22 JAN 2016
Venice, Italy

Lifecycle impacts of Copper nanomaterials released from timber preserving impregnations Workshop Proceedings

An international workshop among experts from Europe, Russia and USA, organized by the EU FP7 SUN and ECONANOSORB projects

Organizers

Just like the city that hosts it, **Ca' Foscari University of Venice** is a crossroads of cultures, fields of research, ideas and creativity. Within its eight departments it realizes advanced research projects and innovative study programmes. Ca' Foscari combines the most traditional areas in the fields of Chemistry and integrated studies on Chemical Sciences, both theoretical and experimental, and a special focus on Nanoscience and Nanotechnology.

The REACH Centre is one of the leading international providers of regulatory guidance, scientific and analytical services, and training to industry in the field of chemicals management and risk assessment. It employees a team of experts in chemistry, (eco)toxicology, environmental and occupational exposure, offering services for EU REACH, equivalent global notification systems, GHS and the EU CLP implementation, Cosmetics, Detergents and Biocidal Products regulations, RoHS and Conflict Minerals, and the developing Nanomaterials regulatory framework.

SUN - Sustainable Nanotechnologies Project - an EU FP7 project, aiming to develop strategies and objectives for safe nanoscale product and process design covering the complete lifecycle and to include the results in guidelines for industries.

ECONANOSORB - Ecological application of nanosorbents on the base of natural and synthetic ionites and carbons) – an EU EU FP7-PEOPLE Project, aimed at supporting and improving human and research potential, expanding research cooperation in European research area, and and overcoming the existing gap between research institution and wood processing industry.

GreenDecision is a spin-off company of Ca' Foscari University of Venice, which aims to transfer academic knowledge and technology to the public and private sectors, and to provide consulting services and training in the fields of sustainability, risk and resilience.

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Background

Nanotechnology materials and products are increasingly being produced for their potential to provide benefits to society. Therefore, although still emerging, nanotechnology has been identified as a Key Enabling Technology by the European Union. One of its important areas of application are metal-based biocides used to protect wood against microbial and fungal decomposition. One prominent example is Copper (Cu), different forms of which (e.g micronized Cu, Copper Oxide) are used in particulate timber preserving impregnations. The use of nanoscale Cu instead of bulk Cu improves the durability of wood against microbial and fungal activity due to: (i) increased effective surface area of Cu, enhancing dispersion stability, (ii) ability to penetrate bordered pits; and (iii) decreased viscosity of formulations. The above properties contribute to easier impregnation and deeper and more homogeneous uptake of reactive biocide into the wood, which allows effective and continuous protection over time.

In contrast to the significant benefits from using Cu nanomaterials in timber preserving impregnations, there are considerable societal concerns regarding their environmental impacts and human health risks. The robust estimation of these impacts and risks requires understanding of what quantities and which forms of Cu are released and what are their environmental and health effects, which is information difficult to obtain due to the lack of methods to measure and characterize the release. In order to address these challenges the European projects SUN, NanoDEN and ECONANOSORB as well as the U.S. Environmental Protection Agency have investigated the environmental impacts and health risks of Cu nanomaterials used in timber preserving impregnations.

Workshop Committees

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Abstracts

Session 1: Release, fate, exposure and effects of nanoscale Copper used in timber preserving impregnations

Chair: Danail Hristozov, University Ca' Foscari of Venice, Italy

Copper-based wood preservative formulations

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Presenter's biography:
The author is Head of Wood Protection Research & Development at BASF Wolman GmbH, Sinzheim, Germany. He obtained his PhD in Chemistry from the Max-Planck-Institute of Polymer Science in Mainz, Germany in 1998 before joining Dr. Wolman GmbH as a product manager for Anti-Sapstain and Vacuum Pressure Preservatives in the same year. BASF Wolman GmbH is part of the BASF Group and a leading European supplier of industrial wood preservatives.

Extended Abstract:
Introduction
For several decades now, Copper-based wood preservatives are dominating the industrial preservation of wood for exterior applications. Europe's wood preserving industry supplies around 6.5 million m^3 of pressure treated wood per year for woodworking, construction, landscaping, leisure wood, agriculture, marine, railway, telecommunication, electricity generation and distribution applications (WEI 2015). This wood is treated with either waterborne products (71%), solvent based products (18%) or creosote (11%) (WEI 2015). The pressure treatment with a wood preservative protects the timber against degradation by biological organisms, and thus largely extends the service life compared to untreated timber.
Copper-based wood preservatives
For several decades waterborne acid wood preservative formulations containing Copper and Chromium have been dominating. From the 1980s until today they are increasingly replaced by alkaline copper-based systems around the world. All Copper-Amine wood preservatives approved in Europe consist of inorganic (basic) Copper Carbonate ($Cu(OH)_2$ x $CuCO_3$) as the main biocide and one or more co-biocides to improve and broaden the efficacy of the preservatives against copper-tolerant fungi. The Copper components are solubilized by employing amines, ammonia or a combination of these. The main co-biocides used in Europe are: Bis-(Cyclohexyldiazeniumdioxy)-Copper (CuHDO), Azoles (mainly Tebuconazole, Propiconazole or both) and Quaternary Ammonium Salts (Quats).
More recently, wood preservatives based on milled and finely dispersed Copper component particles were introduced. They also use a copper component as main biocide, combined with organic co-biocides, mainly Quat or Azoles. These preservatives have gained a significant market share in the North American residential timber market, while use in Europe is still quite limited. These Particulate Copper Systems (PCS) are commonly known as micronized copper, however, the average particle size is well in the nanometre range.
In our presentation, the properties of Copper-amine and dispersed or particulate Copper formulations are reviewed based on literature and own studies. Possible implications on their use as wood preservatives are discussed.

Physical-chemical properties

While the actives of both systems are similar, the chemistry of these formulations is fundamentally different. Copper-Amine are dark blue liquids with a typical pH > 10, whereas the PCS are greenish dispersions with neutral pH. Like all dispersions they show a tendency to settle with time. As particle size distributions resulting from milling processes are typically quite broad, commercially available PCS will likely also contain a fraction of particles with dimensions well below 100 nm and are likely to be classified as containing a Nanomaterial under the EU definition.

Wood penetration and fixation

With Copper-Amine formulations a relatively homogenous distribution in wood cells is achieved and the Copper ions penetrate through cell wall voids. Full sap-wood penetration in European pine species is achieved with optimized formulations. The Particulate Copper systems show a more distinct distribution pattern in wood, limited penetration through smaller pits and possible clogging. Therefore, incomplete penetration of the sapwood of European wood species may be an issue, while other pine species like southern yellow pine used in North America are easier to penetrate (Habicht 2010). Anyhow, no particles can penetrate the wood cell wall but there is evidence that dissolved ionic copper diffuse through the wood cell walls after treatment. A sufficient amount of Copper in the cell wall and especially in the middle lamella is an important prerequisite for protection against wood decay by soft-rot fungi (Freeman and McIntyre 2008).

The fixation chemistries are fundamentally different (Ruddick et. al 2015). For alkaline Copper-Amine there is a fast reaction of Cu^{2+} with carboxylic and phenolic groups from cellulose, hemicellulose and lignin. Partly, also Amines and Quats may react. After saturation of accessible functional groups, the remaining Copper precipitates as basic Cooper Carbonate (BCC) in the wood cells due to the pH change in the wood. The leaching of co-biocides mainly depends on their solubility. In the PCS the Basic Copper Carbonate particles are solubilized by carboxylic groups from cellulose and hemicellulose. Also here the Quat co-biocide may react. After saturation of accessible functional groups, remaining Copper Carbonate stays in the form of particles in the wood cells (Ruddick et. al 2015). The PCS systems are claimed to show lower copper leaching, while the leaching of co-biocides is largely unaffected by the formulation of the copper if the co-biocides are formulated in a similar way as in the equivalent Copper-Amine systems.

Corrosion

For Copper-Amine, both the formulation (working solution) itself as well as the treated wood may be corrosive to mild steel. The extent of corrosion largely depends on the co-biocide (e.g. higher for those containing ionic chlorine) and other additives (increasing or reducing corrosion). Corrositivity of Particulate Copper solutions is usually higher, whereas the treated wood is reported to be less corrosive to mild steel connectors due to the lower availability of Cu^{2+} and lower amine content (Freeman and McIntyre 2008, Habicht 2010).

Biological efficacy

The biological efficacy of Copper-Amine systems cover wood-destroying fungi (*Basidiomycetes* and *Ascomycetes*) and insects (termites, beetle larvae). In general, only Cu^{2+} is bioavailable and thereby effective. The overall efficacy of the treatment is governed by the balance of copper and co-biocide efficacy, the active distribution in the wood, and the leaching, depletion or degradation of the active components over time. For Particulate Copper systems comparable efficacy to Copper-Amine systems are reported in the literature for comparable active compositions (Freeman and McIntyre 2008). Possibly, there is a lower efficacy in short term lab tests of wood treated with PCS due to reduced bioavailability of Cu-ions and a better long-term stability due to lower leaching in outdoor exposures.

