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

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

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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.

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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

84 %, der Prüfkörper (Faserplatte, Laubholz, Nadelholz, Sperrholz, rezyklierte Spanplatte und Spanplatte) entsprachen der EU Richtlinie für Schwermetalle (Umweltzeichen). Die meisten der nachgewiesenen Schwermetalle stammten aus Möbeln und Baustoffen, wohingegen Verpackungen und Prüfkörper unbekannter Herkunft weniger bedenklich waren. Es wurden hohe Konzentrationen an *Cl*, *Pb* und *Cr* gefunden. Das Verfahren hat sich unter bestimmten Einschränkungen als effektiv erwiesen. Weil Altholz in manchen Fällen stark belastet ist und in anderen Fällen eine mögliche Quelle für einen reinen Rohstoff darstellt, sollte seine Behandlung mit großer Sorgfalt erfolgen.

1 Introduction

1.1 The challenge

The use of solid wood and wood-based materials (WBM) on a large scale is demonstrated to be globally desirable due to its sustainable nature and effective role in carbon dioxide atmospheric sequestration (CEI-BOIS 2006, 2009; EU Commission 2004; FAO 2011; IPCC 2007; Miner 2010). However, engineering processes applied to wood materials may compromise their recyclability by changing their chemical composition. In particular, it is supposed that some categories of products (e.g. particleboard furniture) are more polluted than others due to the number and type of processes needed to transform natural wood into those products. In order to preserve the innate sustainability of solid wood, any substance applied to manufacture a wood material should not transform it into dangerous waste. Monitoring the contaminants of wood waste allows to manage and control pollutants transfer to the atmosphere (combustion), soil (land-filling as it is or as combustion ashes) or simply to some WBM such as particleboard.

This work focuses on the elemental analysis of wood residues sampled among wood recycling plants and wood enterprises by using a handheld fast ED-XRF device, basically conceived for materials different than wood, having developed due calibration and procedures.

A survey on contamination levels of wooden materials is also intended either for quantifying not polluted ones that may be combusted as biomass, or as a preliminary step for an automatic sorting process based on ED-XRF technology.

1.2 Monitoring

Wood waste monitoring is relevant since nowadays in Europe and other countries a strict legislation on production and trade of hazardous WBM exists. In detail, Chromate Copper Arsenate (CCA) products are considered dangerous waste by the EU Directive 2000/532/CE (2000), and their commercialization is forbidden according to the EU Directive 2006/139/CE (2006). WBM manufactured before that date may be still installed, because 10 years are considered a short time in comparison with the normal lifespan of preserved wood products. In fact researches showed that since the phase-out of CCA treated wood in 2002, 10–40 years shall pass to have all CCA treated products reaching end-life (Lebow 1996; McQueen and Stevens 1998; Hingston et al. 2002). More precisely, wood waste contaminated with CCA is expected to reach end life and is subsequently forwarded to landfill or combustion at a rate varying from 6 to 10 million m^3 per year in USA within the next 20 years (Jambeck et al. 2007).

Risk of leaching poisonous metals from CCA treated wood has been demonstrated by Shibata et al. (2007). This phenomenon may occur in on-site applications and in landfill, with possible contamination of soil and infiltrated water, as demonstrated by several studies (Shibata et al. 2006, 2007; Stilwell and Gorny 1997; Hasan et al. 2010a, b; Jacobi et al. 2007; Jambeck et al. 2006; Khan et al. 2006a, b; Moghaddam and Mulligan 2007).

Risk exists also for many other elements (mainly *As*, *Cd*, *Cl*, *Cr*, *Cu*, *Hg*, *Pb*,) due to the huge amount of products (varnishes, glues, overlays, etc.) that may be applied to wooden materials.

Monitoring wood waste or biomass pollutants is usually done with Atomic Absorption Spectroscopy (CV, GF, or HG-AAS) or Inductively Coupled Plasma Spectrometry (ICP-OES, ICP-MS) (EN 15297 2011; EU Commission decision 2009/894/EC 2009). These methods require preparation of a specimen (milling, acid digestion) and are therefore time consuming, expensive and their preparation process may introduce other variables into the system. Other measurements are generally allowed after validation. A previous study (Fellin et al. 2011) on the applicability of Infrared spectroscopy to monitoring pollutant on wood residues provided satisfactory results, but lack of information on elementary composition was seen as a challenge.

ED-XRF has been used to trace elements in plants since years (Williams 1976) and has recently been successfully applied to online sorting of wood waste (Hasan et al. 2010a, b). This technology provides simultaneous detection of a wide number of elements analyzed, acceptable reliability, low operational costs, short time (10–600 s) for a single measurement. It can be used to monitor elements with atomic number (Z) higher than 12 (*Mg*) at high concentration (%), higher than 17 (*Cl*) at mid concentration and higher than 22 (*Ti*) for concentrations as low as few (5 ÷ 50) parts per million (ppm). Background and matrix corrections in trace analysis should be carefully evaluated and applied (Sorensen 1981). Preliminary tests have been carried out in order to characterize the instrument backgrounds, the Limit of Detection in wooden matrix and the Signal to Noise Ratio.

1.3 Trace elemental concentration of wood

Naturally, wood is low in inorganic components (seldom exceeding 1 % d.w.), whereas in terms of needles, leaves or bark it may have a much higher concentration (e.g. 2–5 % for bark, d.w.) (Sjöström 1993). Various deposits usually appear as salts of carbonates, silicates, oxalates and phosphates (Sjöström 1993). Most abundant metal components in wood and bark are *Ca*, *K* and *Mg*, followed by *Fe* and *Mn* at common concentrations below 10 mg/kg but occasionally up to 100 mg/kg. Generally *B* and *Cu* are also present in traces.

According to Browning (1967) salts in mature wood are mostly based on *Ca*, *K*, *Mg*. Acid radicals are reported as carbonates, phosphates, silicates, sulphates and rarely oxalates. In ash, the presence of *Fe*, *Mn*, *Al*, *Na* oxides is also mentioned.

