

Destructive and non-destructive methods for the evaluation of chlorinated pesticides concentration and emissions from wooden art objects

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Abstract

Liquid solvent extraction with dichloromethane combined with liquid injection gas chromatography-mass spectrometry (GC-MS) is a well suited method for determination and quantification of chlorinated pesticides in wood tissue. By scaling down the extraction step to micro level, concentration profiles of the pesticides in the wood tissue can be acquired. For this, wood tissue sections with a thickness of 50 μm are prepared with a sliding microtome. The sections are extracted in GC vials with dichloromethane and further analyzed by GC-MS. Chlorinated pesticides can be detected and semi quantified non-destructively on wood surfaces by $\mu\text{-X}$ -ray fluorescence ($\mu\text{-XRF}$). Emissions of pesticides from contaminated art objects can be measured by emission chamber experiments followed by thermal desorption GC-MS analysis of the sampled volatiles. However emission chamber experiments are often difficult to realize, as they are cost intensive, time consuming and the objects need to be transported to the emission chamber. Passive sampling with polydimethylsiloxane (PDMS) can be used alternatively for easy-to-do on-site sampling of pesticide emissions from art objects to further qualify and quantify the emissions by thermal desorption GC-MS.

Introduction

Emissions from wooden art objects, treated intensively mainly during the second half of the 20th century with chlorinated pesticides such as lindane, DDT, and pentachlorophenol may generate critical concentrations of such chemical agents in the indoor air [1, 2]. To prevent conservators from health risks by being contaminated during their daily work and to avoid massive emissions into indoor air of exhibition rooms, decontamination of the art objects for the removal of the pesticides is desirable. Several decontamination methods are described in literature and used in conservator's daily practice [3 - 8]. To measure the effect of a decontamination treatment, suitable analytical methods are needed for detecting the concentration of the pesticides in the wood tissue. Even more, the pesticides concentration profile is of interest to evaluate the distribution of the pesticides from the wood surface into the interior of the wood tissue. Determination of the emissions of the pesticides is also needed to evaluate the contamination risk for the indoor air of museums and conservators studios. Regarding the historical value of art objects non-destructive methods are desirable (and necessary in many cases). In addition, fast and cost-effective methods and mobile sampling is requested to evaluate the pesticide emission in collections containing numerous art objects. In a case study with contaminated oak wood specimens destructive as well as non-destructive methods were used to evaluate the pesticides concentration and emission.

Preparation of test specimens

To provide test specimens as standardized as possible, heartwood samples from *Quercus robur* were treated with a pesticides mix. The wood samples (8 cm x 3 cm x 3 cm, see Figure 1) were placed in a glass vessel. 1,4-dichlorobenzene (DCB, CAS# 106-46-7), γ -1,2,3,4,5,6-hexachlorocyclohexane (Lindane, CAS# 58-89-9) and 1,1,1-trichlor-2,2-bis(4-chlorophenyl)ethane (p,p'-DDT, CAS# 50-29-3) were solved in acetone and the glass vessel containing the wood specimens was filled up to the top and sealed against evaporation. The uptake of acetone solution was measured in advance and the pesticides concentration in the acetone solution was calculated to result in a pesticide concentration in the wood tissue of about 1000 $\mu\text{g g}^{-1}$. After 7 days of impregnation, the samples were removed and placed for two weeks under a laboratory hood allowing the acetone to evaporate.



Figure 1 – Contamination of oak wood specimens in a glass container and storage of the contaminated pesticides under a laboratory hood

Determination of the average pesticides concentration in the wood tissue by liquid extraction, solid phase extraction and GC-MS

For preparation of extraction material, the wood samples were sawn into small cubes with a side length of about 8 mm and grinded with a hammer mill (mesh size 1 mm) to receive a homogenous wood powder. For milling, all the single cubes of a specimen were processed to achieve a ground material that corresponds to the entire initial specimen. 2 g of the wood powder were extracted with an Accelerated Solvent Extraction device (ASE 200, Dionex) with dichloromethane as solvent at 100°C and 100 bar (Heating time: 5 min, Static time: 10 min). Each sample was extracted twice and the extracts of both steps were combined, spiked with an internal standard (hexadecane) and filled up to a volume of 50 ml. For purification of the crude extract 1 ml of the extract was loaded on a silica cartridge (500mg, Accubond) and eluted with dichloromethane to a final elution volume of 10 ml.