Safety

Finally, the some possible implications of the previously mentioned differences between formulations on workers and consumers safety, as well as environmental concerns are discussed. In the manufacturing, transport and impregnation stage, the Copper-Amine formulations are corrosive to skin (high pH, amines), whereas the PCS should be not and do not contain potentially harmful amines. For the

PCS the emissions of nanoparticles in the manufacturing process (closed system, only accidental exposure) should be limited. There might be a possible workers exposure to copper nanoparticles in dusts from dried deposits of the wood preservative (spills, residues remaining in plants).
In the use phase of the wood treated with Copper-Amines the most likely exposure routes to humans are possible hand-to-mouth exposure of wood preservative components from the wood surface and exposure when re-working (sawing, drilling, sanding) treated timber. Emissions to the environment are most likely to be emissions of actives through leaching from treated wood by rain water or soil moisture. The same routes apply to wood treated with PCS, except that the copper leaching might be reduced and both the leachate and the transferred/released surface material or saw dust may contain Copper-based nano particles.
Finally, at the end of the usable lifetime of the timber components, wood treated with chromium free Copper-Amine wood preservatives can be burned in industrial waste incineration facilities. The ashes will contain copper. For the PCS this should also be true, however, the fly-ashes or flue gases may contain Copper nano particles.

Conclusions

To summarize, the chemistries of the current state of the art in Europe, the Copper-Amine systems, and the novel Copper Particulate Systems are distinctively different. Therefore, the important properties of an industrial wood preservative need to be examined. Compared to current Copper-Amine systems, PCS could offer advantages in terms of lower copper leaching, especially at high retentions, the lower content of potentially harmful additives like amines and possibly higher long-term efficacy. However, especially the penetration & distribution in European Wood species, the fixation chemistry and possible effects of a low particle size fraction (Nanoparticles) on workers safety during manufacturing of the preservatives, wood impregnation and handling of the treated wood, as well as emissions during the used phase and at the treated timbers disposal need to be studied carefully.

Keywords: Copper, Copper Amine, Micronized, Nanoparticles, Wood Preservation, Impregnation

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Copper Nanoparticles for Wood Protection: Effectiveness and Remobilisation in the Air

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Presenter's biography:
Chiara Civardi is a PhD student in Civil Engineering at ETH and Empa, the Swiss Federal Laboratories for Materials Science and Technology. Her research interests include wood protection, nanoscience, metal speciation, and X-ray techniques. More specifically, her work examines the effectiveness of micronized copper for wood protection and its fate during timber service life.

Extended Abstract:
Copper (Cu) is essential for the protection of wood in ground contact (use class 4, European Standard EN 335 (2013)), as it has the potential to prevent decay by soft rot fungi. Recently, an innovative wood preservative treatment based on particulate Cu was developed. This is best known as "micronized copper" (MC) and is mainly composed of basic copper carbonate particles, whose sizes range between 1 nm and 250 µm, and an organic co-biocide, either azole (MCA) or quaternary ammonium compounds (MCQ). Despite the misleading name and the broad particle size range, MC mostly contains smaller particles (Platten et al., 2014) and is therefore to be considered as a nanomaterial according to the definition from the European Commission recommendation on nanomaterials (2011).
From its introduction in 2006, MC has been turning into one of the largest scale commercial applications for nanotechnologies (Evans, Matsunaga, & Kiguchi, 2008).
In this paper we investigated the performance and the mechanisms behind the efficacy of MCA against different wood-destroying fungi. More precisely, we assessed:

- the performance of MCA-pressure-treated wood against soft rot fungi, applying the guidelines provided by the European standard ENV 807 (2001)
- the presence of specific nano effects that exert additional toxicity against wood-destroying basidiomycetes, especially if Cu-tolerant, assessing:
    - screening for Cu-tolerance among different wood-destroying basidiomycetes (*A. serialis*, *C. puteana*, *G. trabeum*, *R. placenta*, *T. versicolor*)
    - fungal biomass and oxalic acid production in liquid cultures containing Cu^{2+} ions, MCA, bulk Cu carbonate, tebuconazole and the selective Cu^{2+} ion chelator ammonium tetrathiomolybdate
    - EN 113 (1997) wood mass losses in MCA-, bulk Cu carbonate-, and tebuconazole-pressure-treated wood
- the penetration and interaction of MCA in easily treatable Scots pine and refractory Norway spruce wood, combining elemental analysis on Cu (ICP-OES) with X-ray computed tomography (CT) and EN 113 (1997) tests
- the performance of MC(A)-pressure-treated wood and nanoCuO-coated wood against non-Cu-tolerant, non-azole-tolerant *C. puteana*, by means of the EN 113 (1997) guidelines.

The ENV 807 test on MCA-pressure-treated wood against soft rot fungi indicate that the treatment is effective, and the concentrations required to effectively prevent fungal decay were as low as 0.80%. *R. placenta* showed the highest Cu-tolerance in Cu-amended environments, therefore it was selected for the subsequent studies, as it would provide an indication for possible nano effects exerted by

MCA on highly Cu-tolerant fungi that would reduce the Cu threshold level and would result in effective protection of wood at lower Cu concentration than the Cu^{2+} ion or bulk counterpart. *R. placenta* was able to recognise Cu also as MCA (nano) and can trigger the same Cu-tolerance mechanisms typically shown in the presence of bulk Cu or Cu ions. This indicate that the nanoparticles in the MCA formulations assessed did not provide additional protection against *R. placenta* and the main effectiveness has to be attributed to tebuconazole.
We could not precisely locate Cu in the woody cell wall, i.e. if Cu diffuses into (cell-wall treatment) or only onto it (cell-lumen treatment). The difference is critical for wood protection because wood cell-wall treatments are certainly more effective against white and soft rot fungi. In addition, it was not possible to determine if the Cu present was solubilised or available as unreacted -single or aggregated/agglomerated- particles responsible for a reservoir effect. Cu appeared equally distributed in ray parenchyma and ray tracheids. Most of Cu contained in Norway spruce heartwood is likely to be in the form of fine particles or ions, as indicated by the X-ray CT scans coupled with the ICP-OES analysis, whereas Cu appears in larger clusters in Norway spruce sapwood, and even larger in Scots pine wood. MCA cannot readily penetrate refractory wood species (Norway spruce), which are commonly used in Central Europe. Therefore, the adoption of MCA for the European market would still require pre-treatments such as incising. However the MCA formulations succeeded in protecting refractory wood species against *R. placenta*, and the treated refractory wood was destroyed less than easily treatable MCA-pressure-treated wood.
The samples analysed within the framework of the SUN project consisted of two nano Cu carbonate-based formulations (comparable to MCA), two conventional Cu amine preservatives, and two Cu-based acrylic wood coatings. The mass losses of pressure-treated wood exposed to *C. puteana* were all well below 3% (indicating an effective treatment), independently on the formulation, whereas the coatings could not effectively protect the wood from fungal attack. This difference is mainly due to the nature of the wood treatment itself: while pressure-treatment aims at a homogenous distribution of the fungicide (Cu) across the whole wood volume, coating results in only a superficial treatment, whose shield can be penetrated once cracks occur on the wood surface, due to abiotic or biotic agents.
As long as Cu remains within the timber structure, independently on its size, concentration, or species, it does not pose a risk, as no exposure can occur. However, issues arises once Cu is remobilised. We provided an insight into Cu-amended aerosol release from MCA-pressure-treated wood due to abrasive processes or spore compartmentalisation mechanisms by the Cu-tolerant fungus *R. placenta*.
In addition, we discuss the possibility of Cu-based nanoparticles release from MCA-pressure-treated wood into the air.

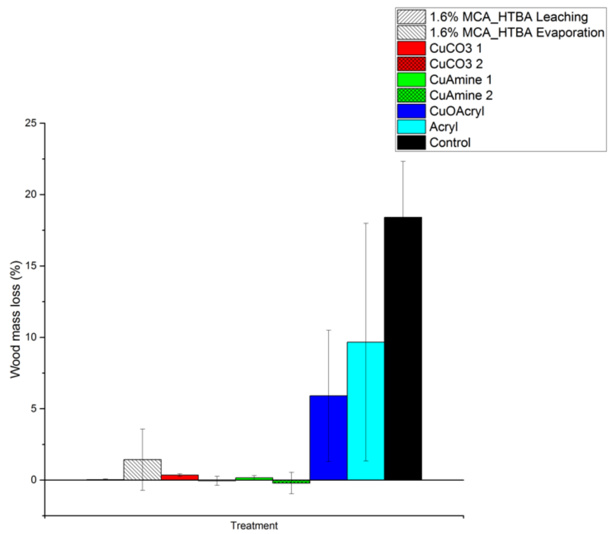

Figure 1. Assessment of nanoCu-based formulations against *C. puteana* 62 and associated mass losses in Scots pine sapwood. Data are represented as mean ± standard deviation of three replicates. Wood mass losses below 3% indicate that the wood preservative treatment is effective, while wood mass losses above that value indicate insufficient protection against basidiomycete attack.