Pendias (2011) points out several studies on trace metals in arboreal plants, while higher concentration was found in herbaceous plants. In other studies (Kloke et al. 1984; Macnicol and Beckett 1985), critical (toxic) concentrations of metals in plant tissues are presented, but those values are argued not to be naturally exceeded by plants. Ellis (1965) reports the constituent elements in wood (*C*, *O*, *H*, *N*, *P*, *S*, *Cl*) and other elements, distinguishing between major (*Ca*, *K*, *Mg*, *Na*, *Si*), minor (*B*, *Mn*, *Fe*, *Mo*, *Cu*, *Zn*), common (*Ag*, *Al*, *Ba*, *Co*, *Cr*, *Ni*, *Pb*, *Rb*, *Sr*, *Ti*) and uncommon (*Au*, *Ga*, *In*, *La*, *Li*, *Sn*, *V*, *Zr*). This work focuses on the most relevant elements of ecologic concern: *C*, *O*, *H*, *N*, *P*, *S*, *Ca*, *Fe*, *Mn*, *Ni*, *Se*, *Sr*, *Zn* and *Zr* are therefore excluded.

1.4 Multi-elemental concentration reference values

Reference values of concentration were searched for each element. In this framework, a range coming from natural concentration and normative limits or threshold of attention was considered as 'reference values'. Indicative reference values are presented in Table 1 as minimum/maximum in nature, and normative concentrations. They are coming from different sources (EN 15297 2011; Ellis 1965; EN 14961-1 2010; Valerio et al. 2009), since no unique one on all elements was found. Reference values for minimum natural concentration were the minimum values found in literature. The elements defined either as uncommon or not reported in literature were indicated as zero. If the lack of an element is not considered as a deficiency for plant physiology, it has been reported as zero as well. The highest reference values for maximum natural concentration were found in wooden biomass excluding abnormal conditions (e.g. plants grown on polluted soils). Selection of normative limits has been done choosing element limits from the most relevant law/standard, if available, and as second possibility switching to the most inherent normative limit. The only existing legal limit is the European Union Commission Decision 2009/894/EC (2009) "limit values of elements and substances allowed in recycled wood fibers for the production of wood-based materials… for the award of the Community Ecolabel for wooden furniture" which rules namely *As*, *Cr*, *Hg* 25 mg/kg, *Cu* 40 mg/kg, *Cd* 50 mg/kg, *Pb* 90 mg/kg, *F* 100 mg/kg, *Cl* 1,000 mg/kg, Pentachlorophenol 5 mg/kg, Tar oils (benzo(a)pyrene) 0.5 mg/kg. The ED-XRF setup allowed measurements on *As*, *Cr*, *Hg*, *Cu*, *Cd*, *Pb*, *Cl*. For the remaining elements, indicative limits were reported, chosen among the most inherent normative ones. As a consequence, limit values for *Ba* and *Sb*, were taken from EN 71-3 (2000) and Directive 88/378/CEE (1988); limit for *Sn* was taken from VDI (2009) and finally limit for *Ti* was taken from EN 14961-1. Stricter limits are in use in some EU countries, e.g. in Germany, wood waste normative (Altholzverordnung 2002) rules namely *Hg* 0.04 mg/kg, *As*, *Cd* 2 mg/kg, *Cu* 20 mg/kg, *Cr*, *Pb* 30 mg/kg, *Cl* 600 mg/kg.

2 Materials and methods

2.1 Sampling

Samples of WBM were collected among recycling centres located in the Trentino region—Italy, wood enterprises located in the Veneto region—Italy, research centres located in Trentino and Quebec—Canada, and also a site

Table 1 Elemental concentration reference values for wooden materials and ED-XRF detection limits (exposure time 15 s, excitation with a Rh tube 45 kV 40 μA)

Tab. 1 Referenzwerte der Elementkonzentration von Holzprodukten und Nachweisgrenzen von ED-XRF (Belichtungszeit 15 s, Anregung mit Rh-Röhre 45 kV, 40 μA)

Element (mg/kg)	As	Ba	Br	Cd	Cl	Cr	Cu	Hg	Pb	Sb	Sn	Ta	Ti
Minimum natural values	0	10.2	0	0	0.9	0.04	2.4	0	0.02	0	0.003	0	0.08
Maximum natural values	4	254	0	5	500	40	200	2	30	0.01	0	0	55
Relevant normative limits	25*	1,000	–	50*	1,000*	25*	40*	25*	90*	60	20	–	50
ED-XRF limit of detection	3	175	3	15	13,000	27	4	5	5	27	22	8	82

Values marked with * are most relevant for the environmental impact

for the storage of railway sleepers in Trentino. Although these specimens were of unknown chemical composition, one known specimen of preserved wood was specifically sampled for verifying the capabilities of the proposed method to sort *Cu Cr As* preserved wood (Chromate Copper Arsenate preservative residues). This strong preservative is still present in many artefacts, and therefore has been considered as a specific case of study.

Specimens were visually described using database descriptor fields (Table 2) according to their *origin*, *type* (solid wood or panel), typology of *material*, v*isual detection of pollution*, *pollutant macro-category* (e.g. varnishes, preservatives etc.) and *pollutant specification*. Due to the heterogeneity of the experimental material, specimens may be classified using more than one descriptor. For instance, a kitchen table may be made of particleboard, two types of glue, veneer overlay, coating varnish. The results of ED-XRF scan may therefore concern either the surface of the specimen or the material along its depth. Penetration depth of ED-XRF measurements is a function of the nature and density of the bulk, and for the set-up used it is in the range of 1–3 cm. Therefore, multi-element analysis results may be related to any of the classification descriptors specified for each specimen, as it would be in an automated process.

2.2 ED-XRF analysis

ED-XRF analysis was carried out with an Oxford Instruments X-MET 5100, X-ray source set at 45 kV 40 μA. The measurement time is inversely proportional to the Limit of Detection (LoD); it has been set to 15 s according to the results of preliminary tests. The measurement time has been set to face either the detection threshold (LoD), expected to be normally below the normative limits for most of the elements, or the accuracy (S/N ratio) and finally the time spent for a single measurement. Moreover the risk of false positives or negatives has been considered as well.

