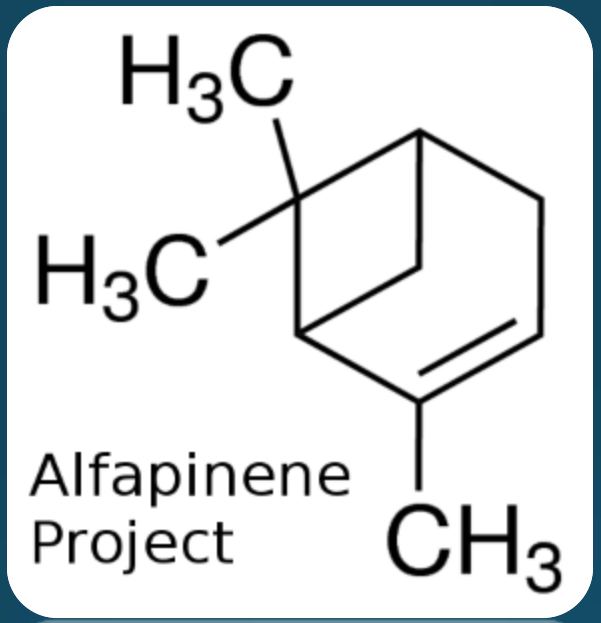
COST Action FP1407 2nd Conference – Innovative production technologies and increased wood products recycling and reuse

Brno, Czech Republic, 29-30 September 2016

Marco Fellin, PhD
Martino Negri, PhD
CNR-IVALSA, Italy
Trees and Timber Institute

Marco Felicetti
Vittorio Monsorno
D.K.Z. srl – Fiemme 3000, Italy



Maintaining wood naturalness: Production of Biocompatible wooden floors and monitoring of Heavy Metals, VOC, and Radiation

Outline

- Introduction
- Sampling
- Materials and methods
- Results
- Conclusions

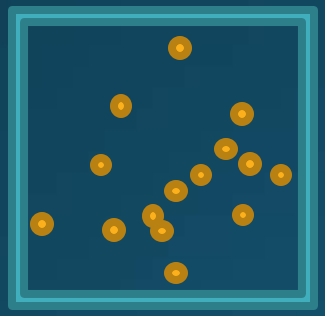
Introduction

- The wood floorings are perceived as natural and healthy materials.
- They are, however, a potential source of indoor VOC's, which may worse the IAQ and human health. Other possible hazards are the presence of radioactive isotopes or heavy metals. It depends on HOW you manufacture it.
- A new generation of biocompatible wood floorings has been tested for the heavy metals, VOC's emissions, radiations and related health impact, together with other brand floorings without evident low-emission attitude.
- The Alfapinene project is a 18 months research project ending in december 2016.

Introduction – Heavy metals

- Pigments, *Ti, Pb, Cr, Cu*...,
- Presence may be naturally originated
- Hazardous for children ingestion and adults inhalation
- They are a challenge for a proper recycling

Introduction - VOC

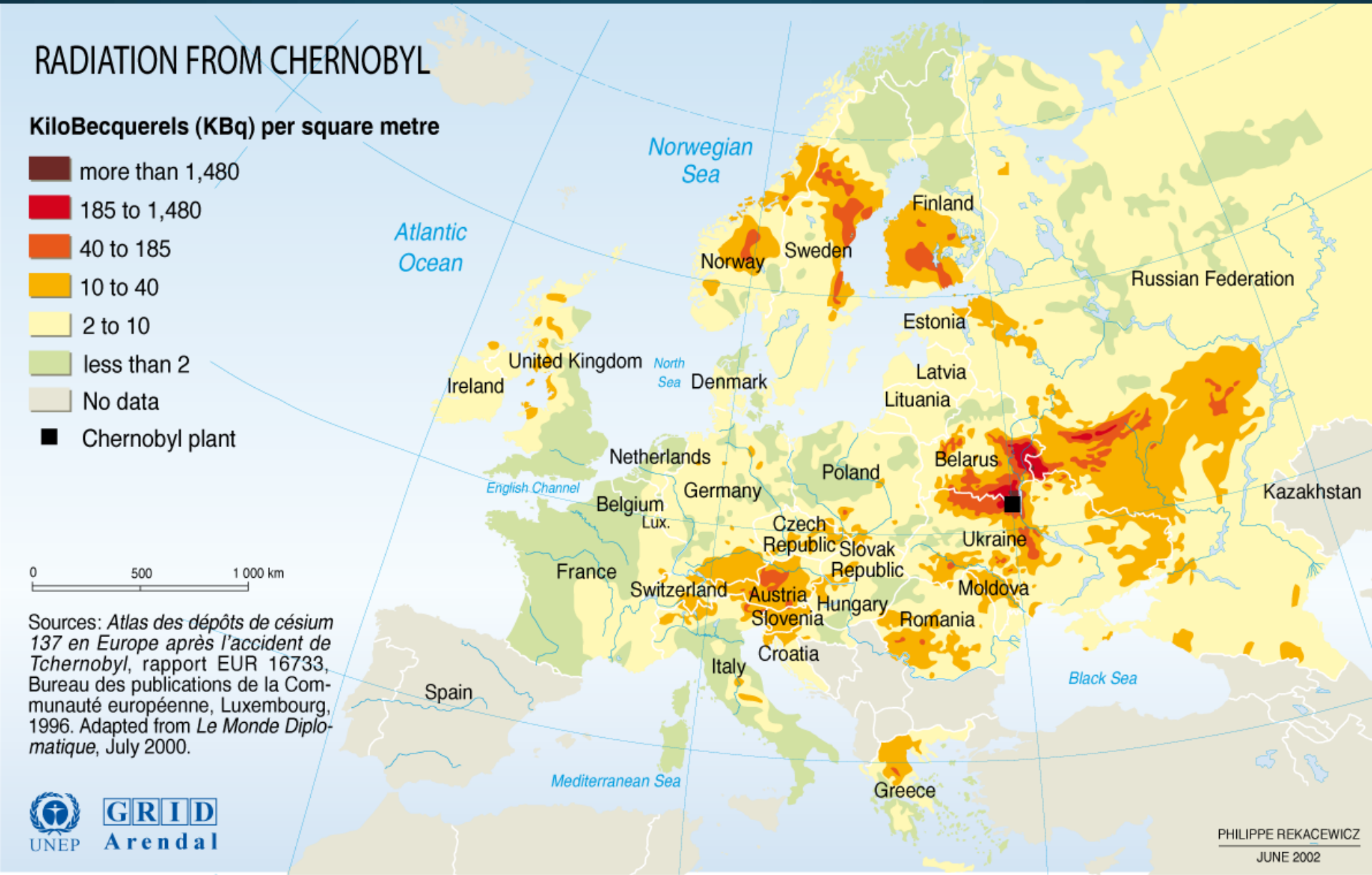


VOC content	VOC emission	VOC concentration	VOC effect
[g/l]	[µg/m³] [mg/hm²]	[µg/m³]	Syntoms
ASTM 2369...	ISO 16000, EN 717, ASTM D6330, ASTM D6670...	Air changes, T, RH, heating, ventilation, air conditioning…	Gender, age, dose, frequency...

Introduction - VOC

- Are VOC good?
- Negative effects: headake, fatigue, skin irritation, nose congestion... The five «Ds» discomfort, dysfunction, disability, disease or death.
- Positive effects: heartbeat slowdown, cancer prevention and therapy, anti-inflammatory, anti-oxidants, decongestant, antimicrobials, help in drugs adsorption, anti-tussive, bronchodilators, mucolytic...
- Important: which molecule, route of exposure (inhalation...), magnitude (concentration), duration (how long?), frequency (how often?), timing (at what age?), gender, age, genetic, health, interactions...

Introduction - Radiation



Sources: UNEP/GRID-Arendal, European Environment Agency; *AMAP Assessment Report : Arctic Pollution Issues,* Arctic Monitoring and Assessment Programme (AMAP), 1998, Oslo; European Monitoring and Evaluation Programme (EMEP); Co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe, 1999. Adapted from *Le Monde Diplomatique, July 2000.*