Acknowledgment: We are indebted to Daniel Heer, Markus Heeb, Bruno Zgraggen, and Angelika Fey for the technical assistance. We would like to acknowledge Prof. Joris van Acker and Dr. Jan van den Bulcke for the expertise with X-ray computed tomography, as well as Dr. Lukas Schlagenhauf, Dr. Cordula Hirsch, and Dr. Jean-Pierre Kaiser that contributed to the abrasion project. The work is financially supported by the Swiss National Research Foundation (Grant No. 406440_141618) and the Transnational Access to Research Infrastructures activity in the 7th Framework Program of the EC under the Trees4Future project (Trees4Future, 284181).

Keywords: Copper-tolerance mechanism, Copper toxicity, Micronized copper azole, Pressure-treated wood, Wood durability, Wood treatability, Wood-destroying fungi, X-ray computed tomography

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Modeling Flows and Concentrations of nano-$CuCO_3$ in the Danish Environment

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Prof. Dr. Bernd Nowack holds a MSc. (1992) and a PhD (1995) in environmental sciences from ETH Zürich. He is leading the "*Environmental Risk Assessment and Management*" group at Empa, the Swiss Federal Laboratories for Materials Science and Technology, and is adjunct professor at ETH Zurich. His current research deals with the chances and risks of engineered nanomaterials, comprising a wide spectrum of different approaches: development and application of methods for material flow modeling, exposure modeling, environmental risk assessment and life cycle assessment; experimental studies about release of nanomaterials from products and investigations about their behavior and effects in the environment. Bernd Nowack has published more than 130 peer-reviewed publications which receive >1400 citations/year. He acted as co-advisor of 15 PhD projects, is founding co-Editor-in-Chief of the journal *NanoImpact* and is Associate Editor of the journal *Environmental Pollution*. He is listed in "The World's most influential scientific minds 2014" from Thomson Reuters in the category "Environmental Sciences/Ecology".

Extended Abstract:
Predictions of environmental concentrations of engineered nanomaterials (ENM) are needed for their environmental risk assessment. Because analytical data on ENM-concentrations in the environment are not yet available, exposure modeling represents the only source of information on ENM exposure in the environment. This work provides material flow data and environmental concentrations of nano-$CuCO_3$ in Denmark, representing the first exposure study to cover this nanomaterial. The modeling is based on probability distributions of production, use, environmental release and transfer between compartments, considering the complete life-cycle of products containing the ENM. The magnitude of flows and concentrations depends on the one hand on the production volume but also on the type of products they are used in and the life-cycles of these products and their potential for release. The use and release of $CuCO_3$ was modeled for a scenario of a future situation where micronized $CuCO_3$ has substituted the $CuCO_3$ used today.
Figure 1 shows the final mass flow model from production to technical and environmental compartments – the major flows are considered to be release during outdoor use and transfer to landfills with construction waste.
The flows can be transformed into average environmental concentrations (Table 1). The results reveal that in aquatic systems $CuCO_3$ has an exposure concentration in the low ng/l range under the assumption that the use as wood preservative becomes important. In soils the concentrations could be in the 20-200 µg/kg range. The results of this study provide valuable environmental exposure information for future risk assessments of nnao-$CuCO_3$.

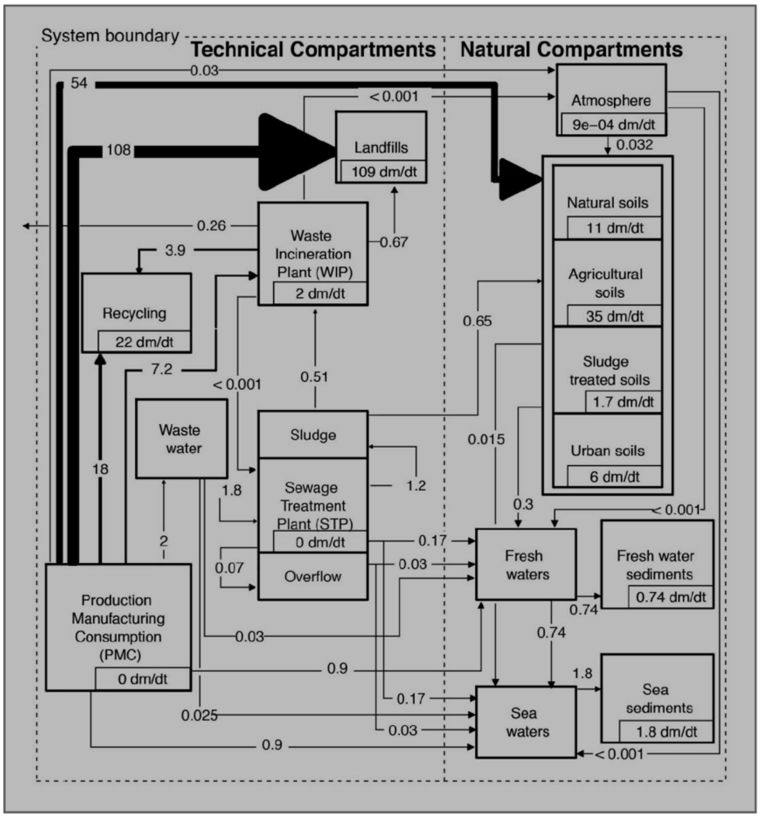

Figure 1. Danish mass flow system of the annual modal values (t/a) of nano-copper carbonate. Boxes show accumulation or transformation.

Compartments (sources)	Concentrations		
	Unit	Mode *median	95% range
Technical compartments			
Sewage treatment effluent	µg/l	1.3	0.3 - 4.1
Sewage treatment sludge	mg/kg	9.1	5.2 - 17.2
Waste mass incinerated	mg/kg	2.0	1.3 - 3.0
Bottom ash of waste incineration	mg/kg	4.4	2.7 - 8.5
Fly ash of waste incineration	mg/kg	22.1	13.2 - 42.3
Natural compartments			
Surface water (fresh water)*	µg/l	0.002	1.2E-04 - 0.006
Sea water	µg/l	3.5E-05	2.0E-05 - 6.8E-05
Sediments (fresh water)*	µg/kg	135.9	6.7 - 321.7
Sediments (sea water)	µg/kg	6.5	3.8 - 12.8
Agricultural soils	µg/kg	4.4	2.8 - 6.3
Natural soils	µg/kg	9.3	5.9 - 19.4
Urban soils	µg/kg	17.0	10.8 - 24.4
Sludge treated soils	µg/kg	7.4	5.0 - 10.7
Air	µg/m3	2.1E-05	4.6E-06 - 3.9E-05

*inconclusive, bipolar (or pluripolar) results or insignifact difference between mode and median

Compartments	Concentrations		
	Unit	Mode *median	95% range
Prediction for 2014			
Sediments (fresh water)*	µg/kg	883.7	43.4 - 2091
Sediments (sea water)	µg/kg	42.2	24.6 - 83.0
Agricultural soils	µg/kg	28.4	18.1 - 40.9
Natural soils	µg/kg	60.3	38.6 - 126.1
Urban soils	µg/kg	110.2	70.2 - 158.6
Sludge treated soils	µg/kg	48.0	32.4 - 69.5
Prediction for 2020			
Sediments (fresh water)*	µg/kg	1845	90.6 - 4366
Sediments (sea water)	µg/kg	88.0	51.4 - 173.4
Agricultural soils	µg/kg	59.3	37.8 - 85.4
Natural soils	µg/kg	126.0	80.6 - 263.3
Urban soils	µg/kg	230.2	146.5 - 331.2
Sludge treated soils	µg/kg	100.2	67.6 - 145.1

*inconclusive, bipolar (or pluripolar) results or insignifact difference between mode and median

Table 1. Concentrations of nano-$CuCO_3$ in technical and environmental compartments in Denmark (left) and concentrations of nano-$CuCO_3$ in environmental sinks in Denmark in 2014 and 2020 (right).

Keywords: Material flow modeling, Environmental concentrations, Probabilistic assessment, Denmark

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Advanced treatment of wastewaters from heavy metals ions by aluminosilicates activated by electromagnetic fields

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Presenter's biography:

Maxim Vyacheslavovich Anisimov finished Voronezh State Academy of Forestry and Technologies (VSAFT), Russia, in 2011 and have degree as an engineer in woodworking. Defended his PhD connected with ecology in woodworking in 2014. In 2014 started working at the Chemistry Department of VSAFT. In 2015 received a Ph.D. He is the author of 44 publications and coauthor of one monograph, 5 of them are refereed in scientific journals of Russia, holder of 2 patent, scholarship of the SAIA, winner of two presidential of Russia scholarships; participant of FP7-program of EU. Research interests include investigation of adsorption and catalytic processes on natural zeolites (klinoptilolite) and clay minerals; development of size of zeolite, using electromagnetic fields for modification sorbents; development of environmental technologies, woodworking, plywood, treatment of waste water.