The parameter of measurement time was considered of great importance foreseeing future application of the system to an on-line wood waste sorting facility or handheld analysis in wood recycling centers, and was therefore chosen as low. The tradeoff with measurement accuracy was acceptable. The LoD of the system is presented in Table 1. LoD for *As*, *Ba*, *Cd*, *Cu*, *Hg*, *Pb*, are satisfactory (higher than 3 times the normative limits); LoD for *Cr*, *Sb*, *Sn, Ta* and *Br* are generally satisfactory for monitoring concentrations as low as 2–3 times the normative limits, and they may be improved increasing the scan time; LoD for *Cl* and *Ti* are not suitable for normative limits, without a large increase of the scan time (e.g. *Cl* LOD of 1,000 mg/kg with 45 min measurement).

Table 2 Descriptor fields of the overall database according to visual sorting divided into groups

Tab. 2 Klassifizierung der Prüfkörper nach verschiedenen, visuell beurteilbaren Kriterien

Origin (*group 1*)	*Pollutant macro category* (*group 5*)	*Pollutant specification* (*group 6*)
Building		
Furniture	None	–
Garden	Glue	Edge glue
Packaging		Fibreboard glue
Not identified		Flakeboard glue
		Laminate glue
Type (*group 2*)		Melamine or PVC glue
Solid wood		Osb glue
Wood-based panel		Paper glue
Mixed		Particleboard glue
		Phenolic glue
Material (*group 3*)		Plywood glue
Cement-bonded panel		Pur glue
Edge		Pvac glue
Fibreboard (MDF-HDF)		Solid wood panel glue
Flakeboard		Solid wood glue
Hardwood		Uf glue
Hollow core board		Veneer glue
Insulating board	Varnish	Coating varnish
Oriented Strand Board		Ink
Particleboard	Metal	Nail
Particleboard recycled		Screw
Plywood		Other metal
Plywood, concrete formwork	Preservative	–
Softwood	Overlay	Veneer
Solid wood panel		Melamine or PVC
Wood plastic composite		Laminate
Visually detected pollution (*group 4*)		Paper
	Mortar/concrete	–
	Dirt	–
	Wood dowel	–
Non detected	Fabric	–
Detected	Plastic	–

Since some elements providing the bulk of wood and of many organic matters (such as *C*, *O*, *H*, *N*) are not detected by XRF, appropriate models shall be provided to the software to take into account the attenuation of the undetectable matrix. Different models are managed as Fundamental Parameters (FP) methods (De Boer et al. 1993; Criss et al. 1978), Empirical methods and Screening methods. For WBM, as in the case of this study, the analysis was carried out using a specific proprietary FP method

designed to perform scans on a typical wooden matrix composed of *C*, *O*, *H*, *N* in proportions of 51, 42, 6.3 and 0.1 % respectively (EN 14961-1 2010).

ED-XRF instrument was set up in bench top position inside an X-ray protection cabinet. Around 40 cm of air at normal conditions provided an effective background. For each specimen, three replications were performed, changing position of the specimen in between in order to investigate most heterogeneous materials (e.g. for the analysis of overlaid particleboard: one measure of particleboard, one of top overlay, one of edge). Metal residues such as nails, screws and other hardware pieces accidentally occurring in the specimen, were accurately removed.

The results of the three measurements for each specimen were therefore recorded on a spreadsheet database and averaged, while the whole spectra was saved for manual data evaluation, if needed.

2.3 Validation process of ED-XRF measurements

The ED-XRF instrument software converts the peaks of α and β energies into elemental concentration using an internal calibration not accessible by users. Despite the accuracy of this analysis, both some false positive and false negative results were experienced, mainly due to false interpretation when reading raw spectra by the instrument software. Analysis of original spectra has underlined that the problem was not irrelevant, and consequently a validation process was elaborated to reduce the margins of mistake due to false positives. False negative results were faced computing the LoD in the process described below.

The validation process of each specimen has been performed using logic functions in a spreadsheet. The process computed the measurement time, LoD, type of material (either homogeneous or heterogeneous among three replicas), single and average elements concentrations, standard deviation, percentage of positive measures frequency, automatically classifying resulting elements as reliable (labelled as "GO") and not reliable ("NO-GO"). A temporary classification for doubtful data ("CAUTION") allowed human control of borderline measures. Those measurements were classified evaluating the three replica scans standard deviations, observing element energy lines in raw spectra, considering specimen heterogeneity and bibliographical-historical occurrence. The validation process is schematized in Fig. 1.

2.4 Data management and statistical analyses

Validated data from ED-XRF instrument were managed using a spreadsheet. The relevant descriptors of Table 2 and the values of elementary composition as validated average of three replica measurements were assigned to each specimen.

Results are presented as number of tested specimens, number and/or percentage of positive specimens over the total, average concentration, standard deviation (st. dev.) and coefficient of variation (cov = st.dev./average × 100) calculated either on all specimens (where not detected elements are reported as zero) or only on positive specimens, minimum (more than 0), first and third quartile, median and maximum values. Concentration values may have been rounded to significant digits. The amount of *Ecolabel* compliant elements (in %) is also reported for detected elements only, namely *As*, *Cd*, *Cl*, *Cr*, *Cu*, *Hg*, *Pb*. The other elements, without mandatory normative thresholds, are consequently always 100 % compliant, and will not be discussed in results according to the mere indicative standard values reported in Table 2.

In order to point out exceptional values occurring within one of the specified descriptors, a cross table analysis was done using IBM SPSS Statistics. Due to the huge amount of data generated, only interesting positive cases are presented in the Results. In particular, the combinations of chemical element and descriptor whose positive frequency is at least 1.5 times the average of the combinations of the chemical element and all descriptors of the same group are shown.

3 Results and discussion

3.1 General overview

A total amount of 336 specimens was collected during sampling: 80 % of specimens (268) came from 11 recycling centres, 12 % (39) from four wood enterprises, 8 % (27) from two research centres, 0.6 % (1) from one site on field. The material was examined with ED-XRF, three replicas per specimen, for a total of 1,008 scans. A total amount of 21 chemical elements was detected, ranging from Z 17 to Z 82 (*Cl* and *Pb*, respectively). The main results concerning the most ecologically important elements are presented in Table 3, reporting both elemental occurrence and concentrations for the whole sampling, while Fig. 2 shows the boxplot of positive specimens. A complete version of Table 3 can be found in Table 1 of the Electronic Supplementary Material (ESM). In Tables 2–6 of ESM and Fig. 4 the essential data divided into descriptor groups are reported.