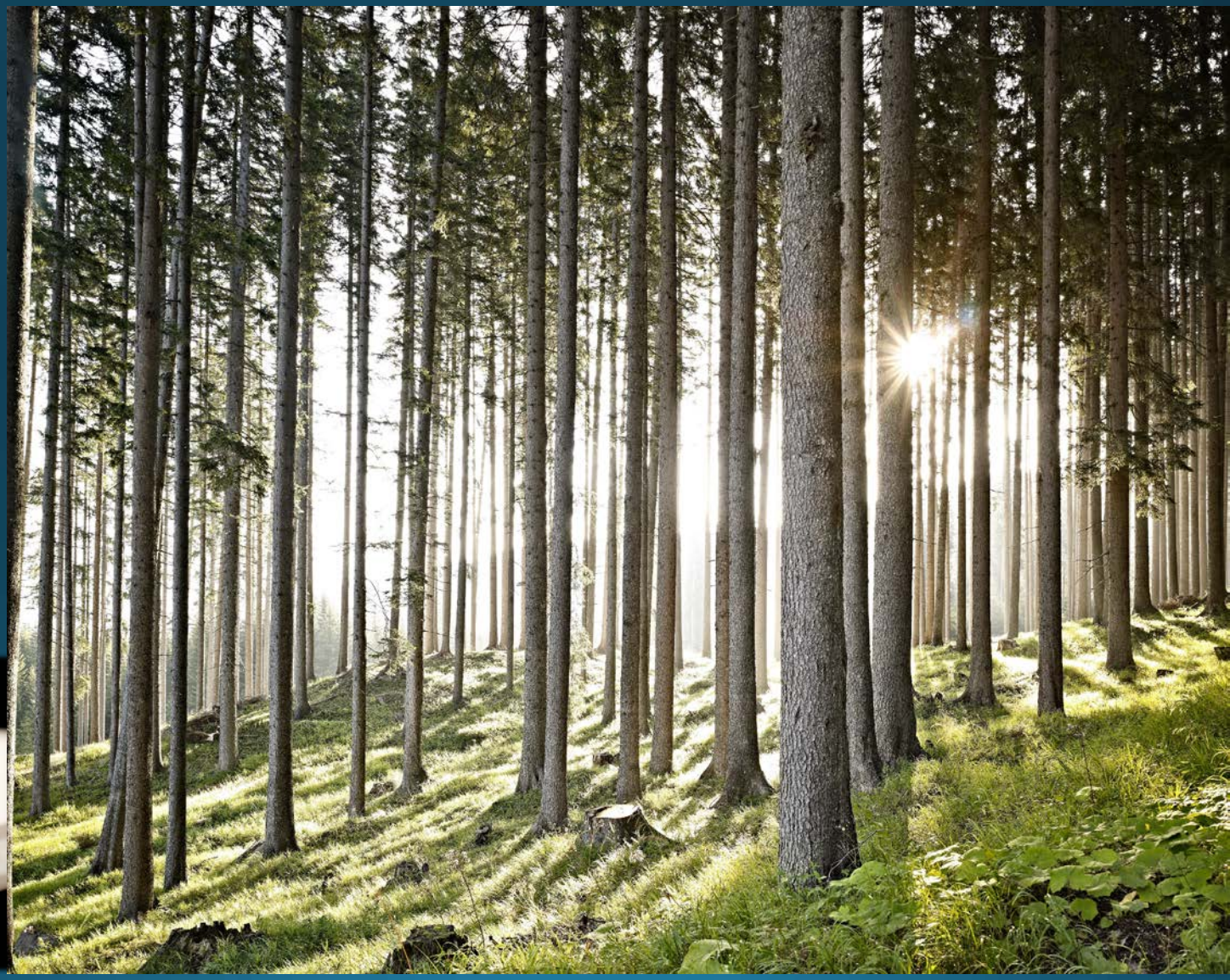
Sampling

- 100 oiled wood floorings:
  - biocompatible floorings, made with vegetable raw materials.
  - other floorings without evident low-emission /eco-friendly attitude.
- 200 wood species in 350 specimens for heavy metals.

Sampling

Biocompatible wood floorings:

- Organic, made with vegetable raw materials. Absence of chemical and petrol derivative product, or any potentially harmful for health.
- Fiemme valley – Italy is famous for its wood because it has luxuriant forests, where Stradivari used to come to bring the timber for his precious violins.



Sampling of natural air


© 2016 Cnes/Spot Image
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
Image Landsat
United Nations Educational, Scientific and Cultural Organization
World Heritage Convention
DOLOMITI
DOLOMITEN
DOLOMITES
DOLOMITIS

Materials and methods - VOC

VOC analysis:

- On biocompatible wood floorings (headspace SPME-MS).
- On other wood floorings (headspace SPME-MS).
- Emissions from wood floorings (Preliminary tests with PID)
- Emissions from wood floorings (ISO 16000, 3 and 28 days).
- Natural “uncontaminated” air (Tenax vials and GC-MS).
- On VOC based pharmacy drugs (headspace SPME-MS).


SPME-MS


SPME-MS


ISO 16000

Materials and methods - VOC

- The identification of the compounds has been done matching chromatograms with the NIST library.
- The health impact of the resulted compounds has been classified using databases from:
  - The International Agency for Research on Cancer (World Health Organization)
  - The AgBB (Committee for Health-related evaluation of Building Products)
  - Toxline
  - Medline
  - The Regulation EC n° 1272/2008

Materials and methods – Heavy metals

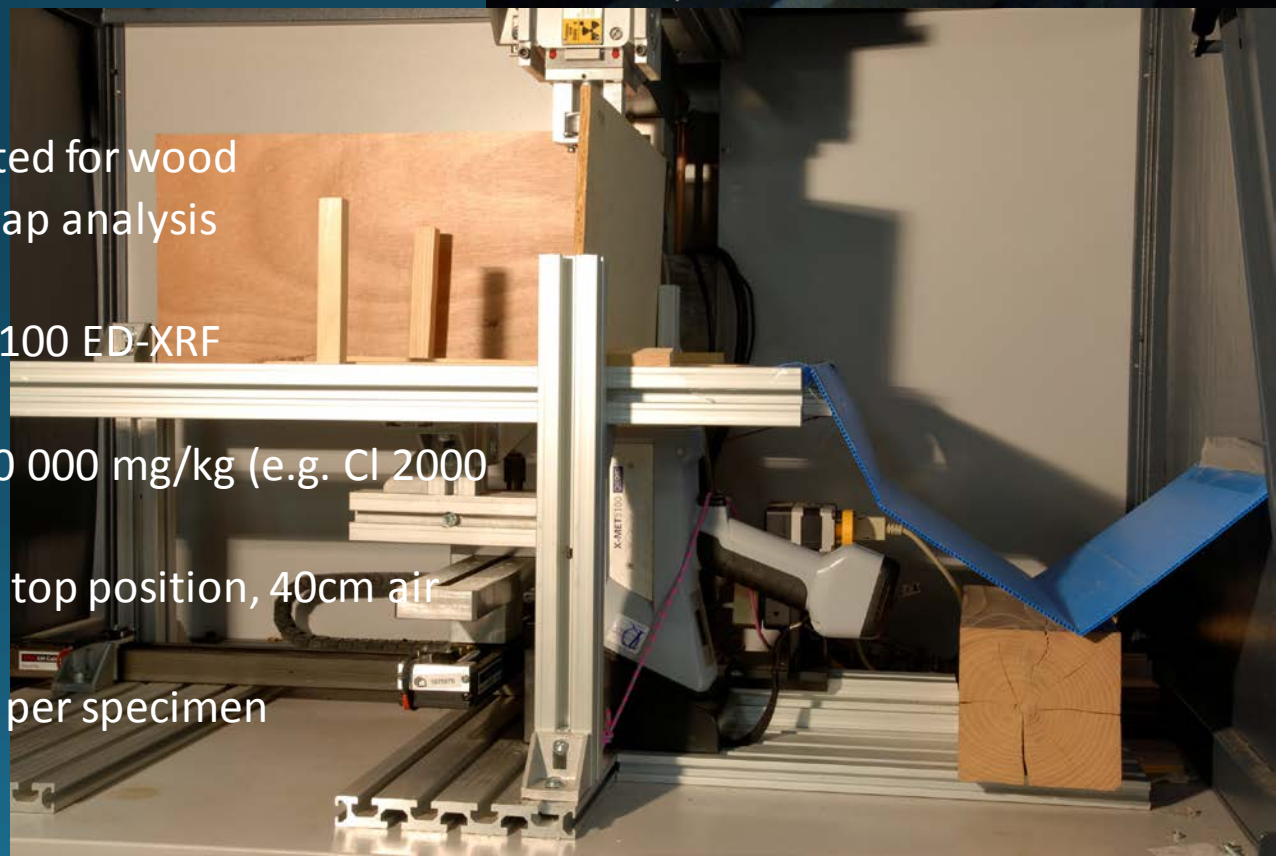
ED-XRF:

- Elements atomic mass > 12 a.m.u. (Mg) (no C, H, O…)
- Quali-quantitative analysis
- Handheld instrument with possible bench top and automation set-up.
- with pretty good accuracy
- Designed for metals, calibrated for wood
- No preparation, fast and cheap analysis

Set-up:

- Oxford Instruments X-MET 5100 ED-XRF
- X-ray source: 45 kV 40 µA,
- Sensitivity: from few to 1 000 000 mg/kg (e.g. Cl 2000 mg/kg Cd 4 mg/kg)
- Measurement set-up: bench top position, 40cm air background
- 6 replicas of 600 s measures per specimen