Extended Abstract:

Contemporary problems of environmental pollution of the hydrosphere by wastewater is becoming increasingly important all over the world, including Russia. In accordance with the "State report «About the condition and Environmental Protection of the Russian Federation in 2014»" one of the essential factors that determine the value of the negative impact on water objects, is the inability to ensure treatment of the total volume of wastewater, the number of which increased from 42895,53 mln. m3/year in 2013 to 43890,8 mln. m^3/year in 2014. To the end of 2015, this amount increased. Priority pollutants in 2014, as well as in 2013 are petroleum hydrocarbons, ions of iron, zinc, copper and other substances. Sorption purification, that effectiveness of which depends on the quality of the sorbent is the very important among the contemporary methods of treatment of waste water. Therefore, the creation and use of new sorbents, which effectively remove organic and inorganic pollutants in form of heavy metals from the wastewater, petroleum products and other toxicants is an urgent task that has a great scientific and practical value.

The purpose of the work: creating of effective sorbent for treatment of sewage water from ions of heavy metals: zinc and copper.

Tasks:

1) Studying the impact of a weak pulsed magnetic field (WPMF) and the electromagnetic field of the microwave (EFM) to the adsorption capacity of clinoptilolite by tons of heavy metals.
2) To determine the optimal treatment regimen of clinoptilolite in WPMF.
3) To determine the optimal treatment regimen of clinoptilolite in EFM.
4) To determine the optimal amount of sorbent.
5) To determine the optimal time of cleaning.

The sorption capacity of the clinoptilolite in native form, is insufficient to ensure the necessary reduction of the concentration of ions zinc and copper. The treatment of the clinoptilolite in WPMF and in EFM was performed in order to improve the adsorption efficiency.

Clinoptilolite is a natural microporous adsorbent, that has active centers of various nature: unshielded (or partially shielded) cations, cation complexes of multiply, hydroxyl groups, Lewis Bronsted acid sites bridging oxygen atoms, defects of the crystal structure. The size and location of the ports are determining for the sorption processes. The zeolite channels frames contain voids forming polyhedra

with channels inside which the volume dimensions are availability 0.6-1.1 nm. The structure of clinoptilolite has 4 types of channels of elliptical cross. Dimensions decimal channels are 0,705 × 0,395, and eight-- 0,46 × 0,395 nm. Matrix clinoptilolite - open carcass, the location of the ion exchange in the open cavities and channels.
The object of the study was Slovak clinoptilolite (K95) with containing rock-forming rocks 95%, particle size ≤ 20 micrometers. The elemental composition of the mineral was determined by the energy dispersion INKA Energy 250. Sample of clinoptilolite is characterized by a high content of K, Ca, Mg. The main cation exchange ions in the clinoptilolite are K+, Na+, Ca2+. Earlier work had shown that the content of exchangeable cations of the zeolite sample relates to the calcium form of clinoptilolite. The amount of silica modulus (Si/Al) for the sample is 5,51.
Preadsorption activation of mineral was carried out in WPMF and EFM.
The greatest effect on the activation of exposure after 48 hours in the mineral processing WPMF has been found in the earlier work.
Models of solution sewage containing copper and zinc ions 0.2 mg / l were used.
This concentration was chosen according to the analysis of the chemical composition of the wastewater of the furniture enterprises in Voronezh area.
The adsorption was carried out during 1, 2, 3, 6, 12, 24 hours.
0,25; 0,5; 1; 2; 4 gram of sorbent were added to 1 liter wastewater.

Method of processing	Natural clinoptilolite		EFM		WPMF	
	Zn	Cu	Zn	Cu	Zn	Cu
The degree of purification of waste water, ŋ, %	4,55	3,85	9,09	31,92	22,73	73,08

Table 1. The degree of purification by natural and activated clinoptilolite of wastewater containing ions of zinc and copper.

On the basis of the results, the treatment in WPMF provides a greater degree of purification in comparison with EFM, more than 2 times. In this regard, a number of studies (MBOH, BET, DLS) conducted to explain this effect.
The analysis of obtained data let us pick out some important theses for this research work. They show the mechanism of the influence of WPMF and EFM to processes of adsorption of non-conductors and effectiveness purification of sewage from heavy metals.
Results:

1) The possibility of increasing sorption capacity of clinoptilolite by zinc ions and copper was determined.
2) Due to the impact of EFM on clinoptilolite the mineral heats immediately (a split second) because of the absorption of the wave's power. Meanwhile the process of the dehydration takes part because of the break in legami intermolecolari between the molecules of water and clinoptilolite's structure matrix. Furthermore during the impact of the field of EFM ions in the structure of zeolite get the direction to the line of force of the field. The frequently change of this direction causes fast friction that leads to emission of heat (heat till 427 K). Dipoles of water move continually perpendicularly to the direction of Hertz wave's movement. When the temperature reaches 373 K it fumes. In total movement of dipole molecule and mineral structures ions causes fast heat of the sample. Power is used to move molecular. Power as a heat is emitted because of the presence of intermolecular friction. This way of removal of moisture from mineral's structure let the appotunity to release from water molecular active centers i.e. the amount of them grows (what was confirmed in the research work).

3) Using of WPMF for activation of sorption processes of clinoptilolite possibly due to the fact that on the surface and within the pore space of the mineral are functional groups having the charge, acting that by WPMF, we can achieve adjustment of structure, to ensure the best effect of adsorption and desorption processes will be completely eliminated. Structuring information about clinoptilolite after treatment in WPMF was obtained in the course of the analysis of the using method and argue in favor of this version.

Acknowledgment: ECONANOSORB project № 295260

Keywords: Clinoptilolite, Zinc, Copper, Adsorbtion, Electromagnetic field of the microwave (EFM), Weak pulsed magnetic field (WPMF)

Hazard and risk assessment of Cu based nanomaterials

Janeck J Scott-Fordsmand

Department of Bioscience, University of Aarhus, Denmark

Presenter's biography:
Dr. Janeck J. Scott-Fordsmand has a vast experience in the ecotoxicology of various chemicals, including nanomaterials. The work has focused on linking effects from the molecular level (biomarkers) to the population and community level. He is an expert in risk assessment advising on various international test guidelines, guidance documents and risk assessment of chemicals; work performed for the various EPAs, EU and OECD. He is co-leading the risk part of the European Nanosafety Cluster and of the nano risk collaboration between EU and US (EU-US CoR).

Extended Abstract:
Introduction
As nanomaterials (NM) are dimensionally and physically different from conventional soluble forms of chemicals, this implies that the metrics with which we relate effects and the type of effects that must be measured are different from those of the conventional chemicals (Scott- Fordsmand et al., 2016). It is further evident that nano-forms are intended for long term use and will mainly end up in solid environmental matrices rather than the pelagic and, hence, for hazard assessment, attention should be given to such environments (Peijnenburg et al 2016). Further, it is well known that Cu based pollution has long term consequences, and that fragmented wood impregnated with Cu may remain in the soil matrix for decades (Nielsen et al 2015).
Discussion
The above also means that there is a need to update the current hazard methods (Amorim et al., 2016). It is important to prioritise the hazard both in direct relation to ecosystem services,
Cu nano hazard
but also in broader ecological aspects. Hazard aspects should include long term aspects such as multi-generation effects over a variety of species covering different environmental compartments. To reduce the cost of testing, it is important to develop short term test systems, e.g. *in vitro* systems that enable a prediction of such long term consequences. Hence, one way forward is to link high throughput approaches to the desired population level adverse outcomes. Although the benefits of integrating various levels of information may seem obvious, this is an even more decisive aspect for NMs. This is the approach taken in the EU's SUN project, where the hazard evaluation is headed by Dr Janeck J. Scott-Fordsmand. Within the SUN project, the focus is on developing novel and more reliable methods for assessing the longer term consequences of nanomaterials, especially with focus on ecosystem services.
Copper based engineered nanoparticles (Cu-NM) also present these novel challenges to the established hazard assessment approach, and because the Cu based materials may also partially dissolve under environmental conditions, the biological effect measures should include both particulate and ionic effect measures. For the terrestrial environment, some studies have been performed by e.g. Gomes et al. (2011) showing differential gene transcription for Enchytraeids exposed to Cu nanoparticles and Cu salts. Based on the gene expression responses, it was possible to discriminate between the two exposure types. Studies using a suit of biomarkers showed that also on the biomarker levels, it was possible to discriminate between exposures to the various forms of Cu, e.g. Gomes et al., 2012. Such different forms of Cu effects are also reflected on the population level (Heckmann et al., 2011, Amorim et al., 2012a, b, Gomes et al., 2015). It is not yet clear whether effects are caused solely by

NM, by ions or by a combination of these, as studies have been showing both that the nano form is more toxic than the salt form and the opposite has also been
shown. This is coupled with the knowledge that although Cu nanoparticles may be oxidised within the environmental matrix, they may still remain mainly as an intact particle due to the protective oxidized layer formed on the surface of the particle (Gomes et al., 2015).

Summary

In summary, given the above indications that Cu nanoforms and salt forms do behave differently and cause different effect types, although overlapping, it should be pursued in the current hazard and risk assessment.

