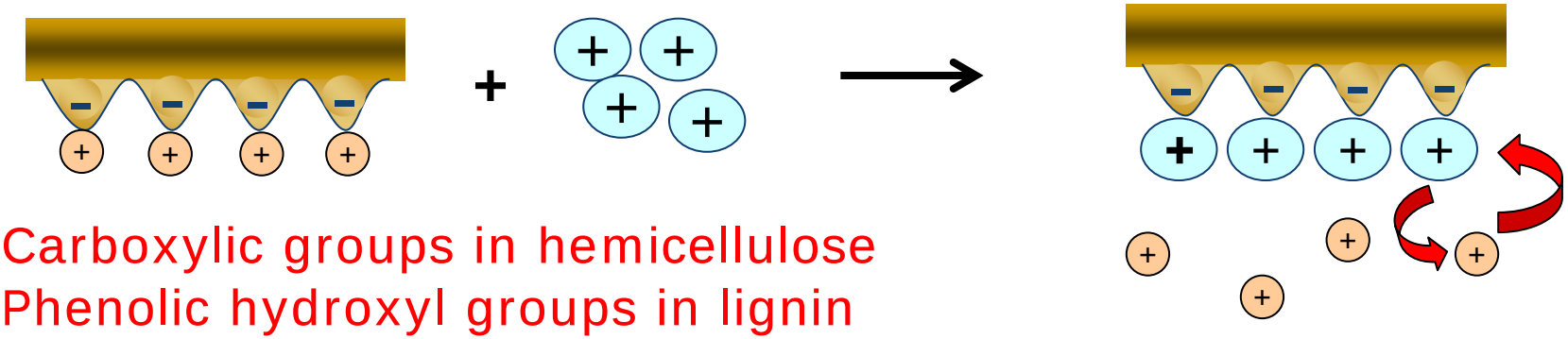
Treated material	Sol. pH	Absorbent
NaOH	pH 2-13 (HNO_3) 100ml sol.	Red pine dust 3g (30-60mesh)
Cu-Mea (Lonza Inc.)		
Cu-Dea/Cu-Tea		

- Treating 48h and washing thoroughly

- Analysis Na and Cu by digestion followed by AAS and Mea with C/N analyzer

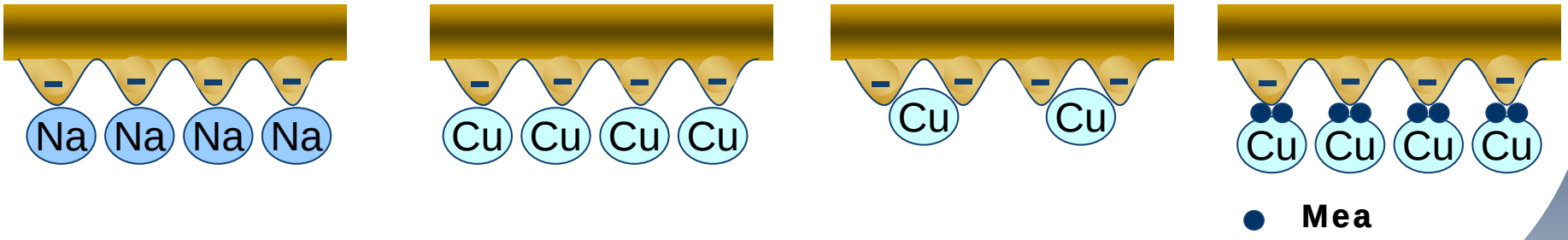
Experimental Method (Cont)