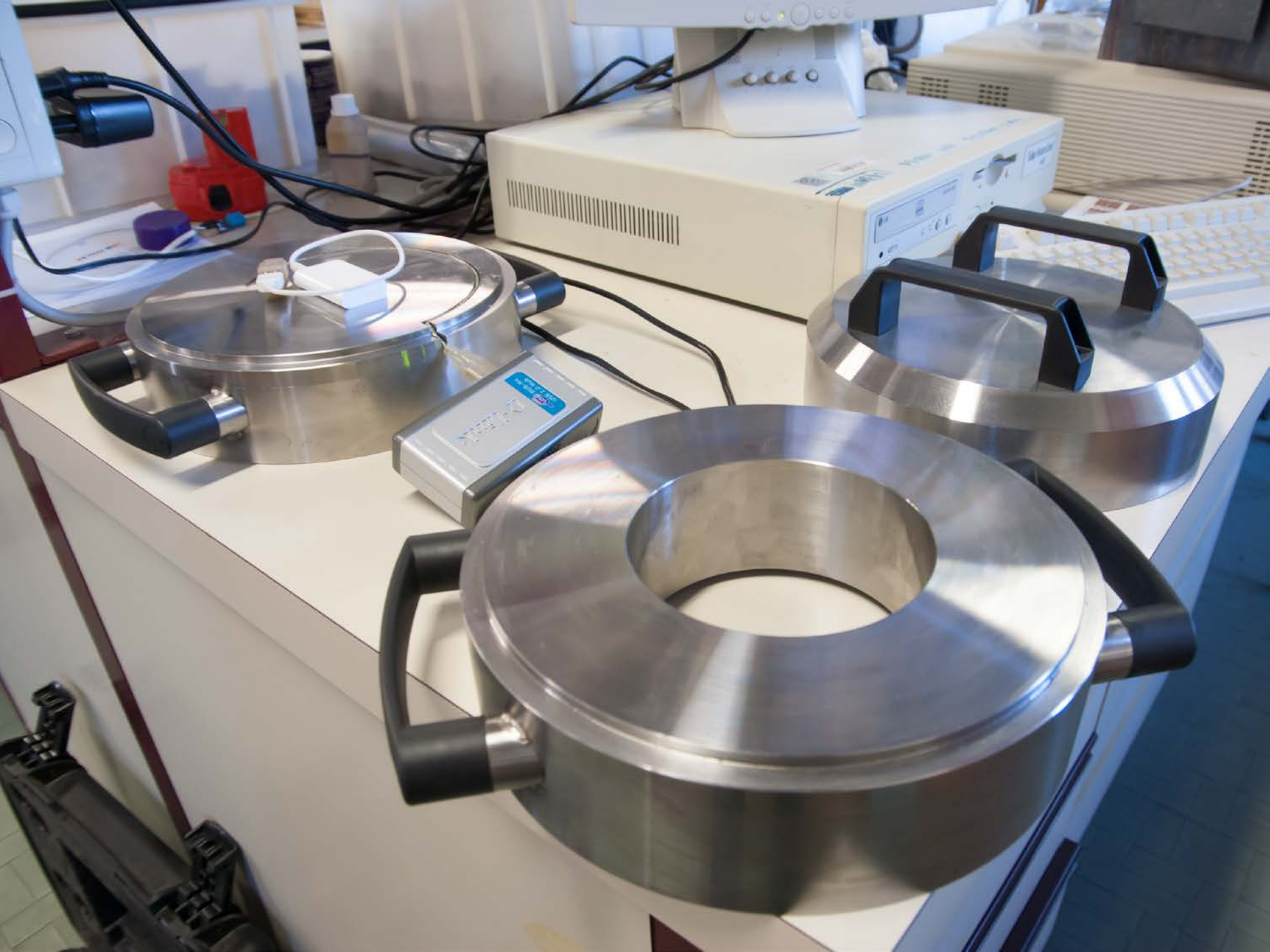
automatic process:
6 spec., 36 meas., 6 hours



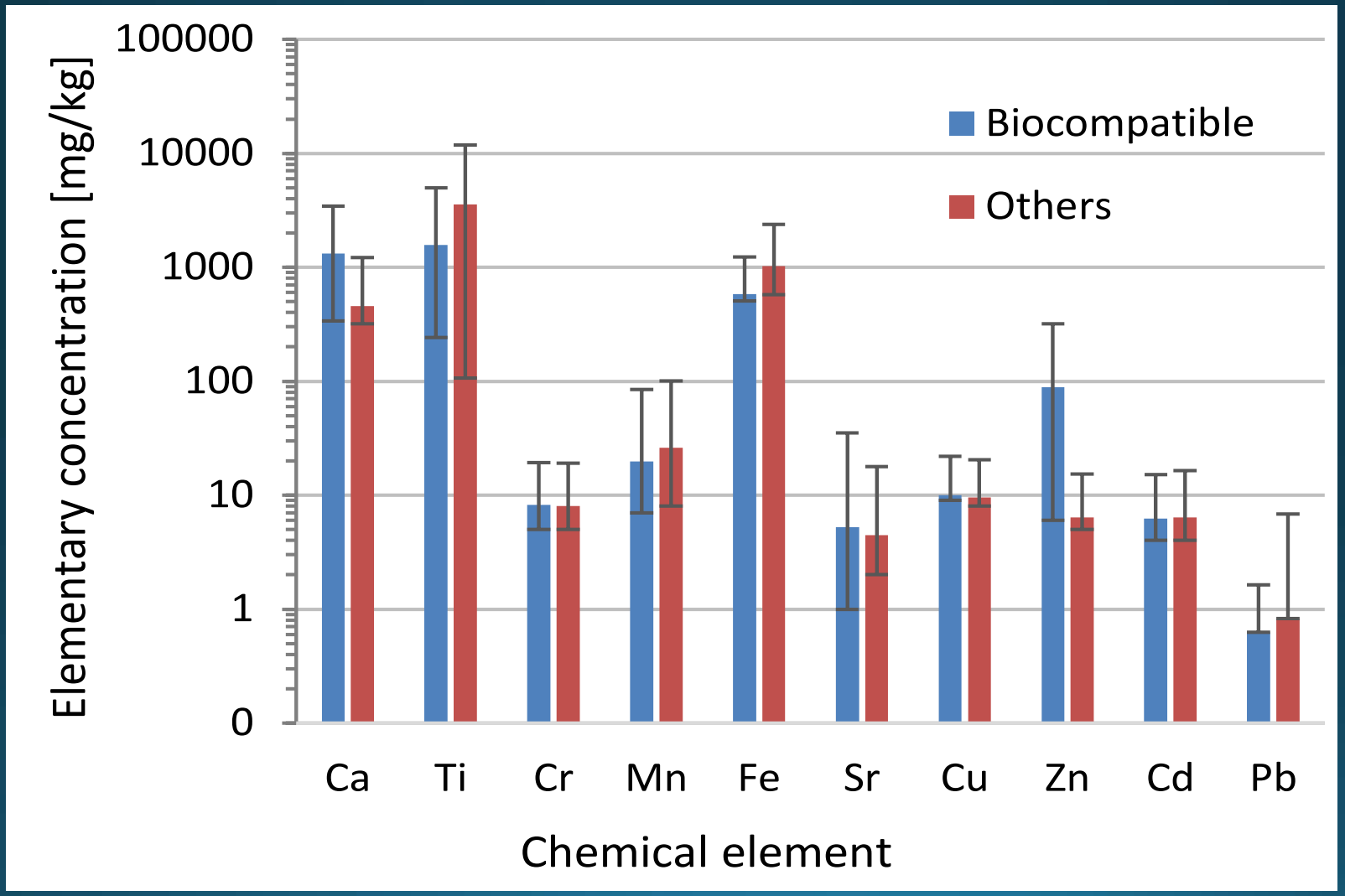
Materials and methods - Radiation

- Pocket geiger type 6;
- 100 mm² First Sensor A.G. X100-7 PIN Ionizing radiation detector;
- X γ rays radiation (β removing the internal shield;
- High sensitive sensor;
- Measuring range (Cs^{137}) 0.05uSv/h～10mSv/h 0.01cpm～300Kcpm;
- USB, microcontrollers (e.g. Arduino), Android, IOS compatible;
- 10 minutes measurements;
- Certification Dutch Metrology Institute;