The automatic validation process registered 66 % positive cases, blocked 22 % of false positive or negative cases, and assigned the remaining 12 % of cases to "Manual data evaluation". After this the positive cases raised from 66 to 75 %.

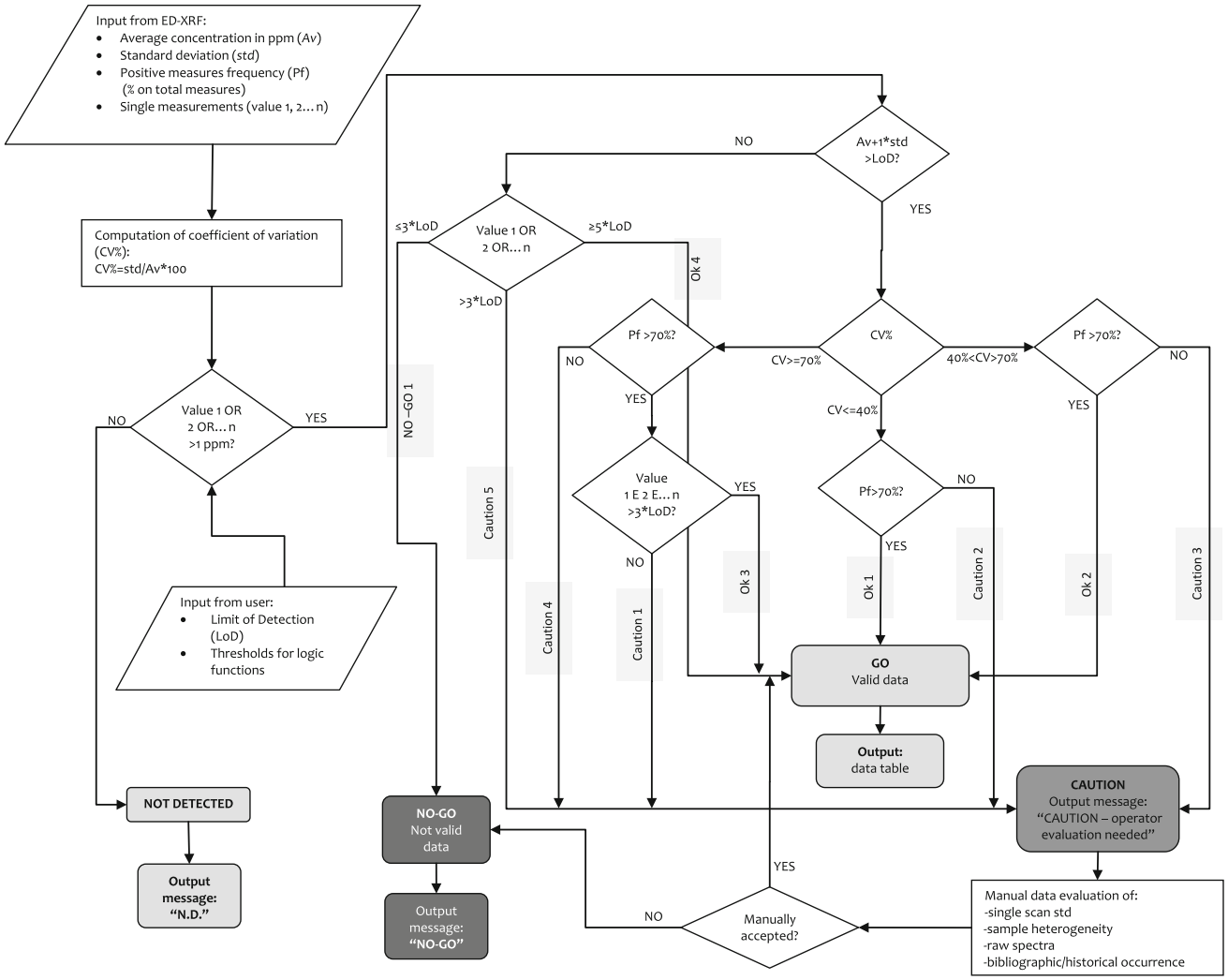

Fig. 1 Schematic presentation of the semi-automatic validation of raw ED-XRF data. Replica scans on non- homogeneous materials
Abb. 1 Schematische Darstellung der halbautomatischen Validierung der ED-XRF Rohdaten. Wiederholungsmessungen an nichthomogenen Materialien

The most frequently occurring elements were *Cu,* and *Ti,* showing frequencies around 36 %, whereas *Pb*, *Sn* and *Ba* were in between 10 and 20 % (17, 12 and 12 %, respectively). *Br*, *Cl*, *Cr* and *Cd* were found in specimens around 3–4 %, whilst *Sb*, *Ta*, *Hg* and *As* ranged from 0.3 to 1.2 %. Highest concentration average values on positive specimens came from *Cl* and *Ti* (160,000 and 18,000 mg/kg, respectively), probably as a result of scans on PVC or white titanium based painted overlays. *Cl* presence may also be caused by high percentage of bark, preservative chemicals, wood exposed to sea water or contaminated during transportation by road salting (EN 14961-1 2010).

The overall concentration range varied from 4 to 421,000 mg/kg.

Cu concentration (ruled by *Ecolabel*) is slightly below the limit (38 and 40 mg/kg, respectively) and more than 3/4 of detected concentrations were within the *Ecolabel* limit; the remaining measurements were over the limit, with few specimens reaching very high concentrations (up to 20 times higher).

Ta presence may occur as a result of processing wood with Tantalum carbide tools. *Ba* in form of carbonate or sulphate may naturally occur (Ellis 1965), however the concentration range detected was higher than the natural value. *Ba* isotope/nuclide shows also the threat of weak radioactivity, not dangerous to animal life.

Br traces may be caused by application of flame retardant (Alaeea et al. 2003), or residues of pesticides (nowadays banned). *Cd* concentration in spruce may naturally range from 0.08 to 1.3 mg/kg dry weight (Lodenius et al. 2000) up to 5 mg/kg (EN 14961-1). Much higher values measured may be caused by paints or plastics (EN 14961-1).