❖ Cation exchange reaction



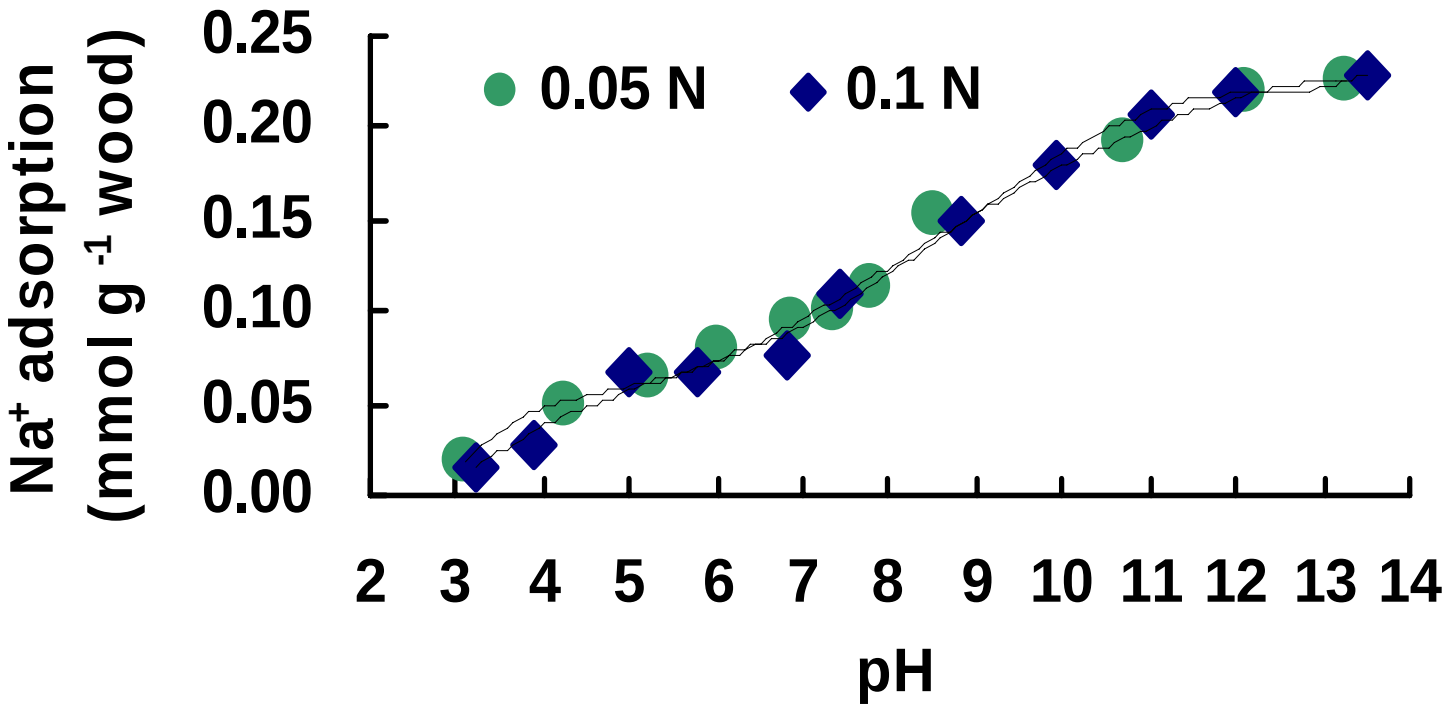
Carboxylic groups in hemicellulose
Phenolic hydroxyl groups in lignin

❖ Outline of Cu adsorption test



Na^+ Cu^+ Cu^{2+} $Cu(Mea)_2^+$

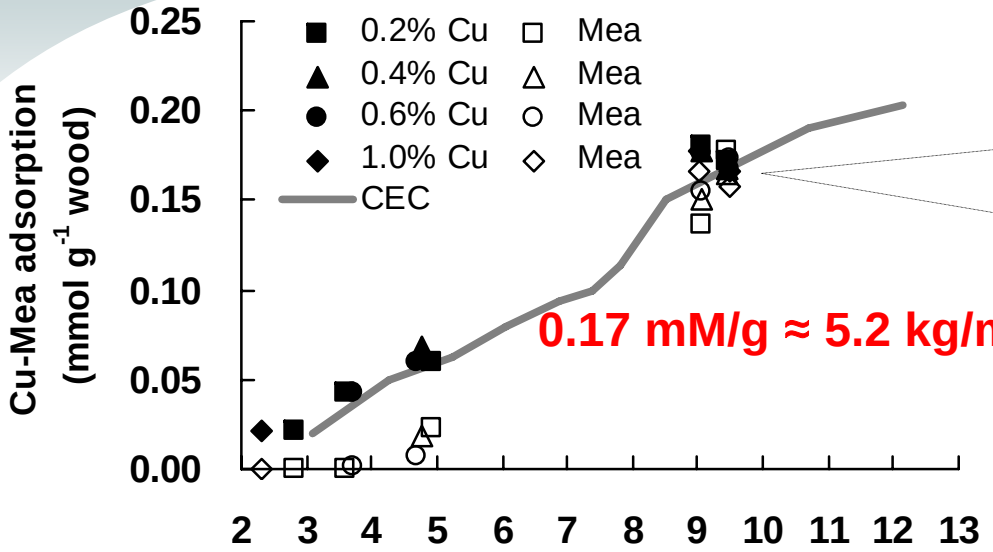
Results : Cation exchange capacity (CEC)