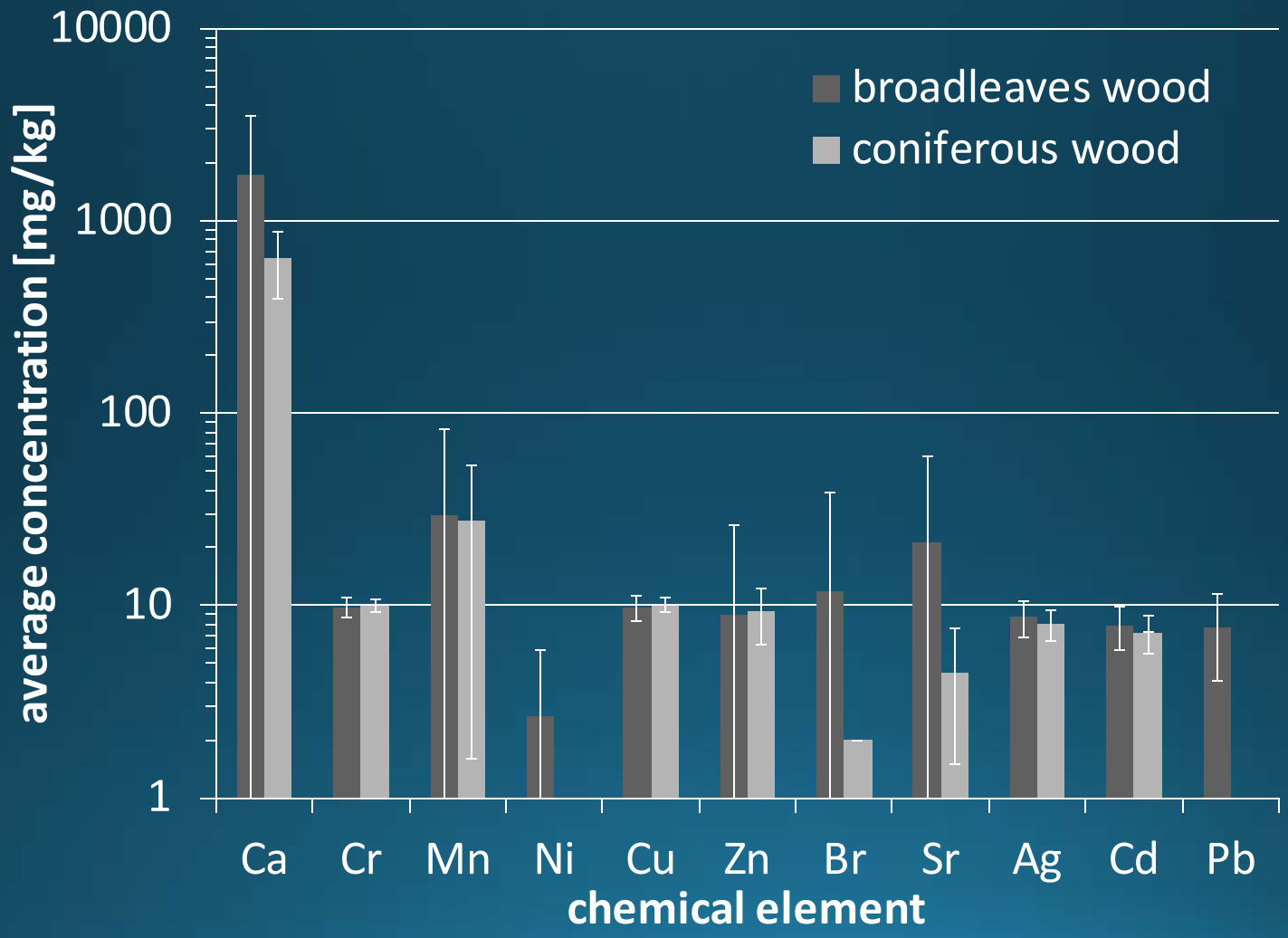
www.radiation-watch.org



Results – Heavy metals in wooden flooring



Results – Heavy metals in natural wood

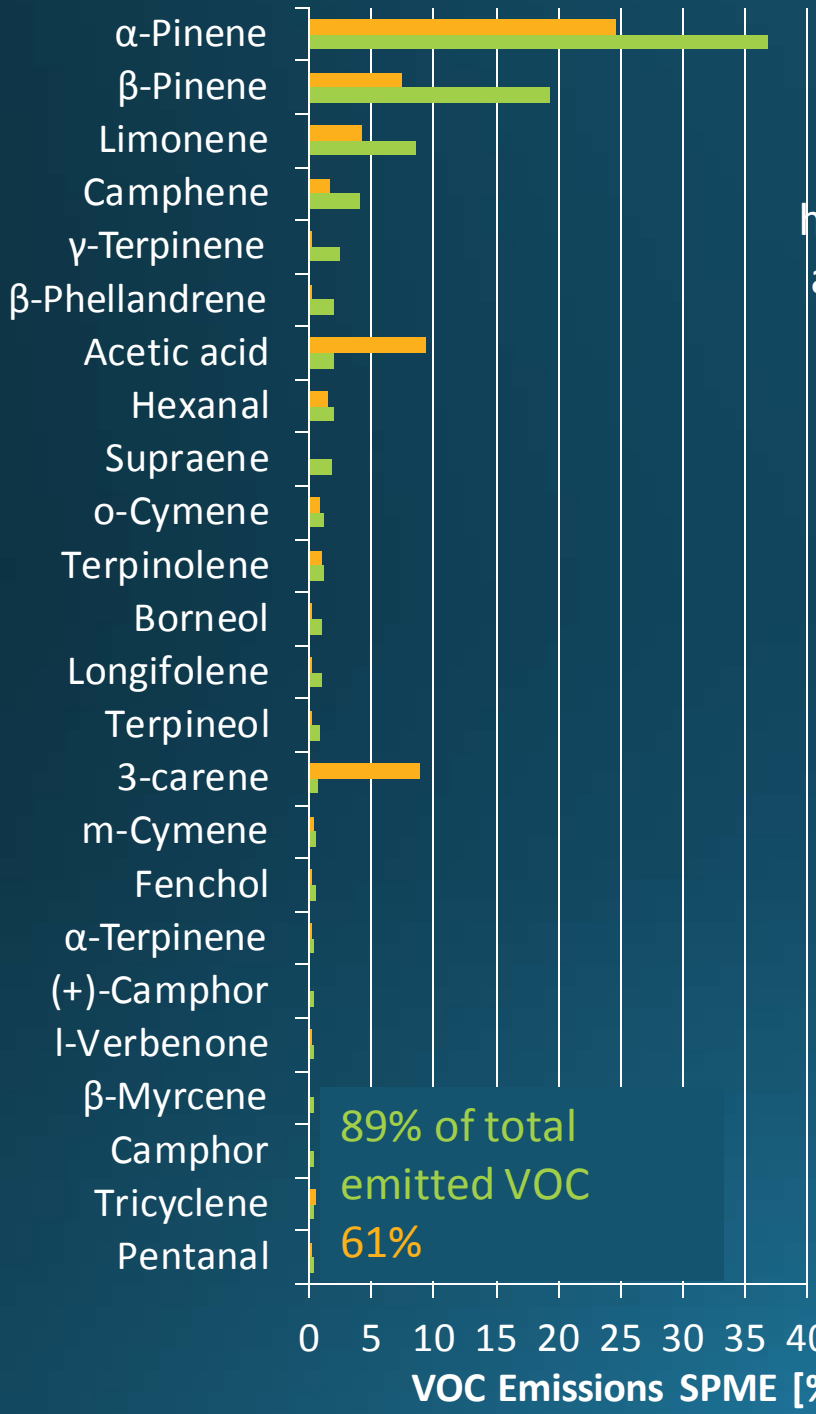


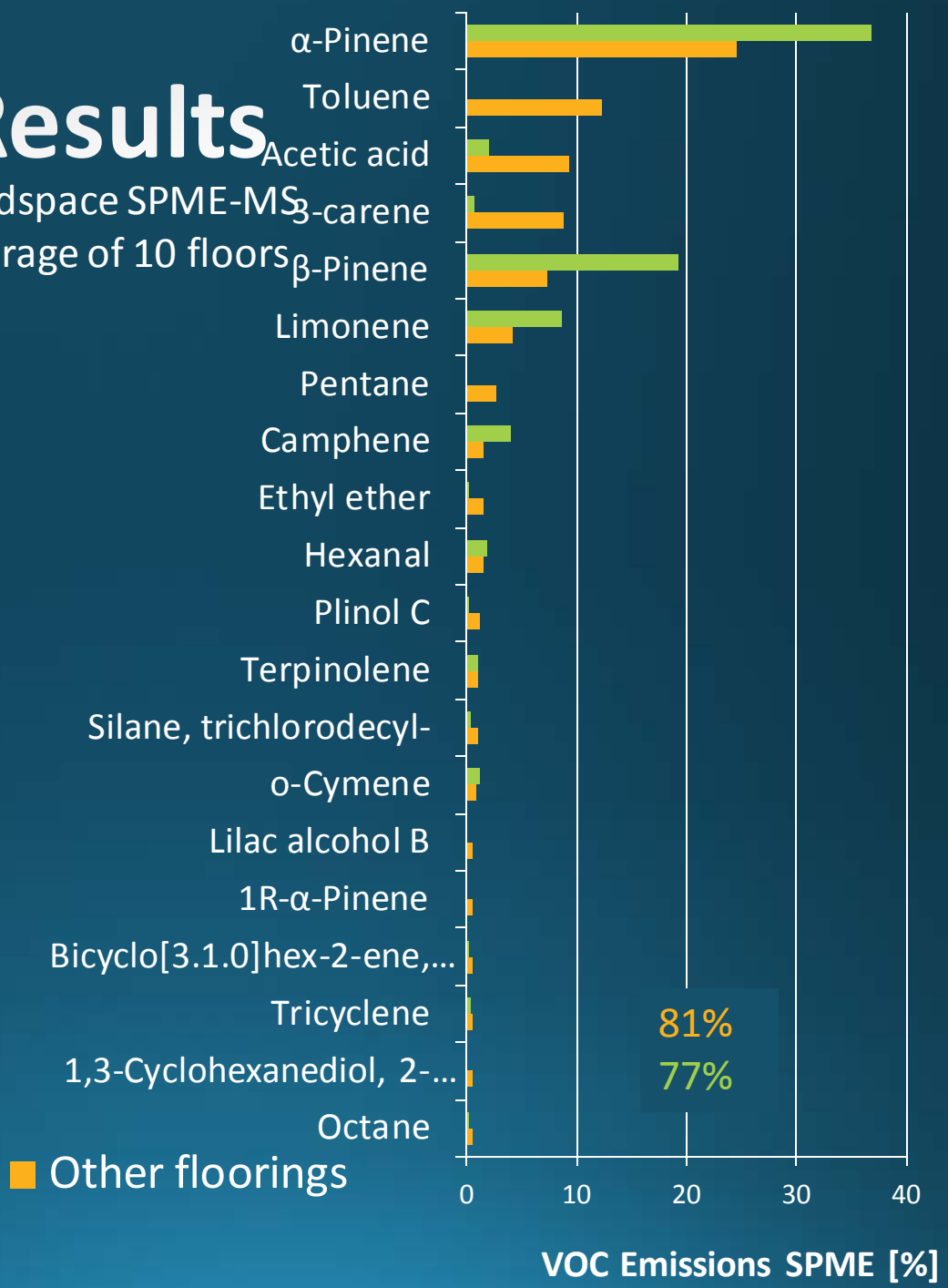
Results - VOC

- International Agency for Research on Cancer (World Health Organization), about 1000 entries: **none found**
- The AgBB red list (Committee for Health-related evaluation of Building Products), about 800 entries: **none found**
- Toxline: both positive and negative health effects for the monoterpenes like α-pinene, camphene, β-pinene, cineole, limonene, camphor, eucalyptol and thujone.
- Medline and Regulation (EC) No 1272/2008, comparison is ongoing.