Keywords: Fun, Science, Nano, Pollution, Tools

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Session 2: Lifecycle impacts of nanoscale Copper used in timber preserving impregnations

Chair: Michael Tsang, University of Bordeaux, France

Certification of a micronized copper wood preservative (MCA) as Environmentally Preferable, based on Life Cycle Assessment

Keith Killpack ***and Gerard Mansell***

SCS Global Services, USA

Presenter's Biography:
Keith Killpack is the manager of the Life Cycle Services program at SCS Global Services. Prior to his current position, he was a Life Cycle Assessment Practitioner at SCS. He holds a Master's degree in Environmental Science and Management and a B.S. in Biochemistry and Molecular Biology from UC Santa Barbara. He has conducted numerous life cycle assessments, analyzing the environmental impacts of various building materials and related products, advanced power generation systems, and recycling systems. He has conducted the life cycle assessment of a whole building- the Caltrans Inland Empire Transportation Management Center. In his role as an LCA Practitioner, he has helped with the development of Product Category Rules for office furniture and steel construction products. Prior to his work as an LCA Practitioner, he worked as an environmental chemist, validating environmental analytical data and working on environmental remediation projects. His Master's thesis reviewed international environmental, health and safety, and product stewardship practices in the nanotechnology field. Prior to his Master's studies, he performed laboratory research for four years at various biotechnology and nanotechnology firms.

Extended Abstract:
Introduction: Micronized Copper Azole (MCA) is a widely commercialized wood preservative treatment process which has been sold in North America since 2008. MCA is a water-based wood preservative which protects wood from fungal decay and termite/insect attack. MCA uses minimally water soluble copper compounds, such as basic copper carbonate. The copper compound is micronized, or finely ground, into a stable dispersion of submicron copper particles with the aid of a dispersant. In addition to micronized copper, MCA also contains a triazole compound, such as tebuconazole.
SCS Global Services has certified MCA as an Environmentally Preferable Wood Treatment Process, based a Life Cycle Assessment (LCA) conducted following ISO 14040, ISO 14044 [1], and a draft US National Standard [2]. The scope of the LCA includes production the wood preservative through delivery to treatment plants. A summary of the life cycle assessment is presented, including the environmental benefits of MCA in comparison to another wood treatment preservative, Alkaline Copper Quaternary (ACQ).
Goal and Scope of Study: The Study followed ISO 14044, and a draft US National Standard for life cycle assessment, to conduct a LCA of Micronized Copper Azole (MCA) in comparison to Alkaline Copper Quaternary (ACQ). The Study sought to determine whether MCA could meet the definition of *Environmentally Preferable*, for the purposes of 3rd party certification as an Environmentally Preferable Wood Treatment Process (EPWTP).

Environmental Preferablility is defined as: *A product which, for all category indicators included in the Life Cycle Impact Assessment profile has lower results than the reference baseline* [2]. For MCA to meet the definition of EPWTP, the life cycle assessment of the treatment chemical must have lower environmental impacts in all impact categories without any trade-offs as compared to the reference baseline, ACQ.

The scope of the Life Cycle Assessment includes the environmental and human health impacts from, 'Cradle-to-Delivered Product'. MCA and ACQ are compared on the basis of wood preservative required to treat one billion boardfeet of lumber. The wood treatment process was assumed to be similar for MCA and ACQ, and was not included in the scope.

Although product use and end-of-life were not quantified in the LCA, the assessment of relative product performance and end-of-life toxicity was an important component of the certification. To assess the product performance of MCA, comparative performance testing of MCA and ACQ was reviewed, including simulated aging tests and in-use stake tests. Performance test data shows that MCA treated wood provides equivalent or improved performance, with reduced copper leaching, relative to ACQ.

Materials and Methods: Life Cycle Assessment of MCA and ACQ wood treatment chemicals was conducted using SimaPro 8 LCA software [3], using a combination of primary data from the product manufacturer and supply chain, supplemented with secondary data using the ecoinvent [4] and USLCI life cycle databases [5].

Life Cycle Assessment was conducted following ISO 14040, ISO 14044 [1] and a draft US National Standard, LEO-SCS-002 [2]. The LEO-SCS-002 standard augments ISO 14044 with a comprehensive list of impact categories, and provides algorithims for site- and region-specific impact assessment. The LEO-SCS-002 draft standard is being developed following the American National Standards Institute (ANSI) consensus process.

Conclusions: Results from the Life Cycle Assessment demonstrate reduced environmental impacts for MCA of between 50% and greater than 90%, in comparison to ACQ. All impact category indicators assessed for MCA show lower values than the reference baseline, thus achieving the status of "Environmentally Preferable Wood Treatment System", as compared to the reference baseline product system. A summary of the LCA results are shown in Table 1.

Impact Category	Units	MicroPro® MCA	ACQ	% Reduction in Impacts
Global Climate Change	Metric ton CO_2 eq.	7,960	77,600	90%
Arctic Climate Change	Metric ton CO_2 eq.	11,800	116,000	90%
Ocean Acidification	Metric ton CO_2 eq.	17,100	168,000	90%
Ocean Warming	Metric ton CO_2 eq.	13,300	131,000	90%
Regional Acidification	Metric ton SO_2 eq.	105	601	83%
Ground Level Ozone Exposures	Persons*hrs*ppb O_3	830	8,370	90%
PM-2.5 Exposures	Persons*hrs*µg/m^3 PM2.5	3.4	39	91%
Risks from Radioactive Wastes	GBq eq.	0.47	4.1	89%
Energy Resource Depletion	MJ eq.	54,600	916,000	94%
Copper Resource Depletion	Metric ton Cu eq.	1,290	2,880	55%

Land Use Ecological Disturbance**	Percent	Negligible	100%	~100%

Table 1. Impact category indicator summary for MCA wood treatment chemical system and comparison to the reference baseline ACQ treatment chemical system.*
**Values calculated per 1 billion board feet of treated wood. Results rounded to three significant figures.*
***Though it was not possible to calculate hectares disturbed, or species loss, and there were no data to suggest that oil plantations were environmentally certified, it was assumed that all land used to produce oils for carboquat production were transformed from its natural baseline condition, with resulting impacts on biomes and species.*

The results of the LCA are also shown as a *Life Cycle Impact Profile* (Figure 1), which shows the impact of MCA relative to the reference baseline wood treatment chemical, ACQ.

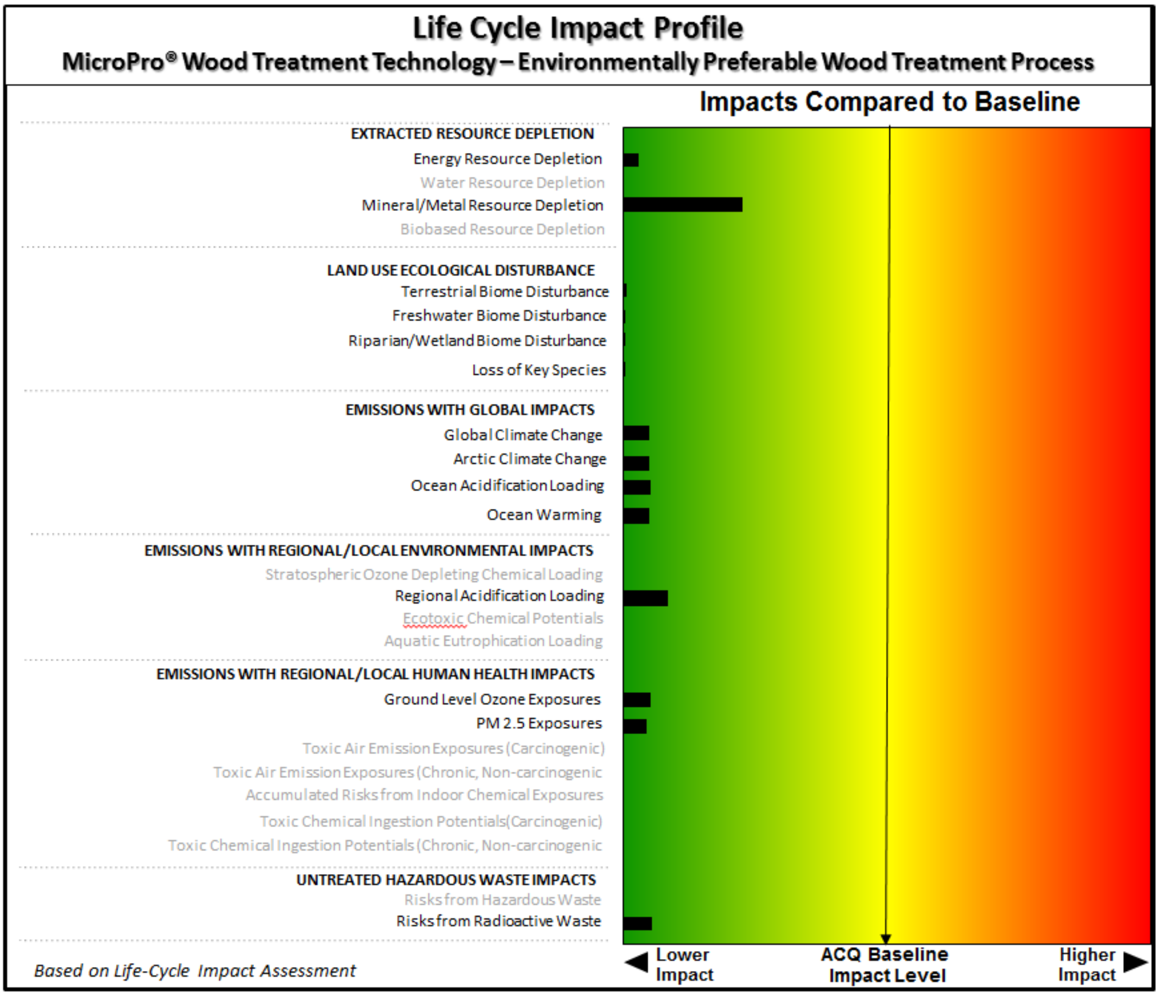

Figure 1. Life Cycle Impact Profile of MCA wood treatment chemical, relative to the Reference Baseline, ACQ wood treatment chemical. The impacts of ACQ are represented by the vertical line in the yellow field. The impacts of MCA are represented with horizontal black bars. Horizontal black bars to the left of vertical line for ACQ show reduced impacts, while any increase in impacts would be shown by a bar extending to the right of the vertical line for ACQ.