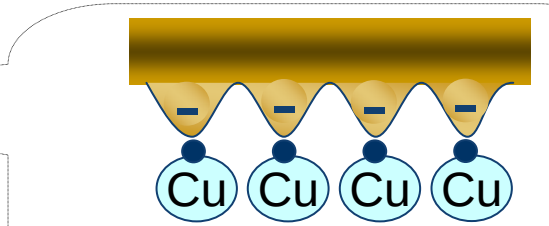
$RCOOH \rightarrow RCOO^- + H^+$: **RCOO-Na**

$ROH \rightarrow RO^- + H^+$: **RO-Na**

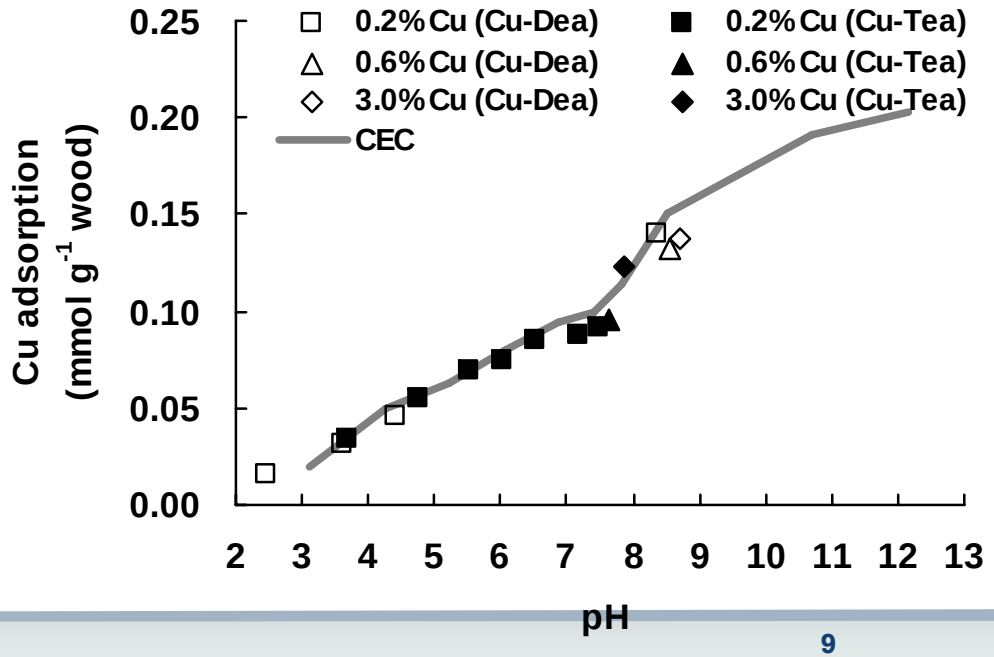
Results : Cu-Mea exchange capacity



0.17 mM/g ≈ 5.2 kg/m³



Cu(MEA)⁺



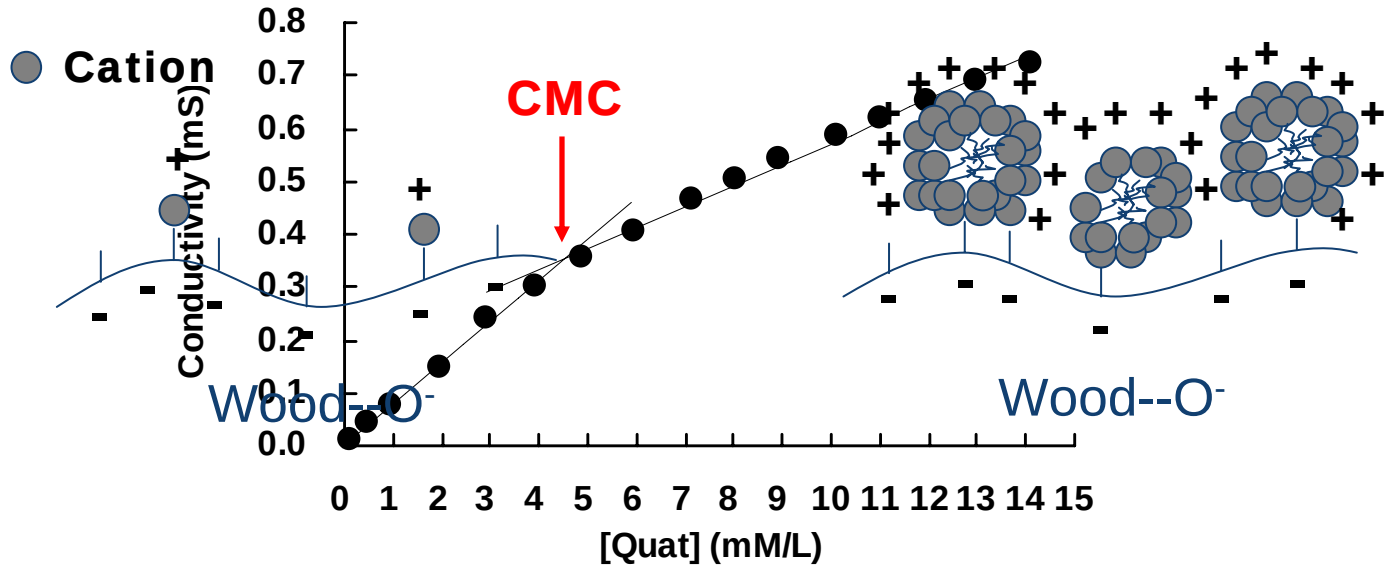
$Cu(MEA)_2^+$ + Wood

↓

$Cu(MEA)^+$ ---- Wood + MEA ↑

❖ Quat

- CMC determination of quat by conductivity method (DW, 1.4% Mea, 2.8% Mea, 0.4% Cu-Mea)