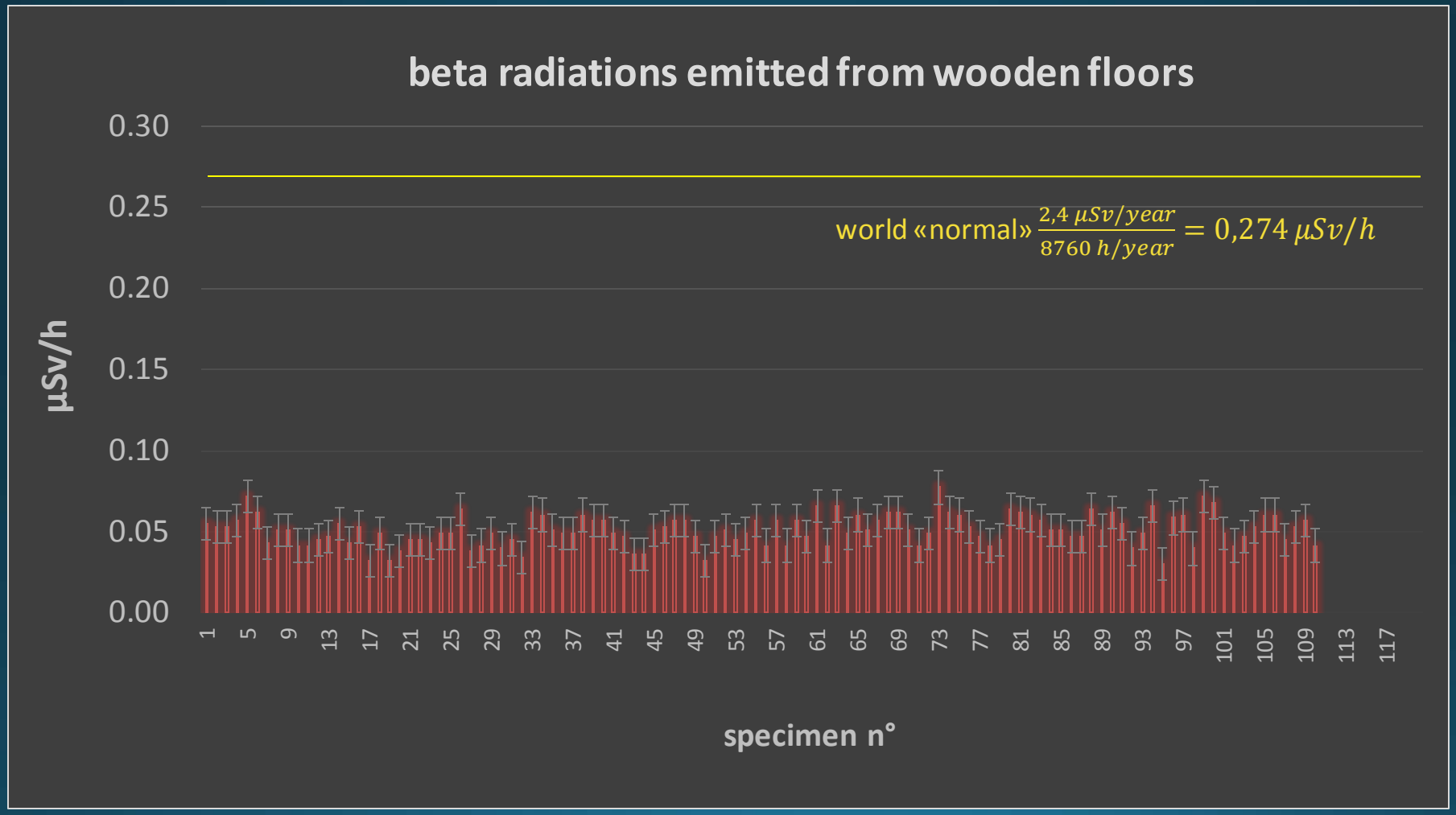
Results

headspace SPME-MS
average of 10 floors

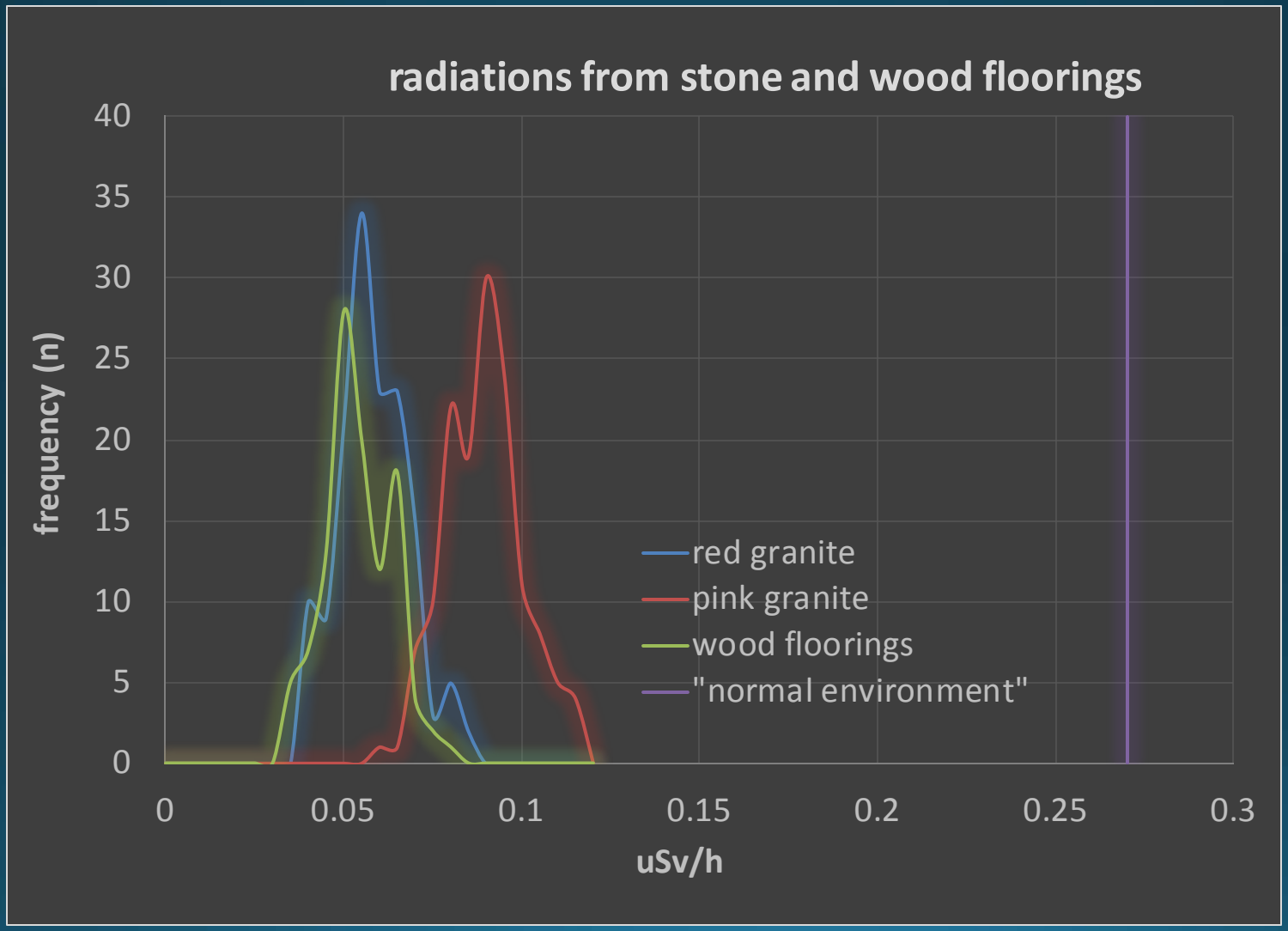




Results - radiation



Results - radiation



Conclusions

- The biocompatible floorings made with vegetable raw materials present no trace of heavy metals, radiation, petroleum-derived compounds. The detected VOC are naturally occurring in wood, and show no evident threat to human health.
- A bibliographic search suggests that some of the VOC emitted by the biocompatible floorings are the same molecules naturally emitted by conifers forests, or found in VOC based pharmacy drugs. (Scientific validation is ongoing).
- The other floorings VOC emissions are completely different, showing molecules with evident human hazard (toluene).
- Actual indoor concentrations are ongoing.

Conclusions

Final OPEN question:

Are the natural-based VOC emitted from these wooden based materials contributing to increase the indoor discomfort, are they neutral or are they improving the air quality?

Acknowledgements

Research funders:

- D.K.Z. srl – Fiemme 3000: Marco Felicetti, Vittorio Monsorno, Luca De Marco
- Fondazione Caritro

SPME analysis:

- Marco Michelozzi, Luca Calamai, CNR-IBBR

- **M. Fellin**, supervisor R. Zanuttini, co-supervisor M. Negri, 2014, *Monitoring wooden materials for recycling*, PhD thesis, Università di Torino, CNR-IVALSA, pp. 182 ISBN: 9788890927317, DOI: 10.13140/2.1.1460.5128.
- **M. Fellin**, M. Negri, R. Zanuttini, 2013, *Multi-elemental analysis of wood waste using Energy Dispersive X-Ray Fluorescence (ED-XRF) analyzer*, European Journal of Wood and Wood Products, (vol.72 issue 2):199-211, DOI 10.1007/s00107-013-0766-4.
- **M. Fellin**, M. Negri, R. Zanuttini, F. Maffei, 2014, *Characterization of ED-XRF technology applied to wood matrix*, Wood Research 59 (4): 2014, pp. 533-546. ISSN: 1336-4561.