Table 3 Multi-elemental analysis of the wood materials tested, whole sampling of 336 specimens
Tab. 3 Multielementanalyse der untersuchten Holzprodukte; 336 Prüfkörper

Element	Positive specimens	Av. Conc. On all specimens	St. Dev.	Cov
Unit	%	mg/kg	mg/kg	%
Ti	34	6,100	16,000	4,700
Ta	1	0.4	4	1
Sn	12	9	32	9
Sb	1	0.5	4	1
Pb	17	86	830	250
Hg	1	0.1	2	1
Cu	39	15	75	22
Cr	4	27	200	60
Cl	4	7,300	41,000	12,200
Cd	3	5	36	11
Br	4	1	13	4
Ba	12	260	1,100	330
As	0.3	0.01	0.2	0.1

Cr, *Cu* and *As* altogether originate from CCA preservative detected in a treated pole; this is the only specimen with all *Cr*, *Cu*, *As* concentrations well above the limits. This specimen is considered as a case study in Sect. 3.3.

All the other specimens (non-CCA treated) showed high concentrations of *Cu* or *Cr*, but the *As* concentration was always within the range of natural values. Presence of *Cr* may also originate from wood machining tool coatings.

Pb is present in concentrations reaching high levels, and this may be caused by environmental contamination, paint or plastic overlays (EN 14961-1).

Even if *Sb* is present in trees since it is relatively easily taken up when present in soil in soluble form (Pendias 2011), the concentrations measured were always higher than natural values. *As* concentration is within natural values and is therefore no source of danger. Concentration range of *Br* is exceeding natural threshold, at least concerning the maximum value.

The concentrations of *Hg* and *Sn* are higher than the maximum natural references; this may be determined by metal deposition during wood working processes. According to the standard limits, most critical elements were *Ti*, *Cr*, *Cl*, *Cd*, *Sn*, with concentrations generally exceeding. *Ba* and *Pb* were found to be around the limits.

Cu and *Hg* were mostly below limits, showing in case of *Cu* high maximum peak. The amounts of *Sb* and *As* were within the standard limits.

Detection limits showed to be effective for monitoring standard compliance for all the elements except for *Cl*, *Ti* and partially *Cr*, *Sb*, *Sn*, *Ta* and *Br*.

3.2 Wood materials descriptor field report

Detailed data analysis was carried out sorting results by the descriptor fields shown in Table 2 among different groups of *origin*, *type* (solid wood or wood-based panel),

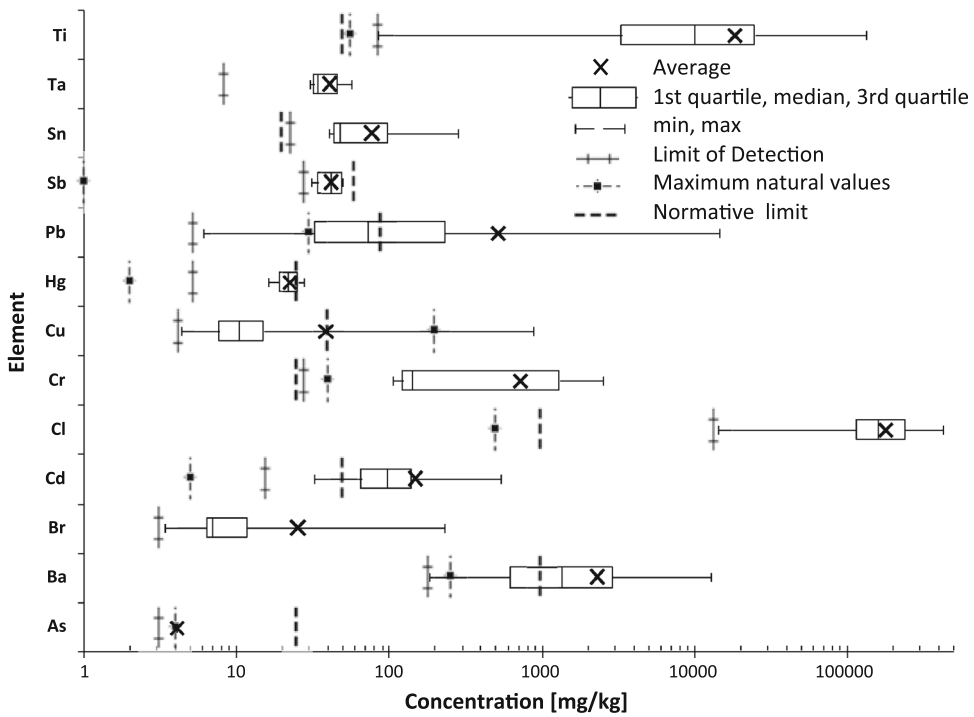

Fig. 2 Boxplot graph of multi-elemental concentrations of the wood materials analyzed, only positive specimens
Abb. 2 Boxplot der Multielementkonzentrationen der untersuchten Holzprodukte; nur belastete Prüfkörper

materials, *visual detection of pollution* (detected/not detected), *pollutant macro category* and *pollutant specification*. Only cases with specimens' number greater than 10 are presented and discussed, as well as only most relevant cases of the group *pollutant specification*.

Results are shown in synthetic tables (Tables 2–6 of ESM; also elements not object of discussion are reported because of their low environmental impact) where only essential data are reported for each group of descriptors. It is worth remembering that results categorized as follows are coming from heterogeneous materials, and therefore their attribution in terms of descriptors is not univocal.