- Zeta-potential of wood particle at different conc. (Model: Zeta plus, 400mesh particle, pH 5-7 at 22℃)



Experimental Method (Cont)

- Determination of quat adsorption capacity and leachability as a function of ADBAC (alkyl dimethyl benzyl ammonium chloride) conc.

Treated solution	ADBAC Conc.	pH	Treatment /leaching
ADBAC	0.005 -100 (mM/L)	9.5 ± 0.2 (Mea)	5 / 10 (days)
ADBAC + 0.4% Cu			

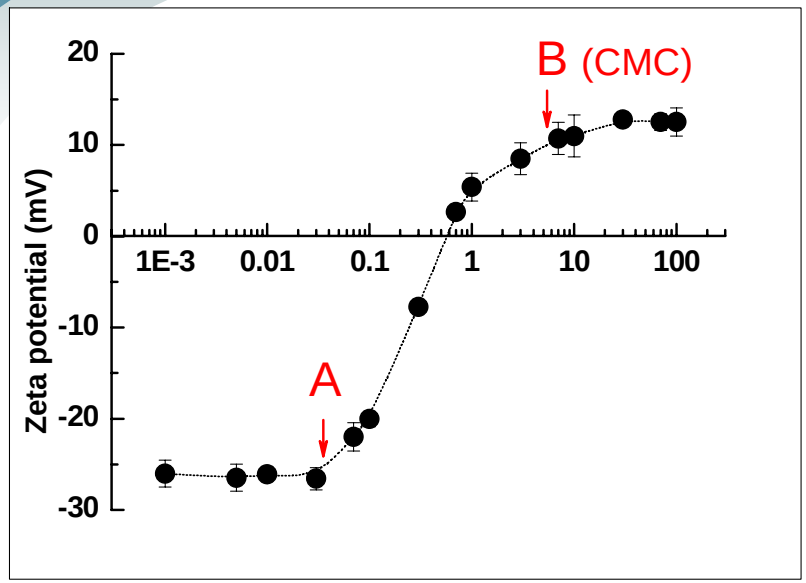
- Analysis quat and chloride by IC after extraction (AWPA A16-93)