Major parameters of the extraction steps were optimized in preliminary studies. In addition to extraction, the wood moisture content was measured by Karl-Fischer-titration.

The pesticides were separated, characterized and quantified by gas chromatography (6890N, Agilent Technologies) and mass spectrometry (5975, Agilent Technologies). A MPS2 sampler (Gerstel) was used for automated injection of 1 μl per sample into a split/splitless inlet in pulsed splitless mode at 200°C. For separation, a 30 m analytical column (DB-5MS, J&W, film 0.25 μm , i.d. 0.25 mm) was used. GC temperature program: 40°C, 0-2 min, 25°C min^{-1} until 260°C at 18 min. The MSD was running in scan mode (50-240 amu, 7.22 scans s^{-1}). For quantification a multi-point calibration of analytical references in GC grade (Sigma Aldrich) was used.

In preliminary tests the above noted method was developed and validated. Different inlet temperatures at the split/splitless inlet were investigated. As shown in Figure 2 and Table 1 an inlet temperature of 200°C showed high MSD intensities as well as low relative standard deviations (RSD). At higher temperatures the DDT starts to decompose and change its structure during injection. At lower temperatures, the evaporation of DDT in the inlet liner is quite poor and the pesticide is not entering the column completely. This results also in higher RSD.

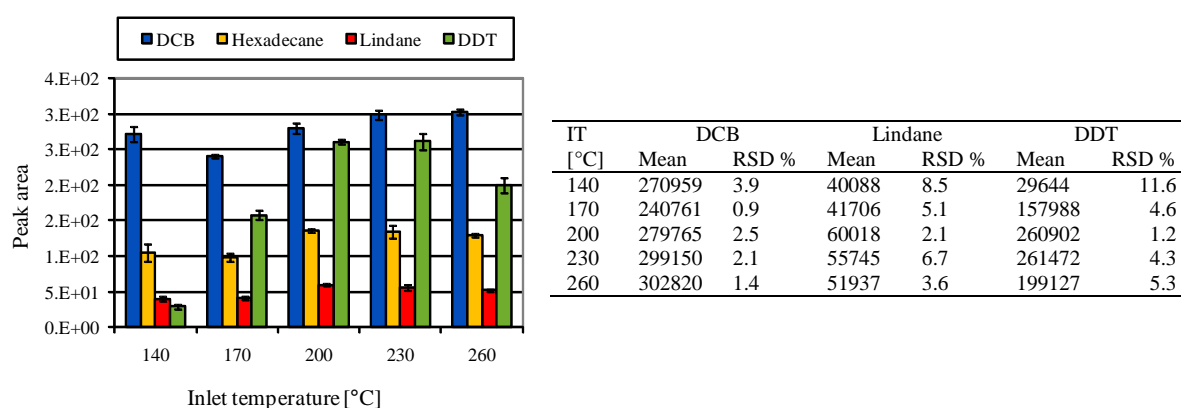


Figure 2, Table 1 - Detector signal at different GC inlet temperatures (IT) with the corresponding relative standard deviations (RSD) for single pesticides and the internal standard hexadecane.(n=5)

The measurement accuracy and the method accuracy were determined with a 200°C inlet temperature method. For determination of the measurement accuracy, a low level standard solution containing all of the pesticides was injected 10 times in the CG system. The RSD of the quantification data was calculated to 5.9% (DCB), 5.8% (lindane), and 4.6% (DDT).

For determination of the precision of the overall method, all single steps of the method including sample impregnation, grinding, extraction, solid phase extraction, filtration and CG-MS were taken into consideration. Therefore, 10 different contaminated specimens were processed and analysed separately. The RSD of the resulting pesticides concentrations were calculated to 8.26 % (DCB), 10.07 % (lindane) and 11.38 % (DDT).