3.2.1 Wood materials classified according to their origin

The group o*rigin* sorts wood-based materials according to the provenance, if identified (Table 2 in ESM). Regarding wood waste originating from *building*, concentration range of all elements exceeded natural levels except for *Br* and *Ba*. Pretty high concentration ranges were shown by *Cr*, *Cl*, *Pb* and *Ba*. Very high maximum value was shown by *Ti*, probably caused by metal hardware/coatings applied to the wood used in buildings. There is no major concern regarding *Cu*, *Br*, *Sn*, while *Ta*, *Sb*, *As*, *Cd* and *Hg* were not detected. WBM originating from *packaging* have a concentration range of all elements exceeding natural values. *Ti* and *Ba* showed pretty high distribution of concentration; *Sn* distribution is mostly above standard limits but reaches a low max of 95 mg/kg, while *Pb* was detected mostly below the *Ecolabel* limit. Only one specimen was positive to *Hg*, below *Ecolabel* limit. There is no major concern regarding *Ta*, *Cu*, *Br*, whereas *Cd*, *Cl*, *Cr*, *As*, *Sb*, were not detected in this group. In WBM originating from *furniture*, all elements exceeded natural values except for *Br* and *Cu*. *Ti* and *Cl* showed very high concentration range, probably due to paintings and overlays. *Cr*, *Cd*, *Sn* and *Hg* showed concentration range above standard limits, *Pb* range was lower with high extreme max values. A quite high concentration range was also shown by *Ba*. *Cu* showed pretty high maximum values probably due to contamination of metal hardware. *Ta* concentration range was higher than standard threshold but limited to about 100 mg/kg. There is no major concern regarding *Br* and *Sb*. *As* was not detected. On WBM with *not identified* origin, few elements exceeded natural values: *Ti*, *Sn* and *Pb*. *Ti* and *Sn* exceeded also standard limits, *Pb* not. Only one specimen was positive to *Cr* and at a high concentration. There is no major concern regarding *Cu*. *As*, *Ba*, *Br*, *Hg*, *Sb*, *Cd*, *Cl*, *Ta* were not detected. Comparing wood materials of various origins there is a neat difference in contamination levels. Most contaminated are materials deriving from *building* and *furniture*, less contaminated are *packaging* and *not identified*. In particular the occurrence of *Ba*, *Cd*, *Pb*, and *Ti* in *furniture* was at least 1.5 times the occurrence average for all descriptors of the same group.

3.2.2 Wood materials classified according to their type

Sorting wood waste among *types solid wood* and *wood-based panels* resulted in similar element concentration ranges (Table 3 of ESM). *Cd* concentration ranged mostly above *Ecolabel* limit for *wood-based panels*, while for *solid wood* a single positive specimen was in that condition. *Cl*, *Cr*, *Ti* ranged for both descriptors above standard limits. *Pb* showed a range mainly within the *Ecolabel*, higher in *solid wood*. *Br* range for both descriptors was mainly not exceeding natural values. *Ba* and *Cu* range for both descriptors was partially exceeding standards. *Sn* and *Ta* showed in both cases a range within hundreds mg/kg. Both descriptors were positive to *Hg*, below *Ecolabel* limits. One specimen was positive to *As* within the *Ecolabel* limits. For both descriptors there was no major concern regarding *Sb*. *Wood-based panels* showed the presence of *Se,* whereas *solid wood* not. Among these two descriptors there were slight differences due to homogeneous distribution of concentration and high maximum values for both descriptors, but less compliancy to *Ecolabel* of *wood-based panels* was observable.

3.2.3 Wood materials classified according to the material

Analysis of WBM classified in *materials* group gave interesting results (Table 4 of ESM): presence of *Cd* was determined only in *particleboard*, *plywood* and *softwood* (respective 13.5 and 1 % of specimens positive). *Ti* and *Ba* presence up to high concentrations was generally revealed across all *materials*. *Cl* and *Pb* were found the most critical elements for *fibreboard*, *Cu* and *Pb* for *hardwood*, *Cl*, *Cd*, *Pb*, *Cu*, *Cr*, *Hg* for *particleboard*, *Pb* and *Cr* for *particleboard recycled*, *Pb*, *Cr*, *Cl*, *Cd* for *plywood*, *Pb*, *Cu*, *Cl*, *Cr* for *softwood*. Highest concentration of *Cd* (250 mg/kg) was found in *plywood* together with highest of *Cl* (421,000 mg/kg), probably due to a scan on a PVC overlay; highest of *Cr* and *Cu* (2,500 and 120 mg/kg, respectively) in *softwood*; highest of *Pb* (14,000 mg/kg) in *softwood* and the only case of concentration of *Hg* above Ecolabel limit occurred on a *particleboard*. Comparing the results of multi-elemental analyses done on different materials, the less contaminated resulted in *fibreboard*, *hardwood*, *softwood*, whereas most polluted were *particleboard*, *particleboard recycled* and *plywood*. In particular, the occurrence by over 1.5 times the average of all materials for the combinations of *Cl* in *particleboard*, and *Br*, *Pb*, *Ti* in *recycled particleboard* is remarkable.

3.2.4 *Wood materials classified according to visual detection of pollution*

Sorting WBM results according to *visual detection of pollution* (Table 5 in ESM), as it would be in an operator based sorting process, showed for *non detected* that only nine chemical elements (three environmentally relevant) were traced among all specimens. In details, *Sn* was found over natural values, *Ti* was over the natural reference only in one case, *Cu* in few cases. Concentration range of *Sn* was completely above standard limit, reaching a maximum of 100 mg/kg. Concentration of *Ti* was detected over natural levels only in one case. *Cu* exceeded the *Ecolabel* limit in max values. Generally this descriptor of WBM collected the less polluted fraction of specimens, as expected. Results on *detected* pollution WBM revealed the presence of *Cr*, *Cl*, *Sn*, *Ti* concentration range above the standard limits. *Cd* showed a range mostly above the *Ecolabel* limits. *Ba*, *Pb* showed a range behavior around standard limits. *As* and *Sb* were completely below standard limits. *Cu* and *Hg* concentration ranges generally were below standard limit, with max peak above it. There is no major concern regarding *Br* and *Ta*. The comparison of these two descriptors (*detected/non detected*) stressed huge differences with clearly polluted specimens multi-elemental concentration ranges far above not polluted ones, as expected.