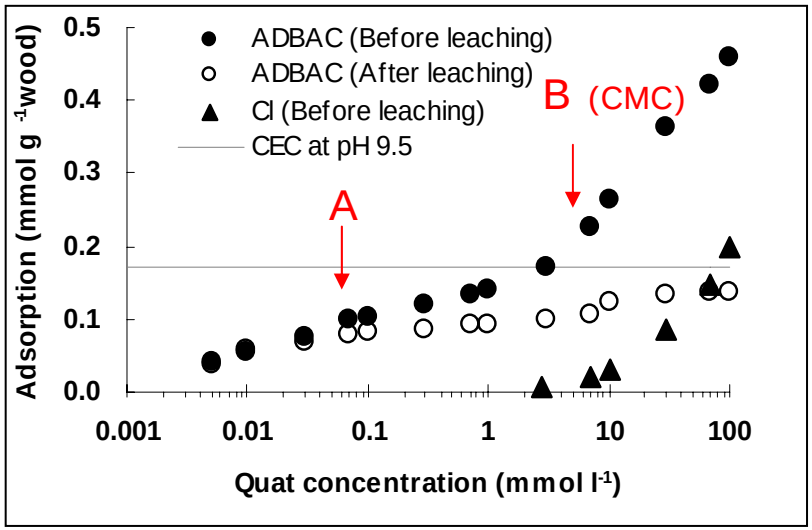
Results : Critical micelle conc. (CMC)

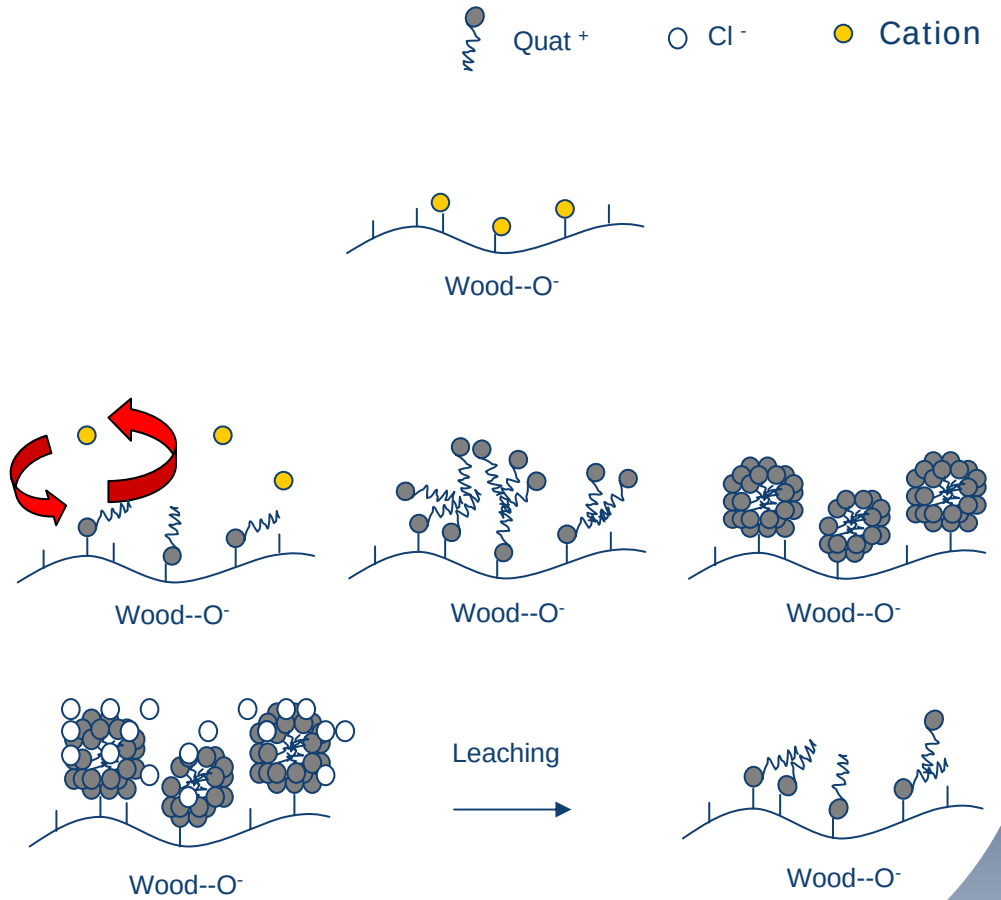
Component	CMC_{ADBAC}		pH
	mmol l^{-1}	%	
DW	4.57	0.160	5.6-7.2
Mea $_{1.4\%}$	3.91	0.137	11.2-11.7
Mea $_{2.8\%}$	2.74	0.096	11.7-11.9
Mea $_{1.4\%}$ + Cu $_{0.4\%}$	0.77	0.027	8.9-9.2

- CMC decreases by adding Mea and Cu
- 0.75 % ACQ sol.(≈ 0.25 % ADBAC) » CMC (0.027 %)
- Micelle always present in practical ACQ solution conc.