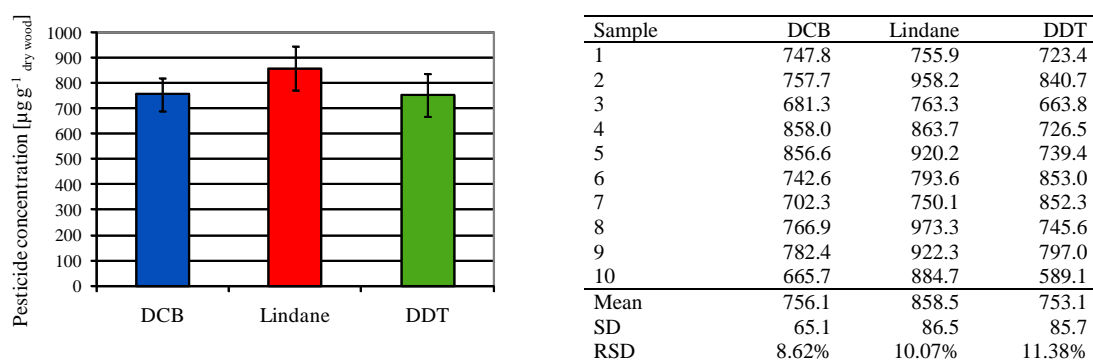


Figure 3, Table 2 - Pesticide concentration in the wood tissue of the contaminated specimens. Values are given in $\mu\text{g g}^{-1}$ dry wood (n=10)

The results display the average pesticides concentration in the contaminated oak specimens, as all of each specimen was ground without fractionation. The method can be used to identify and quantify chlorinated pesticides in wood material precisely. For ground material preparation and extraction amounts of at least some gram of wood material are needed.

Pesticides concentration profiles by micro-extraction and GC-MS

From the contaminated oak specimens thin-cut sections of 50 μm thickness were prepared with a sliding microtome as shown in Figure 4. Two series were prepared:

Radial direction profile: Block A was used for preparing tangential sections with a sliding microtome with a thickness of 50 μm and size of 16 mm x 8 mm. 5 single sections were combined to a fraction (overall thickness 250 μm) and placed into a GC-vial. For extraction the following fractions were chosen 0 mm, 0.5 mm, 1 mm, 1.5 mm, 2 mm, 3 mm, 4 mm, 5 mm, 7 mm, 9 mm, 11 mm, and 13 mm distance from the specimen's surface.

Axial direction profile: Block B was used for preparing cross sections with a sliding microtome with a thickness of 50 μm and a size of 4 mm x 4 mm. About 10 mg of subsequent sections were combined to a fraction. The following fractions were chosen: 0 mm, 5 mm, 10 mm, 15 mm, 20 mm, 25 mm, and 30 mm distance from the specimen surface.

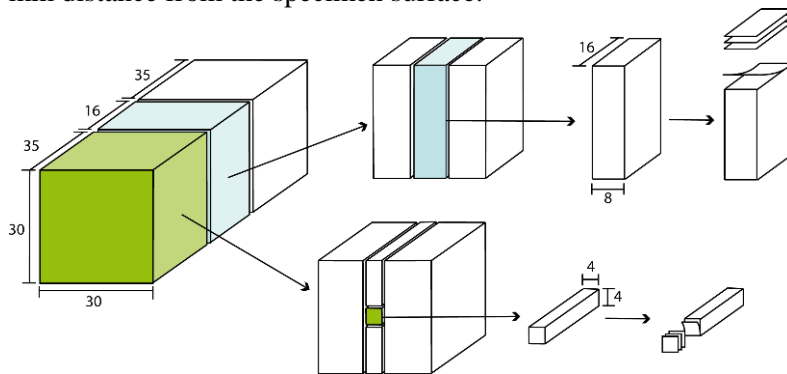


Figure 4 - Sectioning of the contaminated specimens and preparation tissue sections (50 μm thickness) with a sliding microtome for further extraction. Block A:blue; block B:green.