Acknowledgment: Thank you to Koppers Performance Chemicals for providing data for the assessment.

Keywords: Wood treatment, Micronized copper, Life cycle assessment

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How LCA Provides Insight to (Nano)Technology Assessment and Development: Case Study of MCQ-treated Lumber Products

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[2]U.S. Army Corps. of Engineers, U.S.A.

Presenter's Biography:
Michael Tsang is a third year Ph.D. student at the University of Bordeaux working with the life-cycle and sustainable chemistry (CYVI) group. He joined the CYVI Group in November of 2013 after spending two years in Washington D.C. as a research fellow at the U.S. EPA. He has a background in environmental public health, renewable energy, life-cycle assessment, alternatives assessment, risk assessment and decision analysis and has published in these domains in multiple internationally recognized journals. His current research projects include benefit and risk analysis of nanotechnologies, with a particular focus on organic photovoltaic technologies employing fullerene nanomaterials. This work involves the intersection of life-cycle assessment and risk assessment and the methods in which they can be integrated. Michael is also a current student-contractor with the U.S. Army Corps of Engineers where he applies life-cycle assessment on various case studies involving emerging technologies and renewable energy. He received his bachelor's degree in biology from the University of California, San Diego and his master's degree in public health from the University of California, Los Angeles.

Extended Abstract:
Historical trends have shown us that environmental and human health assessments often fall behind the curve of advancements in technology and industrial and consumer product innovation. For example, although tens of thousands of chemicals are registered with the U.S. EPA, only a few hundred human health and/or environmental risk assessments have ever been completed for those same chemicals. In the case of engineered nanomaterials (ENM), the rapid pace of production over the last decade has similarly left a noticeable void in human health and environmental evaluations of ENMs and their associated products. ENMs also pose additional challenges for both data generation/collection as well as the conventional chemical assessment tools that are not specifically equipped to handle all ENM-related human health and environmental considerations.
Life-cycle assessment (LCA) is an environmental management tool defined by ISO 14040:2006 (International Organization for Standardization, 2006a) and 14044:2006 (International Organization for Standardization, 2006b) that tabulates material and resource consumption and waste emissions involved over a product's life-cycle and calculates potential human health and environmental impacts. While LCA is also confronted by ENM-specific data and methodological challenges, it can nevertheless provide a useful method of analysing and quantifying the potential impacts associated with the processing, production, use and disposal of other materials and related processes related to the life-cycle of the ENM-enabled product.
Two previous studies (M. Tsang, Meyer, Hawkins, Ingwersen, & Sayre, 2014; M. P. Tsang, Bates, Madison, & Linkov, 2014) approached the problem of human health and environmental evaluation of micronized-copper treated lumber (MCQ) products that use copper active ingredients down to the nanometer size range from a life-cycle perspective. MCQ treated lumber entered the U.S. market mainly in the early half of the 2000's after a voluntary product restriction of chromated copper arsenate (CCA) lumber from the domestic use of treated lumber due to concerns over the potential toxicity of the product. Since then, alkaline copper quaternary (ACQ) and MCQ are the main product formulations used in the domestic treated lumber market, and nearly 25% of all preservatives used in the

U.S. contain micronized copper by weight. Whereas ACQ treated lumber uses soluble copper species for treatment, MCQ exploits the properties and behaviours of micronized and sub-micronized copper particles in order to treat lumber products. Some studies have shown that MCQ can penetrate different aspects of the wood structures that are important for fungal decay and wood rot, is just as or more effective as ACQ even at lower treatment solution retention rates, has lower rates of copper leaching and is less corrosive to hardware applied to the lumber.

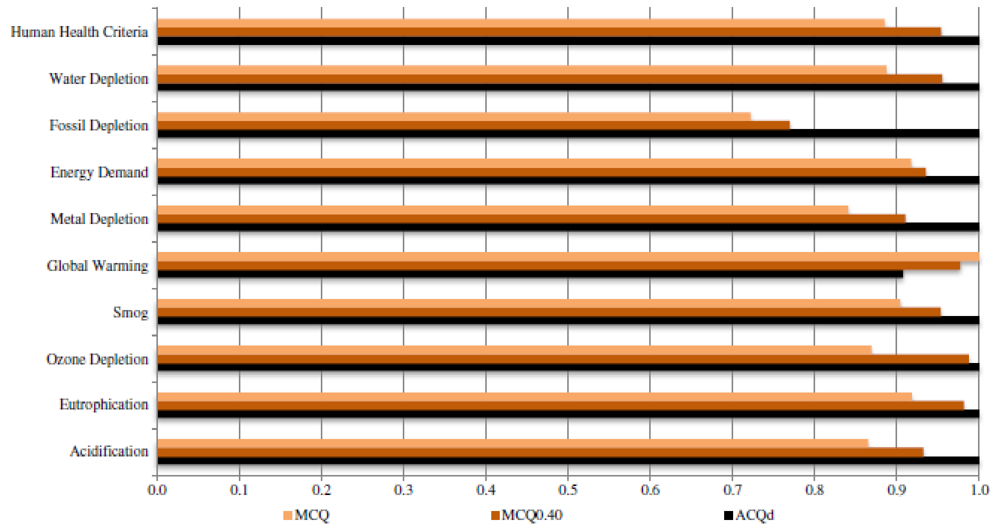

Figure 1. Lifecycle impact results comparing MCQ and ACQ for a raised-garden bed

These potential advantages are also paralleled by the potential adverse environmental and human health effects that sub-micron or nano-sized copper particles might pose across the life-cycle. In order to address these concerns in a more holistic manner, LCA was applied in both aforementioned case studies to further analyse the how the technical and material characteristics of the copper particles might translate into environmental and human health benefits versus the trade-off of potential exposures and toxicity across the life-cycle. The results of the LCA demonstrate some clear advantages for the MCQ product compared with ACQ. Overall, MCQ performed better than ACQ across all impact categories (Figure 1). These reduced life-cycle impacts were mainly due to a few factors, most notably that MCQ does not require the use of a solvent (monoethanolamine) that is required of ACQ. The combined effect of producing and distributing (i.e. transporting) the solvent resulted in ACQ having much greater LCA impacts including global warming potential and energy demand, for example.

Product	Copper leached (mg)	Ecotoxicity (CTU)	Ecotoxicity, metal (CTU)	Human health (CTU)	Human health, metal (CTU)
ACQ_d	35.04	3.69	1,056.67	4.43089E−08	8.00287E−06
MCQ	8.21	3.26	269.31	3.77003E−08	6.31744E−06
$MCQ_{0.40}$	9.66	3.70	314.57	3.77003E−08	6.91209E−06

Figure 2. Results of the ecotoxicity and human health toxicity broken down by metal and non-metal contributions. Note: the results do not include the impacts from the nano copper particles.

However, these results still neglect the potential impacts leading from the direct release, exposure and effects of the copper particles themselves. Non-nano metal leaching drove the majority of the ecotoxicity and human health toxicity impacts for both ACQ and MCQ, although MCQ impacts were

much lower. This was mainly due to the much lower estimated copper that leached from the product. It was also assumed that the majority of copper would leach as ionic copper and not particulate copper. Although this assumption was kept at 95%, there is still room for interpretation on whether the 5% of particulate copper would diminish the ecotoxicity and human health impacts such that there is no longer an advantage for MCQ. Having a clear set of nano-specific results was the main limitation in the approach of using LCA to evaluate the environmental and human health impacts of MCQ. These limitations were present in the form of data accessibility (i.e. ability obtaining pre-existing manufacturing data specific for micronized copper particles or MCQ treated lumber), evaluation-gaps (i.e. lack of knowledge or non-existent data on copper leaching and speciation of the leached matreials) and methodological shortcomings (i.e. lack of tools that can work with the fate, exposure and effects of nanomaterials).
Given these short-comings, the results of these studies still provide useful guidance of sustainable production of nanotechnologies and management of potential human health and environmental impacts beyond what a qualitative assessment and a more narrowly focused risk assessment might produce. Furthermore, these studies also highlight the particular data and methodological gaps that could be addressed in LCA to help inform and promote discussion around the SUN Decision Support System (SUNDS), which aims to provide assessments on nanotechnologies even when data and methodological limitations are present by using an integrated life-cycle approach.