Results :Adsorption of Quat

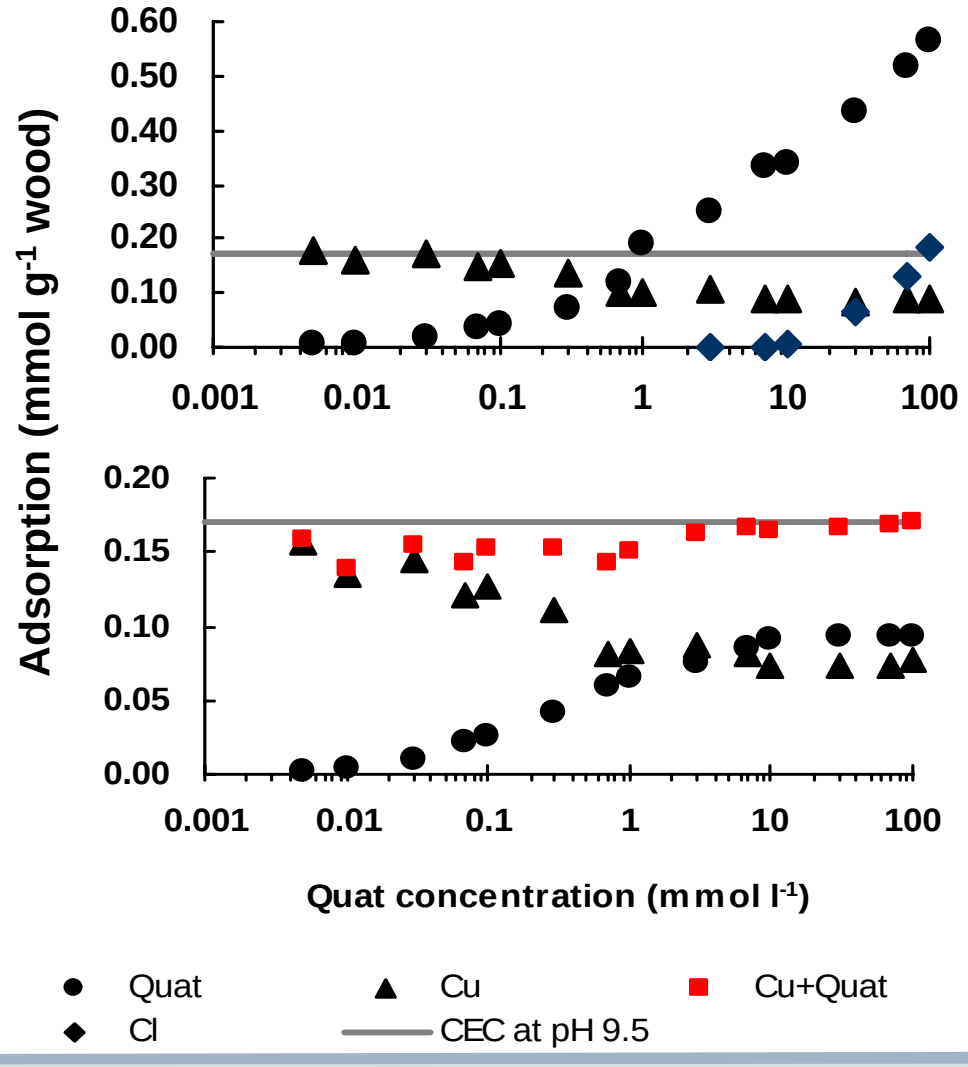






Results :Competition in adsorption

❖ Quat adsorption in 0.4% Cu solution



Conclusions

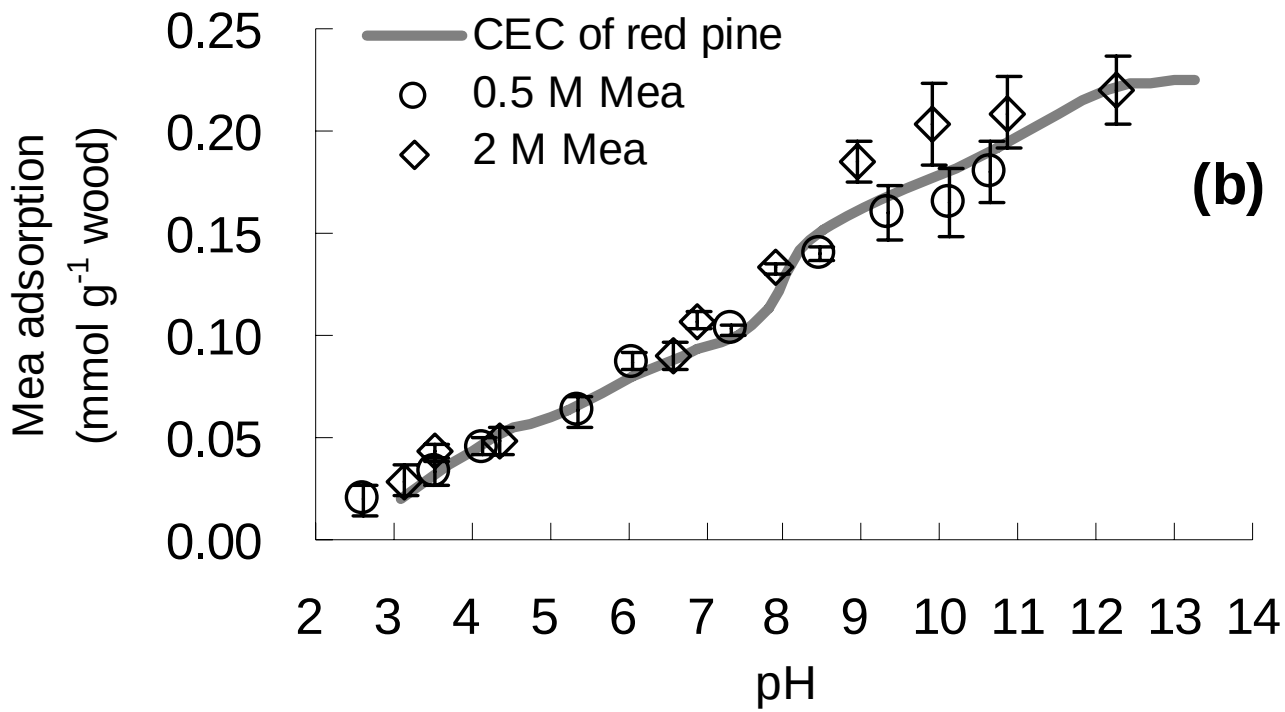
- Wood has increasing CEC as pH increases
- Cu adsorption capacity in red pine was about 0.17 mM/g wood (≈ 5.2 kg/m^3 as a CuO) at pH 9 as a form of $Cu(Mea)^+$
- Quat showed two different adsorption mechanism:
  - Ion exchange reaction at low conc.
  - Aggregation form of adsorption at high conc. (>CMC)
- CMC decreased with adding Mea and Cu
- Anion (Cl-) adsorption was only detected above CMC
- Aggregation form of quat and anion (Cl^-) has low leach resistance
- Quat adsorption does not quite reach the CEC
- Cu and Quat are in competition for the same adsorption sites