3.2.5 *Wood materials classified according to pollutant macro categories*

The descriptor *pollutant macro categories* sorted wood-based materials according to the category of pollutant (Table 6 of ESM). *Non polluted* specimens showed an outstanding behaviour for the absence of contaminants, as it would be expected. 8 % of specimens were positive to *Sn* exceeding natural values. This may be explained by some residuals of nail/screw. *Cu* was within natural values. Regarding all the other *pollutants macro categories* descriptors there is no concern and no major differences among descriptors for the presence and concentration of *As* and *Sb*. Presence and concentration of *Ba* and *Ti* was high for all descriptors, exceeding natural values. High concentrations of *Ti* may be due to constituent of white pigments. Occurrence of *Hg* and *Br* was detected in specimens with *glue* and/or *metal* hardware, with concentrations slightly above natural/normative values. Occurrence of *Cd* and *Cr* was detected in specimens with *glue*, *metal* hardware *overlay*, *varnish*, with high concentrations well above standard/natural values and about 5 % of non-compliance to *Ecolabel*. Occurrence of *Cl* appeared only at high concentrations in all descriptors due to high LoD for this element. These extremely high concentrations are probably due to scans over PVC overlay. Pretty high maximum concentrations of *Cu* were detected in *metal* hardware and *varnish* descriptors. Occurrence of *Pb* is also often high in maximum values and it is the less compliant element regarding *Ecolabel*. Presence of *Sn* was detected in all descriptors, with concentrations ranging always above natural/standard values. *Ta* occurred in the *glue*, *metal*, *varnish* descriptors with maximum concentrations above natural values. Comparing different pollutant macro-categories their multi-elemental analyses showed that most critical contaminants are in *glues*, *metal*, *overlay* and *varnish*. In particular *Cd*, *Cl*, *Ti* in *overlays*, and *Cu* in *preservatives*, were at least 1.5 times the occurrence average of other descriptors of the same group.

3.2.6 *Wood materials classified according to pollutant specification*

Summarized results for the group of *pollutant specification* stressed above average behavior of the combinations *Cd* and *Ti* in *laminates*, *Ti* in *laminate glues*, *Ti* in *melamine or PVC glue* and *Br* in *particleboard glue*.

3.3 Case study: Cu Cr As in preserved wood

The experimental set-up showed to be greatly efficient in distinguishing *Cu Cr As* treated wood from virgin wood. In Fig. 3 raw ED-XRF spectra of specimen preserved with *Cu*, *Cr*, *As*, and virgin wood, both softwood species are compared. Peaks of Ka and Kb energy lines are shown only for the mentioned elements, and they clearly mark differences in the chemical compositions of the materials tested.

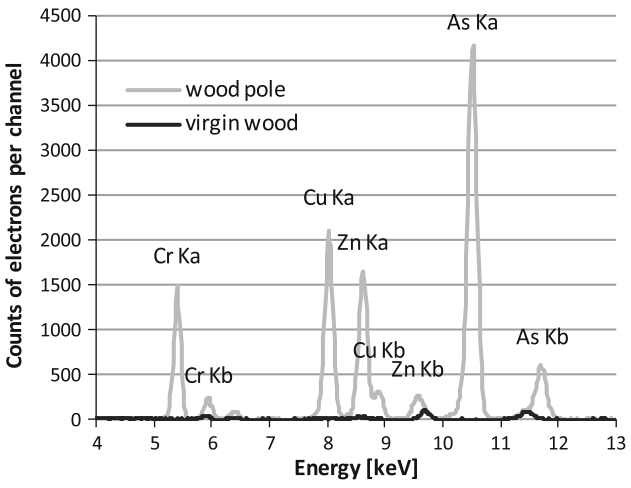

Fig. 3 Comparison of raw ED-XRF spectra of *Cr Cu As* in preserved wood pole and virgin wood
Abb. 3 Vergleich der ED-XRF Rohspektren von *Cr Cu As* imprägnierten Holzmasten und von Frischholz

Preserved telecommunication wood pole measured 2,100, 1,500, 4,100 mg/kg for *Cu*, *Cr*, *As*, respectively, while these elements were not detected in virgin wood. These elementary concentrations are 50-150 times greater than Ecolabel limits, posing serious concern about disposal of this type of products, still installed in working conditions.

3.4 Environmental threat elements according to standard threshold (Ecolabel)

84 % of total specimens accomplished the *Ecolabel* requirements (*Ecolabel* 2009/894/EC), whereas 16 % (54 specimens) have exceeded one or more limits. The elements with higher than the due concentration, in order of frequency, were *Pb*, *Cr*, *Cl*, *Cu*, *Cd* and *Hg*. No specimens were found to be over the limits for *As*, except the CCA treated pole, managed apart as a case study. The average concentrations for exceeding elements were up to 170 times greater than the threshold values. Details are presented in Table 4.

Applying the Ecolabel threshold according to the groups of Table 2 showed that for the *Origin* group the compliance to Ecolabel ranged between 76 and 100 % of cases. Most critical *origin* was found to be *furniture*, followed by *building*. Much less concern is seen in *packaging* and no concern in *not identified origin.* Details are reported in Fig. 4a and Table 2 of ESM (population filtered, 3 "garden" cases excluded). Packaging has a low risk in being heavily contaminated by the manufacturing process (usually heat treatment, metal hardware and labelling). On the other hand, *furniture* and *building* may be manufactured using much more processes (including painting, preservation, overlaying…) and the risk therefore to be considerably more contaminated.

Among the *type* group, there is a noticeable difference among *wood based panels*, most polluted and solid wood.

Table 4 Application of *Ecolabel* EU thresholds to wood waste. Details per element, sample size 336
Tab. 4 Vergleich der Grenzwerte des EU Umweltzeichens mit den gemessenen Werten. Angaben für jedes Element; 336 Prüfkörper

Element	Unit	As	Cd	Cl	Cr	Cu	Hg	Pb
Ecolabel limit	mg/kg	25	50	1,000	25	40	25	90
Average concentration on the whole sampling	mg/kg	0.01	5	7,300	27	15	0.1	86
Positive specimens	n	1	11	14	13	130	2	57
Specimens over the limit	n	0	10	14	13	12	1	23
Concentration in the specimens over the limit	mg/kg	–	160	174,000	700	300	28	1,200
St. dev.	mg/kg	–	140	110,000	790	270	–	3,000
Cov	%	–	92	63	110	88	–	250
Min. over the limit	mg/kg	0	56	14,000	100	48	28	100
Max.	mg/kg	0	530	421,000	2,500	860	28	14,500