WOOD RESEARCH
59 (4): 2014
533-546

CHARACTERIZATION OF ED-XRF TECHNOLOGY APPLIED TO WOODEN MATRIX

Marco Fellin, Martino Negri
Cnr-Ivalsa, Trees and Timber Institute
S.Michele All'Adige, Italy

Federico Mazzei
Tq Technologies for Quality Srl
Genova, Italy

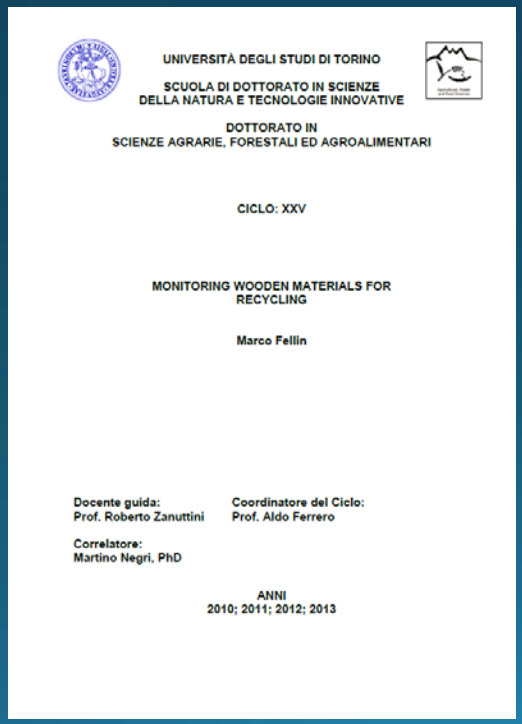
Roberto Zanuttini*
University of Torino Disafa, Department of Agricultural, Forestry and Food Sciences
Grugliasco, Italy

(Received April 2014)

ABSTRACT

The Energy Dispersive X-ray (ED-XRF) Fluorescence is an analyticals technique for detection and quantification of heavy metals, widely used in portable devices basically conceived for metallic alloys. Preliminary tests are needed to use the instrument on different matrices like wood. In this work minimum detection limit (MDL), signal to noise ratio (SNR), repeatability, relationship between measurement time and elements detected, depth of measurement, set-up (background, operator ergonomics and operator X-ray adsorbed dose) have been investigated or tested. MDL varies with time ranging from few thousands (e.g. *Cl*) to few units (e.g. *As*) of $mg.kg^{-1}$. Repeatability error is 5-6 %. Average SNR ranges from 5 to 31 in function of measurement time. The measurement time influences detection of elements. Measurement depth ranges from 15 to 24 mm according to wood density and anatomy. Best backgrounds are air and shield cap. Best set-up is inside X-ray protection cabinet. Radiation leakages have been found in bench top operations. Effectiveness of technique has been proven, with limitations, in multielement analysis of wood-based products.

KEYWORDS: ED-XRF characterization, wood products, chemical composition, multielement analysis.



UNIVERSITÀ DEGLI STUDI DI TORINO

SCUOLA DI DOTTORATO IN SCIENZE DELLA NATURA E TECNOLOGIE INNOVATIVE

DOTTORATO IN SCIENZE AGRARIE, FORESTALI ED AGROALIMENTARI

CICLO: XXV

MONITORING WOODEN MATERIALS FOR RECYCLING

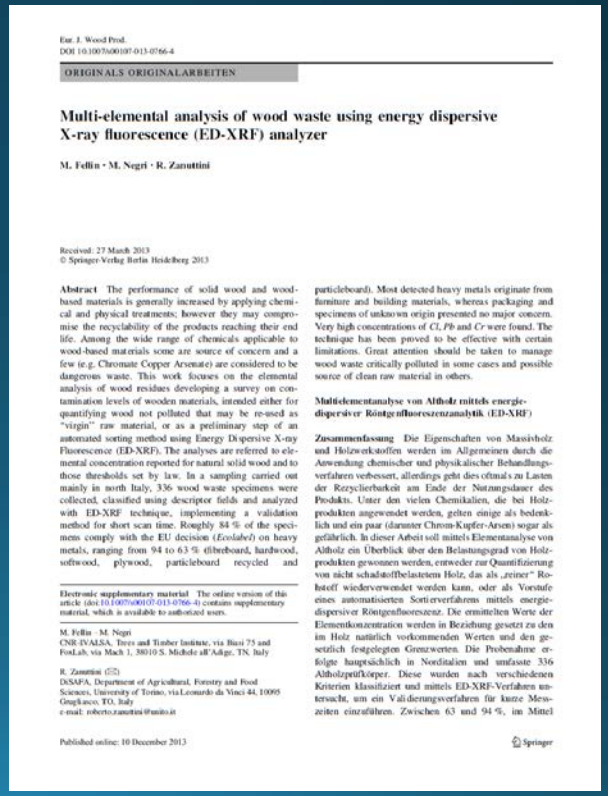
Marco Fellin

Docente guida:
Prof. Roberto Zanuttini

Coordinatore del Ciclo:
Prof. Aldo Ferrero

Correlatore:
Martino Negri, PhD

ANNI
2010; 2011; 2012; 2013



Eur. J. Wood Prod.
DOI 10.1007/s00107-013-0766-4

ORIGINALS ORIGINALARBEITEN

Multi-elemental analysis of wood waste using energy dispersive X-ray fluorescence (ED-XRF) analyzer

M. Fellin · M. Negri · R. Zanuttini

Received: 27 March 2013

Abstract The performance of solid wood and wood-based materials is generally increased by applying chemical and physical treatments; however they may compromise the recyclability of the products reaching their end life. Among the wide range of chemicals applicable to wood-based materials some are source of concern and a few (e.g. Chromate Copper Arsenate) are considered to be dangerous waste. This work focuses on the elemental analysis of wood residues developing a survey on contamination levels of wooden materials, intended either for quantifying wood not polluted that may be re-used as "virgin" raw material, or as a preliminary step of an automated sorting method using Energy Dispersive X-ray Fluorescence (ED-XRF). The analyses are referred to elemental concentration reported for natural solid wood and to those thresholds set by law. In a sampling carried out mainly in north Italy, 336 wood waste specimens were collected, classified using descriptor fields and analyzed with ED-XRF technique, implementing a validation method for short scan time. Roughly 84 % of the specimens comply with the EU decision (*Ecolabel*) on heavy metals, ranging from 94 to 63 % (fibreboard, hardwood, softwood, plywood, particleboard recycled and particleboard). Most detected heavy metals originate from furniture and building materials, whereas packaging and specimens of unknown origin presented no major concern. Very high concentrations of *Cl*, *Pb* and *Cr* were found. The technique has been proved to be effective with certain limitations. Great attention should be taken to manage wood waste critically polluted in some cases and possible source of clean raw material in others.

Multielementanalyse von Altholz mittels energiedispersiver Röntgenfluoreszenzanalytik (ED-XRF)

Zusammenfassung Die Eigenschaften von Massivholz und Holzwerkstoffen werden im Allgemeinen durch die Anwendung chemischer und physikalischer Behandlungsverfahren verbessert, allerdings geht dies oftmals zu Lasten der Rezyclierbarkeit am Ende der Nutzungsdauer des Produkts. Unter den vielen Chemikalien, die bei Holzprodukten angewendet werden, gelten einige als bedenklich und ein paar (darunter Chrom-Kupfer-Arsen) sogar als gefährlich. In dieser Arbeit soll mittels Elementanalyse von Altholz ein Überblick über den Belastungsgrad von Holzprodukten gewonnen werden, entweder zur Quantifizierung von nicht schadstoffbelastetem Holz, das als „reiner" Rohstoff wiederverwendet werden kann, oder als Vorstufe eines automatisierten Sortierverfahrens mittels energiedispersiver Röntgenfluoreszenz. Die ermittelten Werte der Elementkonzentration werden in Beziehung gesetzt zu den im Holz natürlich vorkommenden Werten und den gesetzlich festgelegten Grenzwerten. Die Probenahme erfolgte hauptsächlich in Norditalien und umfasste 336 Altholzprüfkörper. Diese wurden nach verschiedenen Kriterien klassifiziert und mittels ED-XRF-Verfahren untersucht, um ein Validierungsverfahren für kurze Messzeiten einzuführen. Zwischen 63 und 94 %, im Mittel

Electronic supplementary material The online version of this article (doi:10.1007/s00107-013-0766-4) contains supplementary material, which is available to authorized users.