Bild 15

O1 Owner; 2010-04-14

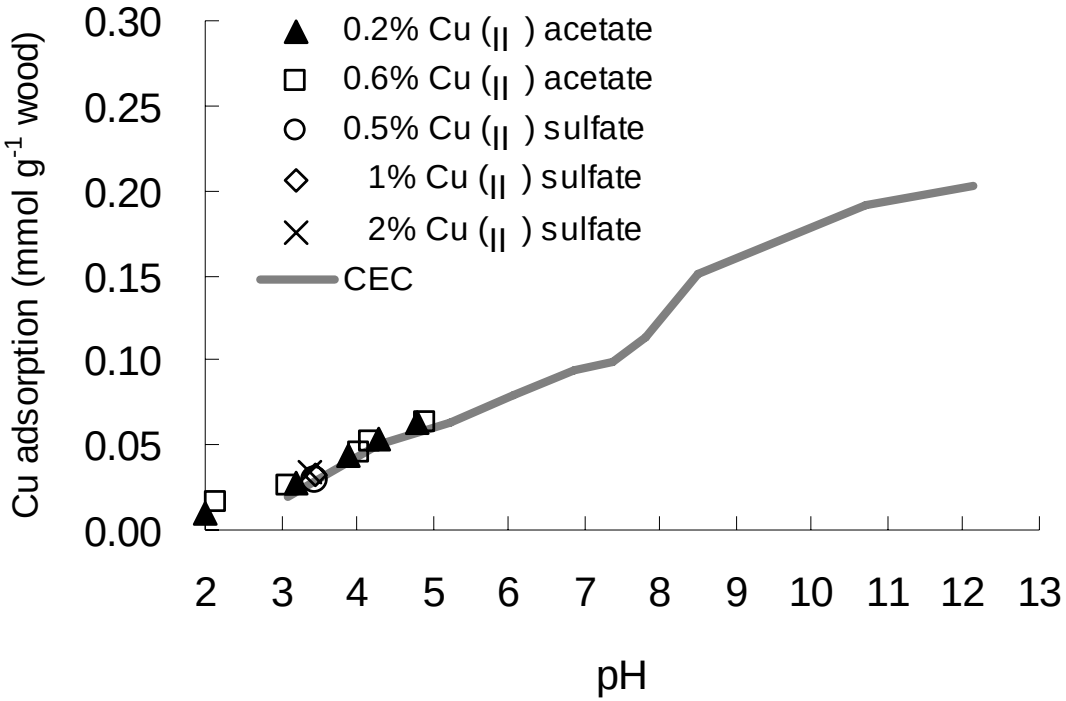

Thank You!

MEA adsorption and CEC



$$NH_3 + CH_2CH_2OH \leftrightarrow NH_2CH_2CH_2OH + H^+ \qquad (pKa \approx 9.5)$$

Cu adsorption (without MEA)



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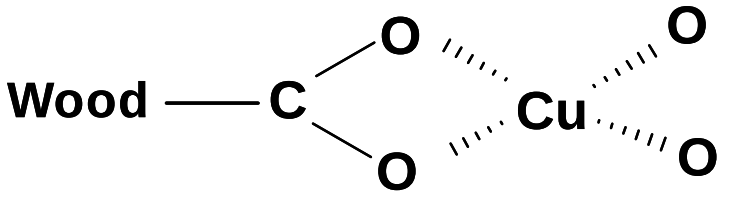
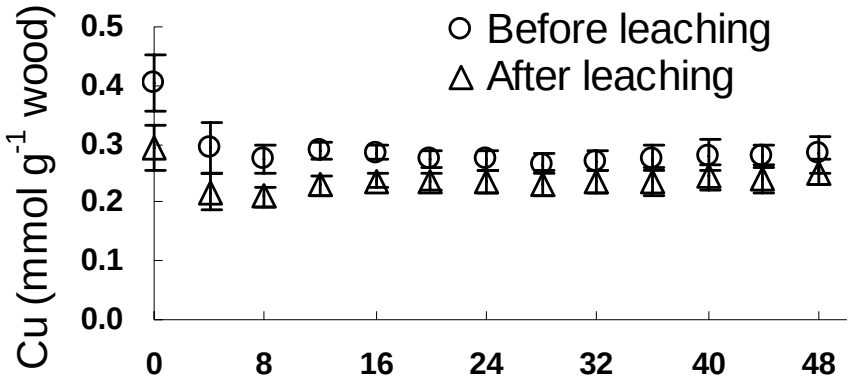
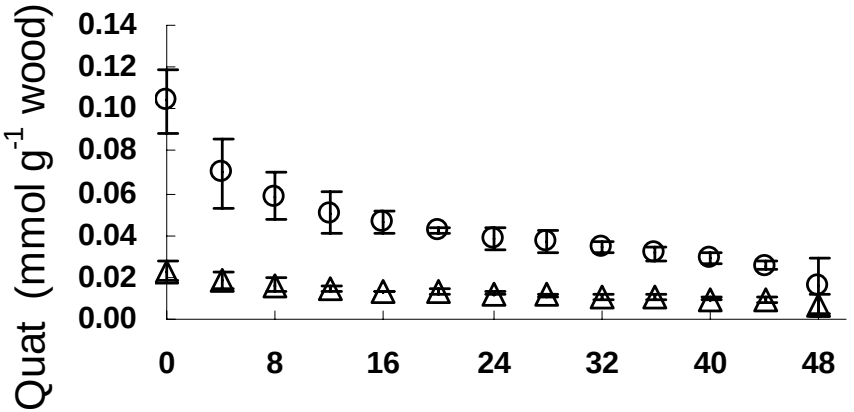


Red pine (30x60x100mm) treating with 2%

Longitudinal penetration





Radial penetration