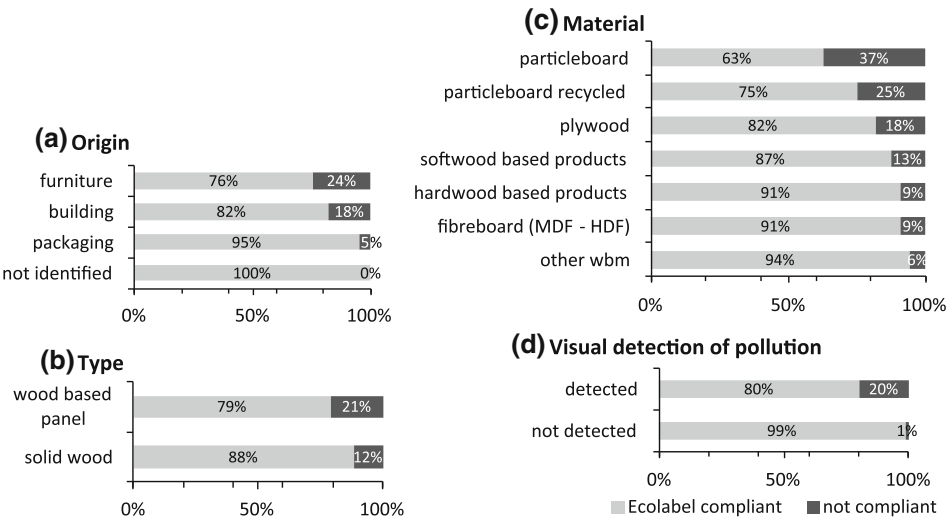

Fig. 4 Application of *Ecolabel* thresholds to wood waste. Graphical details for material groups
Abb. 4 Prozentuale Erfüllung der Grenzwerte des EU Umweltzeichens des untersuchten Altholzes. Darstellung für verschiedene Materialklassen

Details are reported in Fig. 4b and Table 3 of ESM (both groups contain eight specimens constituted of solid wood glued to a panel). Also for this group the most polluted fraction is the one belonging to more engineered products.

Among the group of *materials*, the compliance to Ecolabel ranged between 63 and 94 % of cases. *Materials* with specimen amount lower than ten were grouped in a so called descriptor "*other WBM*", comprehensive of panels *edge*, *flakeboard*, *Oriented Strand Board*, *plywood concrete formwork*, *solid wood panel* and *wood plastic composite*. 94 % specimens of this "*other WBM"* descriptor were Ecolabel compliant. 87–91 % of Ecolabel compliance was found in *fibreboard (MDF–HDF)*, *hardwood, softwood.* 63–82 % of Ecolabel compliance was found in *particleboard*, *particleboard recycled, plywood*. This categorization generally tends to emphasize that most engineered WBM are more polluted. Moreover it is noticeable either the non-irrelevant pollution of soft-hardwood, or the cleanliness of the highly engineered *other WBM*, even if there is a weak statistic relevance for these cases. Observing the soft-hardwood specimens seems that the cause of pollution is due to hobbyist applied chemical treatments more than industrial. Details are reported in Fig. 4c and Table 4 of ESM.

Applying Ecolabel threshold to the visual detection of pollution group allows checking how reliable the visual detection process is in comparison to the automated one. Among all visually polluted specimens, "only" 20 % are effectively not Ecolabel compliant, and a remaining 80 % may still be used as a raw "green material". On the contrary, one specimen visually non-polluted resulted to have a concentration in *Cu* well over Ecolabel threshold. This may be caused by some copper based preservative, whose color was not noticeable in the much discolored specimen. Details are reported in Fig. 4d and Table 5 of ESM.

The WBM examined for this research present a noticeable tendency of being more polluted as far as they belong to more engineered products. There is a clear trend in all *type, origin and material* groups.

4 Conclusion

ED-XRF technique was found to be effective for fast, cost reduced and reliable multi-element measurement of wood waste. Set-up was effective in investigating accurately most of the elements, even if the detection limits for *Cl*, *Cr*, *Sn*, *Ti* were found to be higher than the concentration required for analysis according to reference standards. The parameter of measurement time was kept as low as possible foreseeing future application of the system to an on-line wood waste sorting facility, or to manual sorting in wood recycling centers. Measurement reliability was challenged with great care, developing a completely new validation method, preliminary tests, computation of LoD and background.

As a general overview, in many cases both natural reference values and standard limits were widely exceeded; even extremely high values of *Cl*, *Pb* and *Cr* (421,000, 14,000, 2,500 mg/kg, respectively) were found in specific specimens.

Most contaminated WBM originated from *building* and *furniture*, less contaminated from *packaging* and *not identified* source. Classifying WBM into *types* (as *wood-based panel* or *solid wood*) showed no significant difference in multi-elemental concentrations. Among the descriptor group of *materials*, the most polluted one resulted to be *particleboard*, *particleboard recycled* and *plywood*, whereas less contaminated ones were *fibreboard*, *hardwood*, *softwood*. Classifying specimens into *visually detected polluted* or into *not polluted* stressed a huge difference in elemental concentrations, with *pollution detected* specimens far above the *not detected* ones, as expected. Comparing different macro categories of pollutant, multi-elemental analyses showed that most critical contaminants were *glues*, *metal*, *overlay* and *varnish*. 14 % of overall specimens were therefore exceeding *Ecolabel* limits, whereas the remaining 86 % showed concentrations of *As*, *Cd*, *Cl*, *Cr*, *Cu* and *Pb* below the threshold. This major fraction is *Ecolabel* compliant for use as a raw material for particleboards for the investigated parameters.

The examined WBM showed a noticeable tendency of being more polluted as far as they belong to more engineered products. This indicates that more care should be taken in manufacturing processes to maintain the natural recyclability of wood.

Visual sorting of wood waste materials into "descriptors" and "groups" helped in organizing research work and better evaluation of the results, nevertheless it provided precious suggestions for understanding the pollution related problems and orienting future research.

Methodology demonstrated to be effective in sorting polluted and non-polluted wood waste, and particularly in sorting *Cu Cr As* treated wood. Limitations were found in monitoring low concentrations of *Cl* and *Ti* and partially for *Cr*, *Sb*, *Sn, Ta* and *Br.*

The results related to the pollution measured on WBM showed that upgrading the performance applying either chemical or physical treatments can provide critical issues in the management of their end life.

These results underline how engineered wood products may present critical pollutants. They also allow to figure that part of the monitored wood-based materials, which will be treated as wood waste according to law, is without dangerous concentrations of critical elements, and may be used as "green" biomass either as a raw material for

particleboard panels or for other processes including combustion.

In conclusion, research showed that correct assessment of the end life for WBM is an interesting challenge that needs to take into account at the same time the risk of the presence of hazardous chemical elements and their potentiality as a source of non-contaminated material.

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