Keywords: Engineered Nanomaterials, Life-cycle Assessment, Micronized Copper Quaternary, Alkaline Copper Quaternary, Lumber Treatment, Multi-criteria Decision Analysis

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Environmental impacts of nano and non-nano copper based wood preservatives systems

Tom Ligthart [1] ***and <u>Michael Steinfeldt</u>*** [2]

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Presenter's Biography:
Michael Steinfeldt is a diploma'd engineer, and is senior scientist at the University of Bremen, Faculty of Production Engineering since 2005. His main focus of research is environmental valuation, methods of technology assessment, and life cycle assessment. Current research themes are green and sustainable nanotechnologies.

Extended Abstract:
Softwood that is exposed to the environment in temperate moist climates will rot within a couple of years. Wood preservation can extend the lifespan of these uses of softwood. This case study within the framework of the SUN project studies two different nanocopper wood preservation techniques, one based on nanoCuCO3 and one on nanoCuO, and compares the environmental impact of these systems with that of a conventional wood preservation technique.
The investigation addresses the use of softwood as façade panelling that is not protected from the elements. The nanoCuO preservative is added to an acrylic paint base which is then applied to the softwood. The façade panelling is repainted during its service life. The nanoCuCO3 sub-case uses nano-sized CuCO3 in an impregnation solution to impregnate softwood. The wood is further left untreated during its service life. This is also the case for the conventional wood preservation based on the impregnation of wood with an alkaline copper quaternary ACQ. The Functional unit of the case study: The provision of 1 m2 of an exposed softwood exterior cladding during 1 year by a balanced service life of the application of 20 years.
The life cycle stage of the wooden façade (see Figure 1), starts with the production of the softwood planks and wood preservation products. The wood is than treated with the preservation products and the protected wood is installed at the façade of the building (a certain installation loss of the treated wood is included). The installed softwood planks need repainting during the service life for the nanoCuO case. For the other two cases no treatment is needed. From the exposed wood the wood preservation products will partly leach during their service life. When the wooden planks have reached the end of their service they are manually removed and send to a municipal incineration plant.
In the SUN project the following life cycle stages are distinguished:
1a Production of functional products
1b Production of other products
2 Manufacturing of nano-enabled product
3a Use of product, functional product related
3b Use of product, other product/processes related
4a End-of-life functional product related
4b End-of-life other products related

The life cycle impact assessment (LCIA) is based on the recommended ILCD impact categories (European Commission, 2012) and on ReCiPe midpoints (Goedkoop et al., 2013) combined with shadow prices (Bruyn et al., 2010) for ease of comparison.

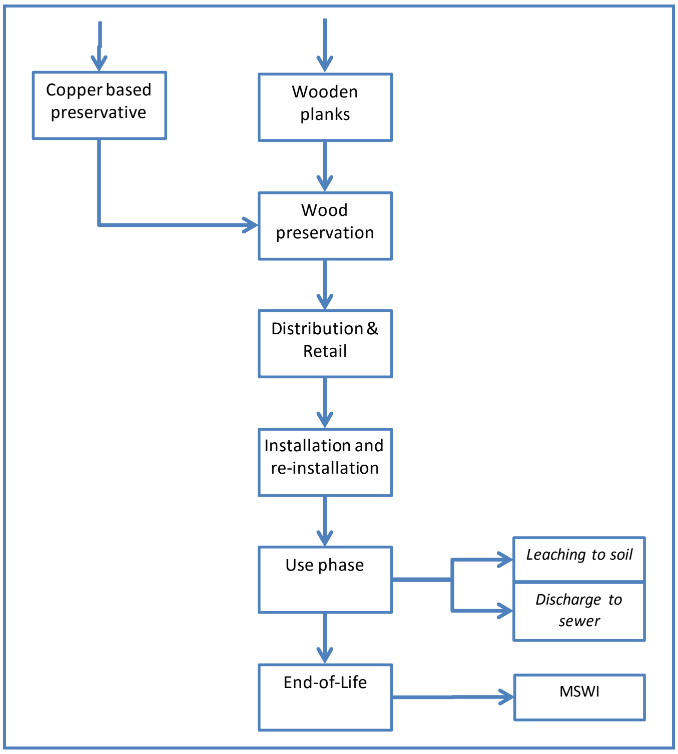

Figure 1. The life cycle of the softwood façade cladding.

Selected results

In Figure 2 the environmental impact of 1 m^2.y-1 CuO painted wooden cladding is shown. The total impact is calculated to be 191 mEUR. The biggest contribution is caused by the agricultural land occupation of the wood production. Furthermore the transport is the second biggest contributing process, with the same reasons as with the ACQ treated wood. The environmental impact of the CuO treatment is caused by the paint, rather than the micro CuO in the paint. The installation losses, the use phase and the disposal are not great contributants in the total impact.

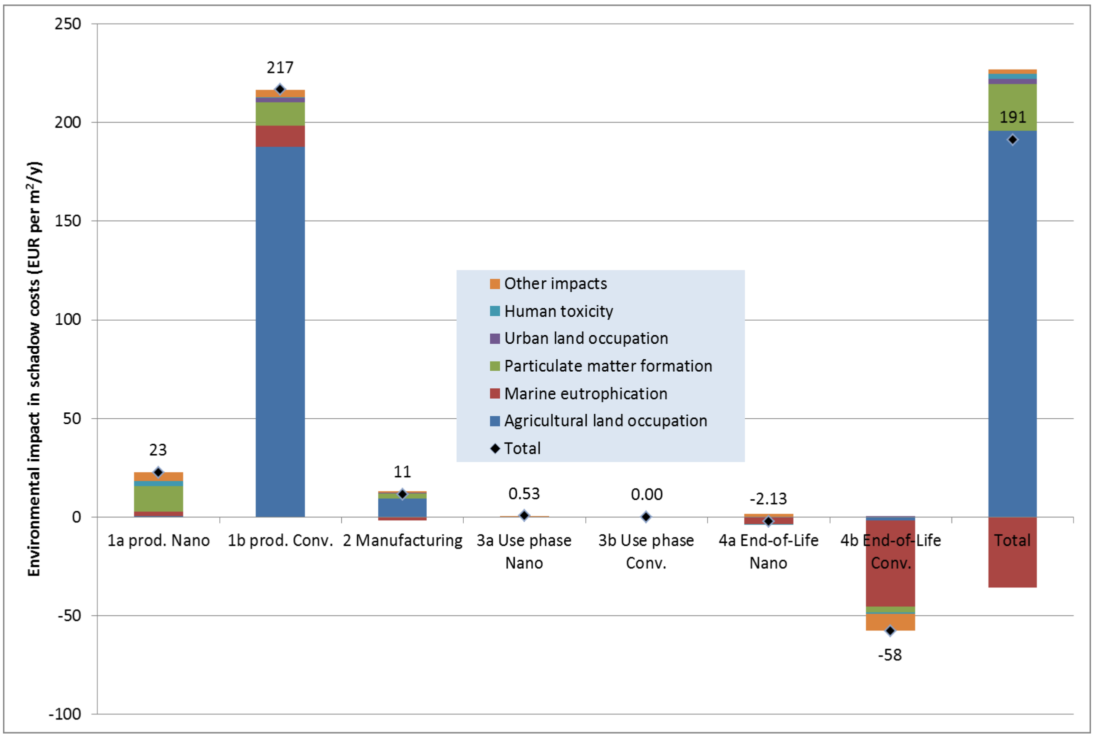

Figure 2. Environmental impacts of 1 $m^2.y^{-1}$ CuO painted wooden cladding

Since the impact of the wood is the main impact for the wooden cladding, it's difficult to see the differences in the impact between the different methods of treatment. Therefore, in Figure 3 a sensitivity analysis is presented where the wood is left out of the product system.