M. Fellin · M. Negri
CNR-IVALSA, Trees and Timber Institute, via Biasi 75 and FoxLab, via Mach 1, 38010 S. Michele all'Adige, TN, Italy

R. Zanuttini (✉)
DiSAFA, Department of Agricultural, Forestry and Food Sciences, University of Torino, via Leonardo da Vinci 44, 10095 Grugliasco, TO, Italy
e-mail: roberto.zanuttini@unito.it

Published online: 10 December 2013

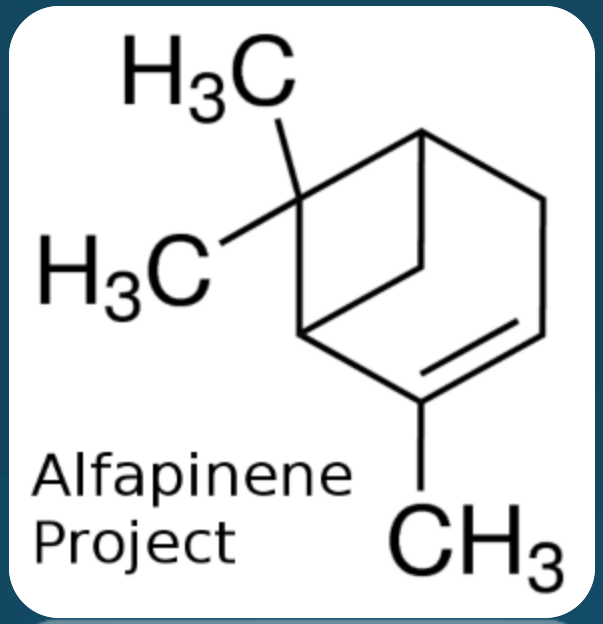
Springer

COST Action FP1407 2nd Conference – Innovative production technologies and increased wood products recycling and reuse

Brno, Czech Republic, 29-30 September 2016

Marco Fellin, PhD
Martino Negri, PhD
CNR-IVALSA, Italy
Trees and Timber Institute

Marco Felicetti
Vittorio Monsorno
D.K.Z. srl – Fiemme 3000, Italy



Questions?

fellin@ivalsa.cnr.it

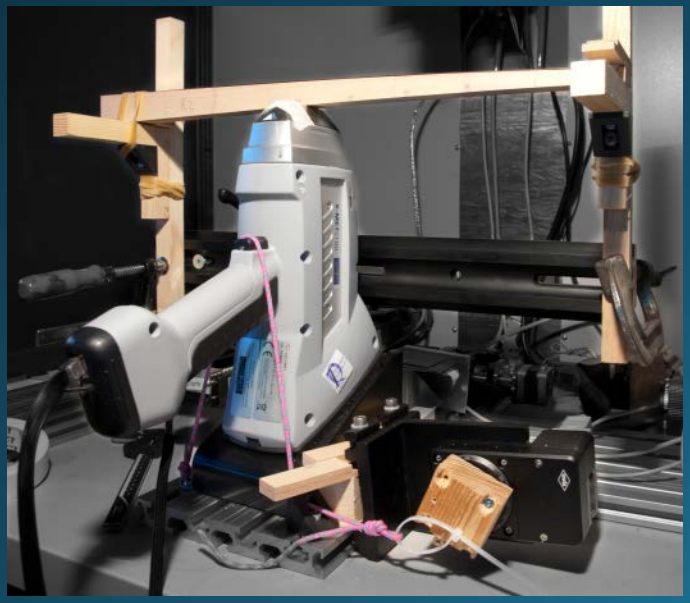
Maintaining wood naturalness:
Production of Biocompatible wooden floors
and monitoring of Heavy Metals, VOC, and Radiation

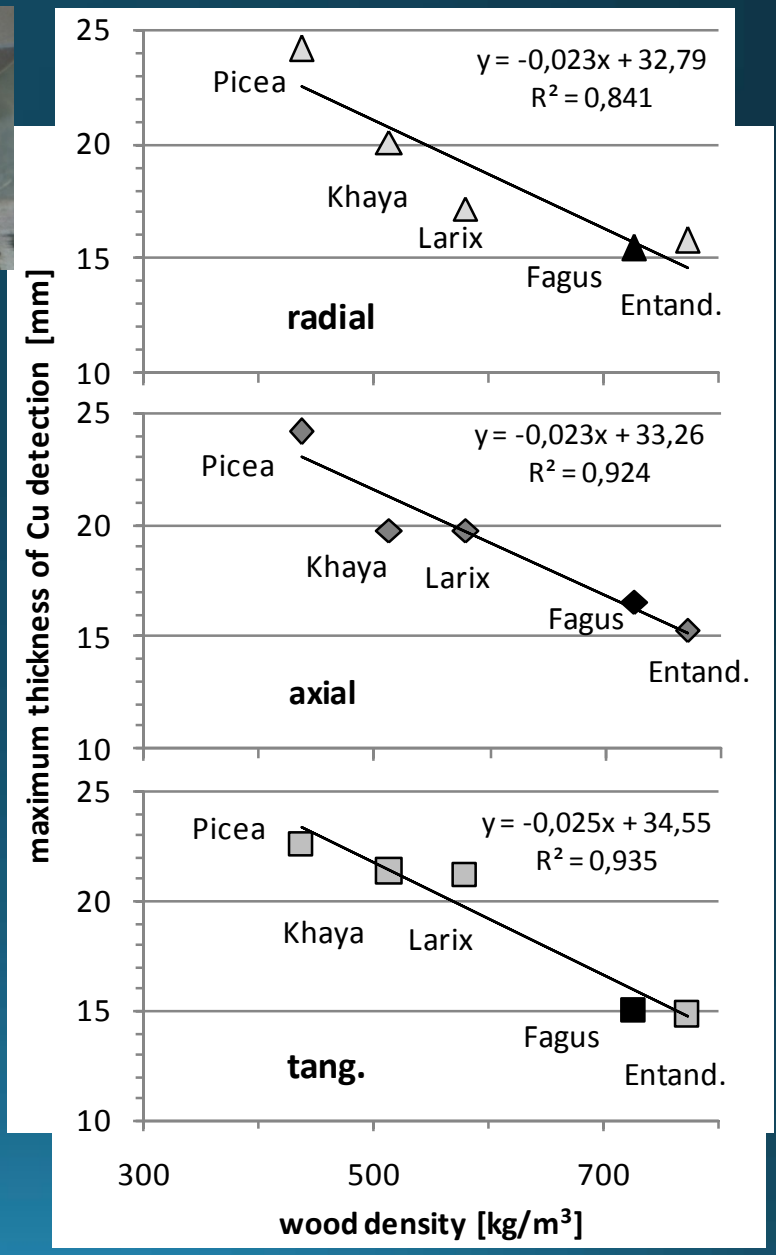
Addendum

How does *end life wood* looks like?

Test 5: maximum detection thickness

Cubes
3 anatomical directions of wood,
5 wood species
Wedges
3 anatomical directions of wood,
2 specimens for anatomical direction,
1 wood specie (*Fagus Sylvatica*)
22 measurements along the changing thickness
11 replicas
total of 1452 measurements





Test 6: Set-up and radiation leaks

case	Set-up				Radiation leakage					Operations	
	orientation	Specimen (1 cm spruce)	protection	back-ground	distance of measurement [m] 0,1	0,3	1	emissions µSv/h	maximum exposure [hours/year]	Operator ergonomics	Max specimen size [cm]
1	upward	no	cabinet	Air	x			0,1	10000	low	60x60x30
2	upward	no	shield cap	Cap	x			0,1	10000	average	8x4x2,5
3	down-ward	no	enclosure	Plate	x			0,1	10000	average	40X40x20
4	down-ward	yes	none	Plate	x			12	83	good	Unlimited
5	upward	yes	none	Air	x			29	34	good	Unlimited
5a	upward	yes	none	Air		x		3	333	good	Unlimited
5b	upward	yes	none	Air			x	0,1	10000	good	Unlimited
6	horizontal	yes	none	Air	x			70	14	average	Unlimited
6a	horizontal	yes	none	Air		x		14	71	average	Unlimited
6b	horizontal	yes	none	Air			x	0,3	3333	average	Unlimited