Figure 5 - Wood tissue sections placed in GC vials for pesticide extraction

The wood sections of each fraction were placed in a GC vial (1.5 ml volume) and 1 ml dichloromethane was added as an extraction solvent. The vials were immediately closed with PTFE sealed caps (Figure 6) and placed in a benchtop shaker for 24 h. The extracts of each cycle were removed from the vials with a syringe and combined after filtration through a 0.45 μl PTFE filter. The extraction cycle was repeated once. (In preliminary studies up to 5 subsequent cycles were investigated and each cycle was analyzed separately. The first two cycles contained $\geq 99\%$ of pesticides extracted). The extracts of the two cycles were combined and filled up to an overall volume of 10 ml. For pesticides quantification the same GC method was used as described above.

The results show a complete penetration of the wood tissue by the DCB, while lindane and DDT were more retained by the wood tissue during impregnation. In radial direction (into the tangential surface) lindane and DDT penetrated only to a depth of about 2 mm (Figure 6, left). As result of the higher penetrability of the wood tissue in axial direction, lindane and DDT can be detected to a depth of about 10 mm to 15 mm from the specimen's surface (Figure 6, right).

The micro extraction technique allows the analysis of very small amounts of sample materials (samples of some mg are enough). If combined with a schematic preparation of thin sections with a sliding microtome, a concentration profile of single substances in the wood tissue can be achieved.

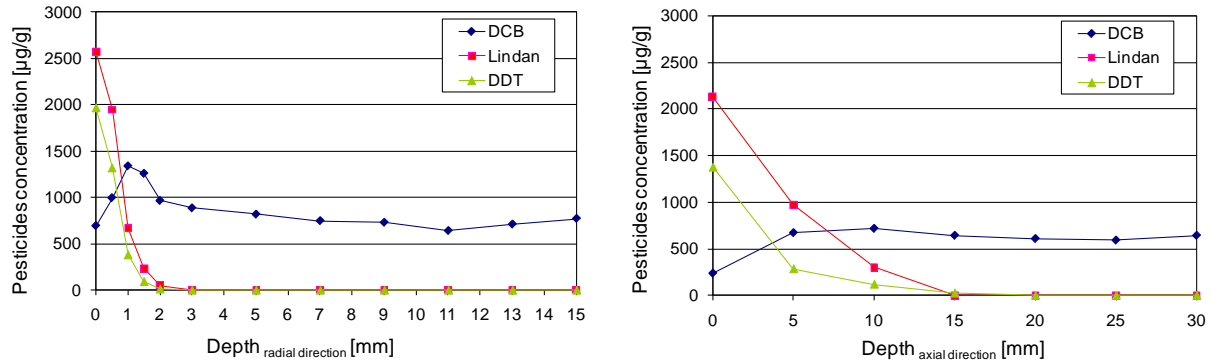


Figure 6 - Concentration profiles of pesticides in the contaminated samples following radial direction (left) and axial direction (right) into the wood tissue

Cl detection by μ -X-ray fluorescence (μ -XRF) investigations

The Cl ions of the chlorinated pesticides on sample surfaces were quantified, by detection the X-ray fluorescence of Cl ions after high-energy X-ray excitation. The measurements were performed as single point measurements as well as line scans using a Eagle III spectrometer (EDAX, X-ray tube: rhodium target), Voltage: 20 kV, current: 120 μ A, 200 s live-time for the excitation, spot size 50 μ m, for line scans a distance between single points of measurement of 100 μ m were chosen. All spectra were acquired under air atmosphere and room conditions. In preliminary investigations high vacuum provoked pesticides evaporation during measurement of single pesticides present in the samples (e.g. DCB with a high vapor pressure of about 0.17 kPa). The use of normal air atmosphere for avoiding pesticides evaporation drastically impaired the detection limit. This can be explained by the scattering of the emitted fluorescent x-rays by molecules in air, not attaining the detector. Nevertheless the detection of Cl counts can be used for a relative comparison of chlorinated pesticide concentration. By cutting a contaminated wood block lengthwise into two halves, concentration profiles of the pesticides were acquired on a tangential surface (Figure 7). The results correspond to the concentration profile as measured by micro-extraction and GC-MS. Exact quantification as well as qualification of the present pesticides is not possible by μ -XRF.