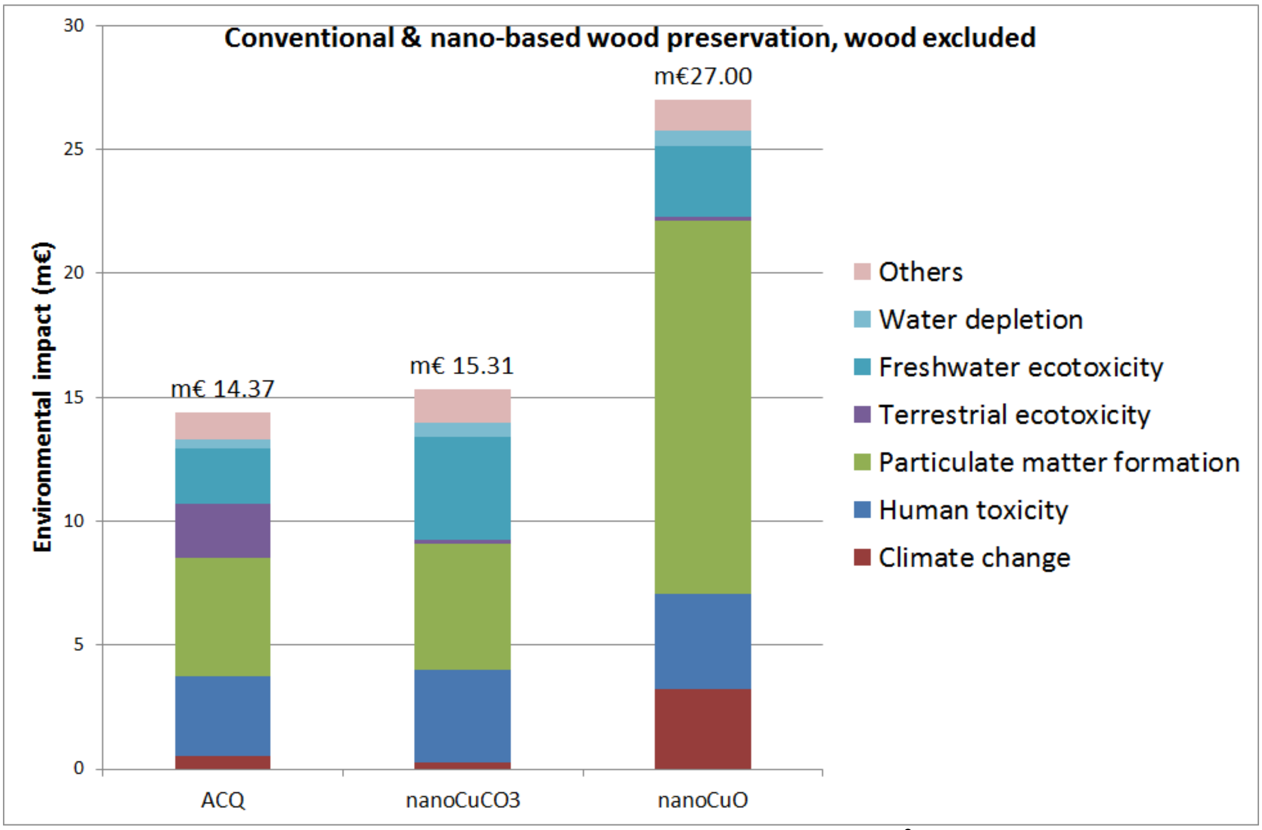

Figure 3. Environmental impact of the three treatment systems for 1 m^2.y-1 cladding, excluding the wood from the product system.

The differences between the treatment methods are now better visible. The production of the CuO paint shows the largest environmental impact, the treatment with ACQ the lowest and CuCO3 shows an intermediate impact. The production of the functional materials shows the largest contribution for nanoCuO and nanoCuCO3. For the ACQ-D system production and end-of-life of the functional substances have comparable contributions to the different environmental impact categories. For the CuO paint the end-of-life shows also an avoided environmental impact, due to the energy recovery from the acrylic base in the MSWI.

Summary

The impact of wood dominates the environmental profile of all investigated systems. The specific contribution of nanoCuO itself is almost negligible, the paint is more important. Compared to ACQ and nanoCO3 impregnation, nanoCuO coating is performing less.

Acknowledgment: This works was sponsored by the European Commission [SUN Project Number: 604305].

Keywords: Life Cycle Assessment, Environmental impacts, Wood preservatives, Shadow prices

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Invited Speech

Modification of Polycondensation Resins with Mineral Adsorbents for Environmentally Friendly Wood Products

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Prof. Ing. Ján Sedliačik, PhD. is a teacher and scientific investigator at the Technical University in Zvolen, Faculty of Wood Sciences and Technology, Slovak republic. Doctoral degree graduated at the Technical University in Zvolen, in 2000, with the work titled: Optimization of the bonding process of environmentally friendly plywood materials. Author of 14 international patents in the area of application of polycondensation resins for wood based materials and author of 25 scientific works. Co-investigator of FP5 European project solving new technologies of processing and application of collagen hydrolysates for application in polymer resins and co-investigator of FP7 project ECONANOSORB.

Extended Abstract:
Urea-formaldehyde (UF) adhesive is one of the most often used polycondensation adhesives in woodworking industry. One major disadvantage of the adhesive is the fact that during manufacturing process of bonding of wood products, during all the time of using them in residential buildings, and using of adhesive mixtures, toxic formaldehyde is released from the bonds. Formaldehyde pollutes working and living environment and the atmosphere. The research is aimed on modification of UF adhesive with mineral adsorbents to reduce formaldehyde emission. Alluminosilicates montmorillonite, palygorskite and zeolite were used to modify the resin. The presence and structure of active centres in minerals make the best conditions for formaldehyde sorption. The mineral sorbents were activated by temperature or by pulse electromagnetic or microwave fields in order to improve adsorption capacity for formaldehyde. Mineral sorbets were added in amount of 3 % of into the adhesive mixtures. Physicochemical properties of liquid adhesives, strength of adhesive joints, formaldehyde content and emission of formaldehyde from plywood were measured. The experimental results showed that activation of sorbents enables to improve the adsorption capacity for formaldehyde. The addition of activated sorbents into the UF adhesive reduces the formaldehyde emission without lowering the adhesive joint strength and properties of the adhesive mixtures are not changed.

Type of modifier	Emission of fd [mg/m^3]	Standard E1 [mg/m^3]	Decrease [%]
UF resin (reference)	**0,097**		**0**
UF resin + Montmorillonite natural	**0,077**	**<0,124**	**21**
UF resin + Montmorillonite heat activated	**0,079**		**19**

UF resin + Montmorillonite pulse electromagnetic field (PEF)	**0,085**		**12**
UF resin + Montmorillonite heat + PEF	**0,073**		**25**
UF resin + Montmorillonite microwave field	**0,065**		**33**
UF resin + Palygorskite natural	**0,067**		**31**
UF resin + Palygorskite heat activated	**0,059**		**39**
UF resin + Palygorskite pulse electromagnetic field	**0,074**		**24**
UF resin + Palygorskite heat + PEF	**0,056**		**42**
UF resin + Palygorskite microwave field	**0,043**		**56**
UF resin + Zeolite natural	**0,087**		**10**
UF resin + Zeolite heat activated	**0,065**		**33**
UF resin + Zeolite pulse electromagnetic field	**0,081**		**16**
UF resin + Zeolite heat + PEF	**0,074**		**24**
UF resin + Zeolite microwave field	**0,049**		**49**

Table 1. Formaldehyde emission from plywood stated by the chamber method according to EN 717-1

The addition of mineral sorbents lowers the formaldehyde emission from plywood samples. It was proved, that activation process of minerals increases the sorption capacity of formaldehyde. The addition of non-activated, natural minerals into the resin has also significant influence on formaldehyde emission.
All tested samples of plywood fulfil requirements of the standard for the formaldehyde emission class E1. Based on obtained results can be stated, that the addition of natural and activated mineral sorbent has the influence on formaldehyde emission from plywood. From non-activated, natural minerals, the highest influence has the palygorskite (lowering of emission down to 31 %), montmorillonite (lowering of emission down to 21 %), and the influence of natural zeolite is less expressive (lowering of emission down to 10 %). Heat activation of aluminosilicates increases the conditions for formaldehyde sorption. The emission of formaldehyde after heat activation of sorbents is lowered down to 19 % for montmorillonite, down to 39 % for palygorskite and down to 33 % for zeolite. The best results for formaldehyde emission are after activation of mineral fillers in microwave field. Activated montmorillonite lowers toxicity of adhesive down to 33 %. Sorbents palygorskite and zeolite activated by microwaves lowers the emission of free formaldehyde down to 56 % resp. 49 %.
The shear strength of glued joints, as the main parameter of mechanical property of wood based panels, meets the requirement of the standard EN 314-1 (1 MPa). The strength of reference plywood based on resin without the mineral sorbent was 2,4 MPa. Adhesive mixtures with the addition of aluminosilicates obtained the strength within the interval from 1,9 to 3,1 MPa. This is explained by anisotropic structure of wood, and there is no significant influence of mineral sorbents on shear strength properties of plywood.
Natural and activated sorbents have no influence on UF resin mixture properties, or their influence is very weak. All proposed methods of activation are efficient, the best results of activation are after microwave treatment. All methods of formaldehyde measurements proved the sorption ability of minerals, the most important emission tests, chamber and desiccator, confirmed the decrease of formaldehyde emission from plywood up to 50 %. Palygorskite and zeolite are the most suitable mineral sorbents of formaldehyde.

Acknowledgements: This research was supported by a Marie Curie International Research Staff Exchange Scheme Fellowship within the 7^{th} European Community Framework Programme, project PIRSES-GA-2011-295260, “ECONANOSORB”.

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-14-0506.

Keywords: Adsorbent, Urea-formaldehyde resin, Modification, Mineral filler, Plywood

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Acknowledgements

The SUN and ECONANOSORB Projects acknowledge the financial support of the European Commission under the Seventh Framework Programmes
FP7-NMP/ 2013-2017- Grant agreement no. 604305
and
FP7-PEOPLE/ 2012-2016 – Grant agreement no. 295260