Introduction

PARADOX: Certain VOC are freely sold and largely used

Introduction

PARADOX: Certain VOC have positive effect on health

real pharmacy shelf

Introduction

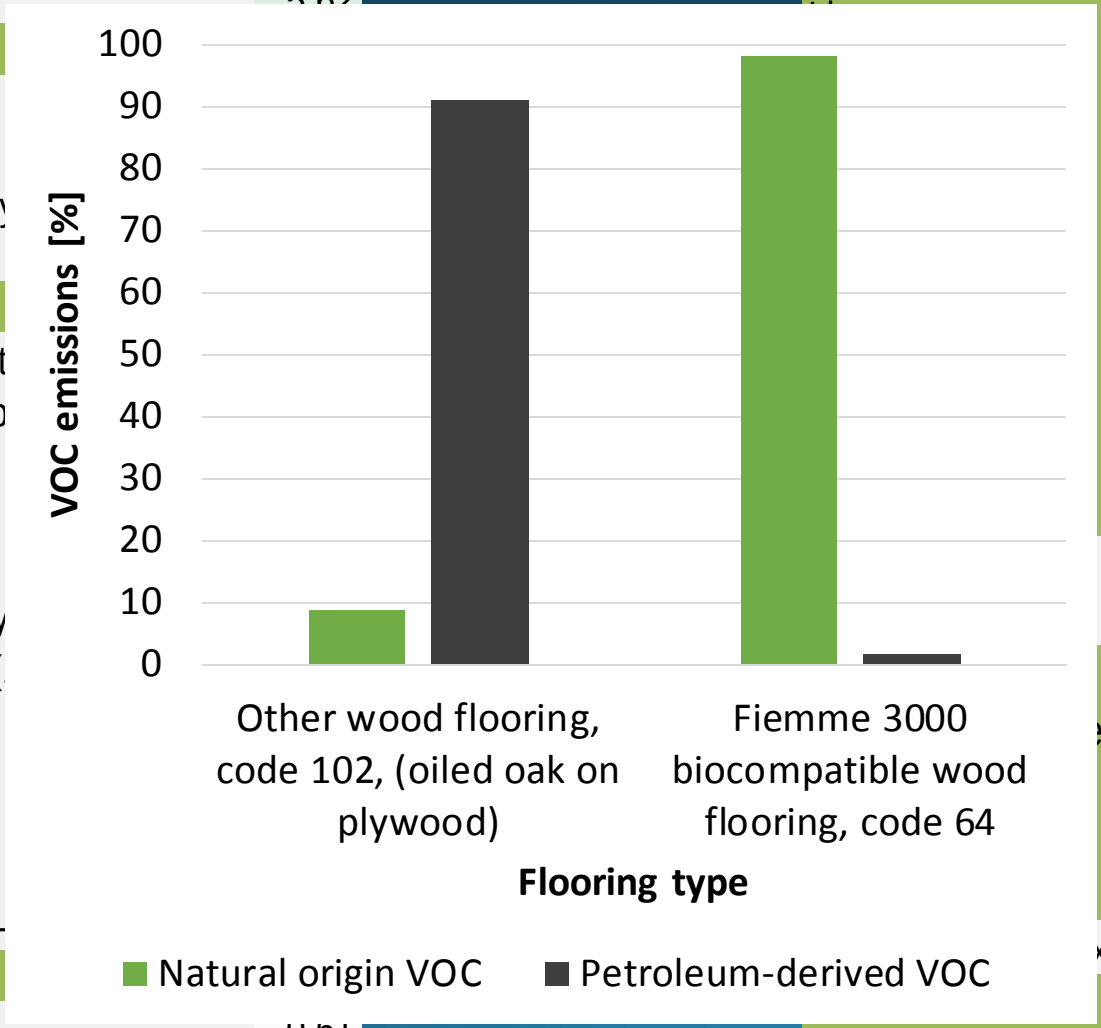
PARADOX: Certain VOC are carcinogenic/hazardous and limited/banned

Results

headspace SPME-MS comparison of two floors

Other wood flooring, code 102, (oiled oak on plywood)	
Compound name	Area (%)
Acetic acid	25,71
Pentane	12,52
Ethyl ether	6,88
Plinol C	5,62
Limonene	
CO2	
Silane, trichlorodecyl-	
Cyclotrisiloxane, hexamethy	
Lilac alcohol B	
1R-α-Pinene	
1,3-Cyclohexanediol, 2-met	
p-Trimethylsilyloxyphenyl-b	
Hexanal	
Vinyl acetate	
Octane	
2-Furanmethanol, 5-etheny	
Cyclohexanol, 1-methyl-4-(	
Propylene Carbonate	
Toluene	
1-Pentanol	
Nonane	
1,6-Anhydro-2,4-dideoxy-β-	
β-Pinene	
3-Octen-2-ol	0,61

Fiemme 3000 biocompatible wood flooring, code 64	
Compound name	Area (%)
α-Pinene	32,43
β-Pinene	16,06
γ-Terpinene	10,98
	10,52
	7,30
	3,38
	3,10
	2,73
	2,01
	1,81
	1,52
	1,10
	0,66
	0,60
	0,59
	0,45
	0,45
	0,42
	0,30
	0,25
xy-4-methyl-1-(1-m	0,25
	0,22

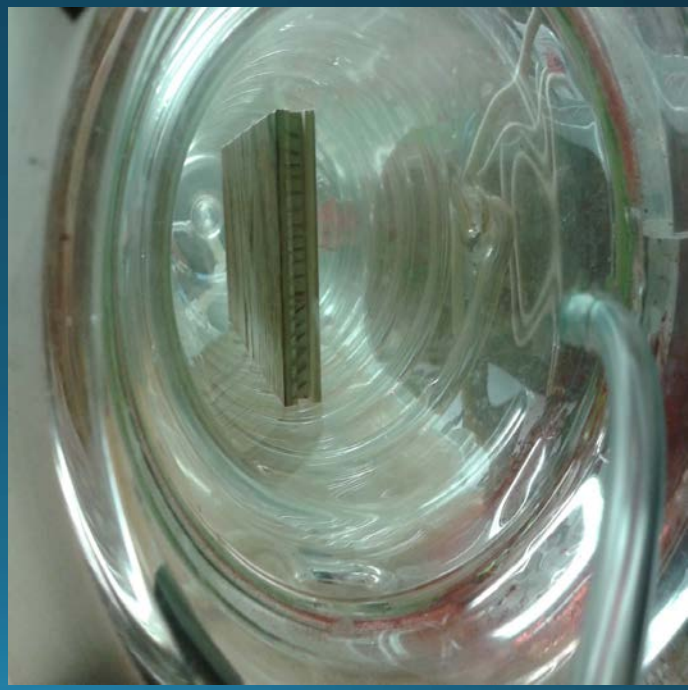


Results

Actual indoor concentrations preliminary tests:

- Climatized standard glass chamber
- Parallel measurements: TVOC emissions with PID analyzer + VOC qualification from SPME GC-MS
- Example:
  - PID detects TVOC: 330 ppb of isobutylene
  - SPME provides a list of compounds and proportions

Compound		SPME Area	Response Factor PID	Molecular Weight	Concentration of single VOC	
name	CAS number	(%)		g/mol	ppb	µg/m³
α-Pinene	80-56-8	32,4	0,27	136,237	28	158
β-Pinene	127-91-3	16,0	0,17	136,237	14	79
Limonene	138-86-3	10,5	0,9	136,237	9	51
Terpinolene	586-62-9	7,3	0,6	136,237	6	36
Terpineol	98-55-5	1,1	0,8	154,25	1	6
3-Carene	13466-78-9	0,7	0,5	136,1	1	3
Acetic acid	64-19-7	0,6	36	60,052	1	1
				TOTAL VOC	60	335

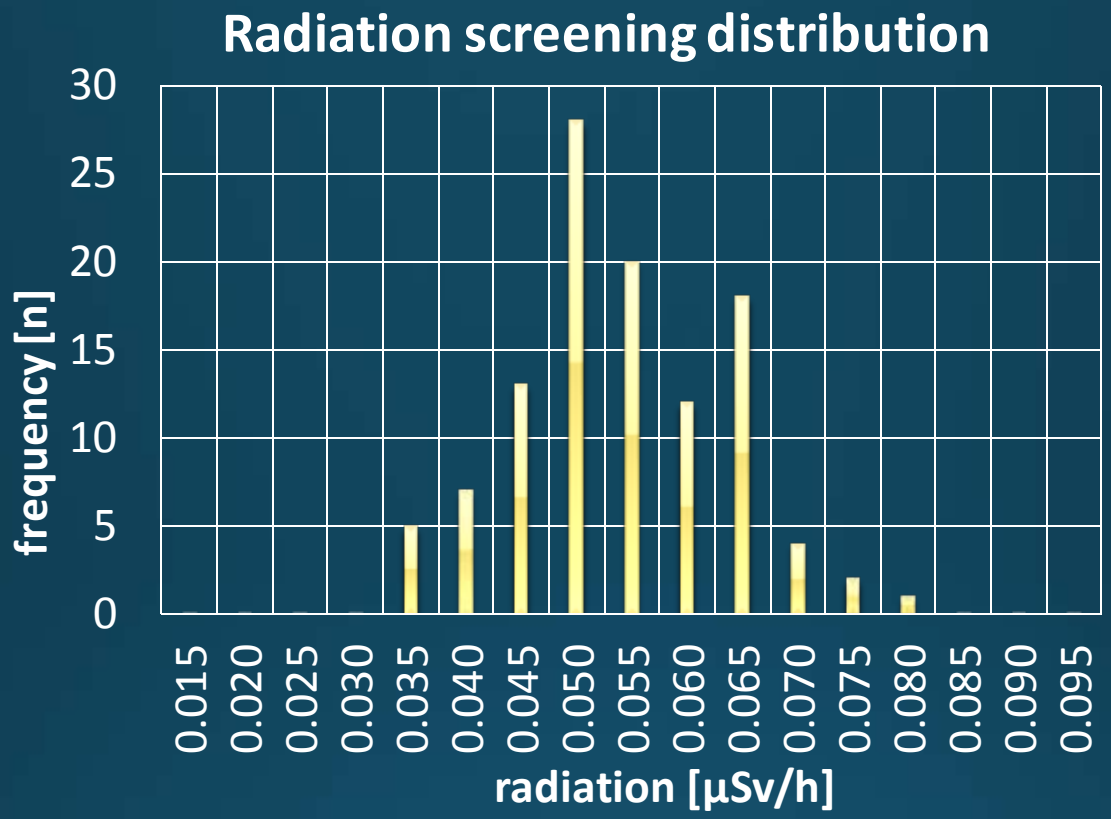


Results

- Actual indoor concentrations:

Preliminary tests TVOC emissions	15 – 350 µg/m^3	3 days
Preliminary tests TVOC emissions	2 – 30 µg/m^3	28 days
UNI EN ISO 16000-9	*measurements are still ongoing*	

- Comparison with the natural air VOC: Limonene, α-Pinene, Ocimene, Acetic acid, Acetone, Phenol… Benzene!
- Comparison with the pharmacy VOC: measurements are still ongoing.



	µSv/h
min.	0,030
max.	0,077
5° perc.	0,036
Mean	0,051
Median	0,051
95° percentile	0,066