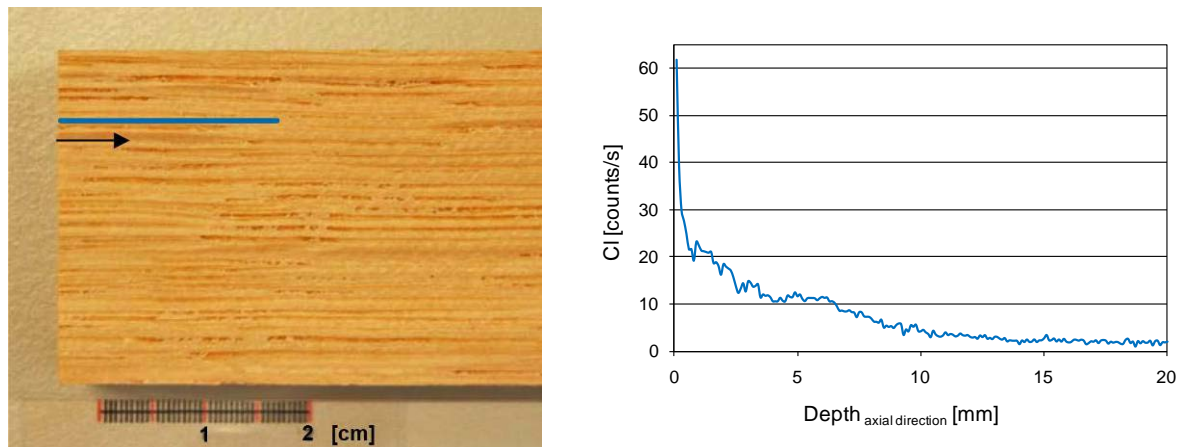


Figure 7 - μ -XRF line scan on a prepared tangential surface of a contaminated specimen for Cl detection in the wood tissue. Left: Line scan path on the sample surface. Right: Cl counts per second along the line scan path measuring Cl concentration. Before measurement, the contaminated specimen were cut lengthwise in two equal parts and the inner tangential surface used for line scanning as shown left.

Pesticides emission detected by analysis of emission chamber air

Emission chamber experiments were performed following EN ISO 16000-6 and -9. Glass desiccators (volume 23 l) were used as emission chambers. A constant air flow (23 l h^{-1}) was led through the chamber, resulting in an air exchange rate of 1 h^{-1} . As the chambers were loaded with 1 uncovered piece of test specimens and 10 uncovered pieces of test specimens the resulting loading factor was 0.49 $m^2 m^{-3}$ and 4.9 $m^2 m^{-3}$, respectively. The resulting area-specific airflow-rate was 0.2 and 2.0 $m^3 h^{-1} m^{-2}$, respectively. Air samples were collected using sorption tubes filled with approx. 200 mg of

Tenax TA (mesh 60-80) using a sampling pump with electronic flow controller (Flec). Using a flow rate of 100 ml min⁻¹, 5 l of the chamber air were collected on the sorption tubes for further analysis. The tubes were thermally desorbed with TDS4 (Gerstel) and after cryofocussing at -30°C (KAS4, Gerstel) separated with a DB5ms column in a GC (Agilent 6890, splitless) and detected with a MSD (Agilent 5975), operating in scan mode (amu 60-300). Analytical references in GC grade (Sigma Aldrich) were used for multi-point calibration of the system. Before starting the chamber tests, the samples were placed for three months under a laboratory hood for ensuring an overall evaporation of the acetone and reaching a constant emission level of the pesticides.

DCB, lindane as well as DDT emission were detected in the chamber air (Table 3). With 10 specimens placed in the chamber, the emission increased as expected. Following decreasing vapor pressures from DCB, over lindane to DDT, the emission decreased consequently. The measured concentration of the DDT was close to the detection limit of the method. To achieve higher concentrations of the pesticides in the chamber air, air samples were taken after 24 h without air exchange. The DCB as well as the lindane showed much higher concentration in the indoor air – in contrast to the DDT, which was still very low concentrated (Table 4).

Table 3 - Concentration of pesticides in chamber air with an air exchange rate of 1 h⁻¹ exchange after 3 days of equilibration

Amount of specimens loaded in the chamber	Emission chamber concentration [$\mu\text{g}/\text{m}^3$]		
	DCB	Lindane	DDT
1	15.6	0.05	0.06
10	119.1	0.56	0.10

Table 4 - Concentration of pesticides in chamber air without air exchange after 24 h

Amount of specimens loaded in the chamber	Emission chamber concentration [$\mu\text{g}/\text{m}^3$]		
	DCB	Lindane	DDT
1	130.90	0.30	0.04
10	227.68	1.24	0.13

PDMS passive sampling of pesticides emission

For development of an easy-to-do, cost-effective and on-site sampling of pesticide emissions from wooden art objects, small sized passive samplers (Gerstel-Twister™) with polydimethylsiloxane (PDMS) coating were used (Figure 8 left). These passive samplers are normally successfully used for stir bar sorptive extraction (SBSE) of non-polar compounds such as pesticides in mostly aqueous samples. After SBSE the sampled compounds can be measured via thermal desorption and CG-MS. We used the passive samplers for sorptive sampling of pesticides in the atmosphere of closed emission chambers. For first experiments 23 l-desiccators without air exchange were used and placed in a constant climate providing a room temperature of 23°C. The desiccators were loaded with 1 piece and 10 pieces of the contaminated samples and the Twisters were installed, lying open to the desiccators' atmosphere on a watch glass (Figure 8, right). After an exposition times of 1, 2, 4, and 7 days, the Twisters were removed, placed in empty sorption tubes and analyzed following a thermal desorption GC-MS method as described above for the emission chamber experiments.

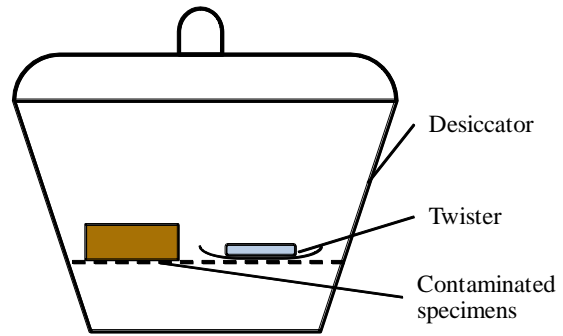
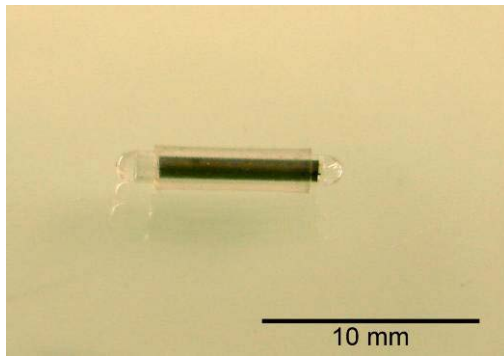


Figure 8 - Picture of a Gerstel-Twister, coated with PDMS (left) and experimental setup for passive sampling of pesticide emission in a 23l-desiccator (right)

DCB, lindane, and DDT were detected on the twisters in amounts of up to 1060 ng (DCB), 156 ng (lindane) and 18 ng (DDT) (Figure 9). The differences can be explained by the decreasing vapor pressures from DCB to DDT. The collected amount of DCB does not increase by longer exposure times, while the DDT can be detected in much higher amounts after 7 days of sampling. Lindane showed similar emission pattern as the DDT, but was detected in about 10-fold higher concentration if compared to DDT. Although the method needs to be validated in following experiments, the twisters have proven their ability of passive sampling of the chlorinated non-polar pesticides.

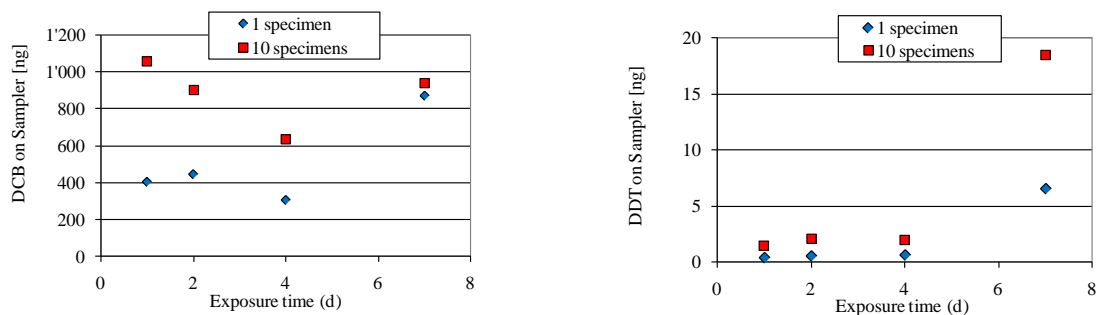


Figure 9 - DCB (left) and DDT (right) concentrations on passive samplers after exposure to chamber atmosphere for 1, 2, 4, and 7 days

If compared to a sorption tube used in the emission chamber experiments (5 l of chamber air were sampled on the Tenax tube), same amounts of DCB were detected on the twisters. In contrast to that, much higher amounts of lindane and DDT (factor of about 20) were collected on the Twisters. This can be explained by the slow evaporation of the lindane and DDT in contrast to the DCB. Further experiments will be conducted for method validation and field trials in the Collections Center of the Swiss National Museums are planned to use Gerstel-Twisters™ as on-site samplers exposed to the atmospheres of glass covered wood art object surfaces.

Conclusion

The methods used in this case generate results necessarily needed to evaluate chlorinated pesticides concentration in the wood tissue and emission from wooden art objects. The main pros and cons of the methods can be summed as shown in Table 5.

Table 5: Major pros and cons of the different methods

Method	Pros	Cons
Liquid extraction + GC-MS	Pesticides can be indentified and quantified precisely	Time consuming (grinding, extraction), ≥ 2 g of sample materials needed
Liquid micro extraction + GC-MS	Pesticides can be indentified and quantified, only some mg of sample materials needed, contamination profiles can be generated	Time consuming (cutting, extraction)
μ -XRF	Non-destructive, fast (point measurements)	Time consuming (line scans, mapping), no identification of pesticides
Emission chamber	Emissions can be identified and quantified	Time consuming, cost expensive (transport of art objects to the chamber, chamber experiment)
Passive sampling	Emissions can be identified, easy-to-do sampling,	Quantification (?)

References

1. Schieweck, A., Salthammer, T. (2006): Schadstoffe in Museen, Bibliotheken und Archiven, Fraunhofer, Braunschweig, 173 S.
2. Sirois, P.J., Johnson, J., Shugar, A., Poulin, J., Madden, O. (2008): Pesticide Contamination: Working Together to Find a Common Solution. The current State of Affairs. Canadian Conservation Institute.
3. Jelen, E., Weber, A., Unger, A., Eisbein M. (2003): Detox Cure for Art Treasures, Pesticide outlook, 14, 7-9
4. Unger, A. (2003): Detoxifizierung Holzschutzmittel belasteter national wertvoller Kunstobjekte mit Farbfassungen und Oberflächenveredelungsschichten am Beispiel des Epitaphs von Döben und des Heiligen Grabes des Stiftes Neuzelle. Abschlussbericht DBU Az. 17314, 64 S.
5. Dignard, C., Helwig, K., Mason, J., Nanowin, K., Stone, Th. (2008): Preserving Aboriginal Heritage: Technical and Traditional Approaches. Canadian Conservation Institute.
6. Odegaard, A., Zimmt, W. (2008): Pesticide Removal Studies for Cultural Objects, Canadian Conservation Institute.
7. Tello, H., Jelen, E., Unger, A. (2004): Bericht über eine Detoxifizierung von ethnologischem Sammlungsgut an den Staatlichen Museen zu Berlin, VDR-Bulletin 1.2004.
8. Winkler, K., Föckel, A., Unger, A (2002): Das Vakuumwaschverfahren, Dekontaminierung belasteter Hölzer im Einbauzustand, Restauro 108, 339-343.

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