DOI: 10.1002/masy.200650604

Degradation of PEG in the Warship Vasa

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Summary: The distribution and ageing of polyethylene glycol (PEG) in the Vasa warship has been examined and compared with other archaeological shipwrecks which have also been impregnated with PEG. The distribution of the PEG has been characterised using a variety of mass spectrometric and FT-IR techniques. Our results show that the PEG after 30 years is still in a reasonably good condition, with a molecular weight distribution that resembles fresh PEG. Only minor levels of degradation products were found. It seems that the PEG preserved wood contains an increased amount of formic acid and the results suggest that it originates from the PEG. Acetic acid is also present; this probably originates from the wood.

Keywords: formic acid; mass spectrometry; molecular weight distribution; poly (ethylene glycol)

Introduction

The Vasa warship sank in 1628 and was, after more than 300 years on the seabed in the Stockholm harbour, re-discovered and brought to the surface in 1961. Over the next 29 years it was conserved: the entire hull was impregnated using different molecular weights of polyethylene glycol (PEG), the water was eventually removed and the hull dried out. In 1990 the entire ship was presented to the public in a purpose built museum, in which the average number of visitors reaches 850000 per year. The past few years has shown that the presentation of the Vasa is not without problems. The position of the ship on the bottom of the harbour has led to deposition of especially sulphur, in different reduced forms, in the hull, which is well described by Fors[1]. Over the years this has gradually oxidized in air, which has resulted in the formation of sulphuric acid[2], leading to an increased acidity of the wood.

Another acid source may be the wood itself, where especially oak is well known to contain acetic acid in high amounts, leading to a lowered pH[3]. Also PEG has been mentioned as leading to an increased formation of formic acid, either as a result of solvolysis[4], or as a result of PEG degradation[5,6]. In all cases, an increased acid level is of concern because of its possible hydrolytic effect on the wood or, for the small organic acids, because they easily evaporate and lead to the probable corrosion in the surroundings, even at the low ppb levels[7]. To discuss the formic and acetic acid origins in PEG treated wood we have compared the formic and acetic acid levels in the Vasa with other shipwrecks which have been found in different locations but all impregnated with PEG during the conservation treatment.

Also the fate of PEG structure is of interest, as an eventual breakdown of the PEG may lead to a decreased average molecular weight, which in turn leads to a decreased melting point and a softening of the polymer, again leading to less stabilisation of the degraded wood. Furthermore, the smaller the polymer the higher the hygroscopicity which under humid conditions may lead to seeping out of the impregnation agent and/or migration and

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recrystallisation of salts in the conserved hull.

In this review we present the results obtained so far about the distribution of PEG in the Vasa and its possible degradation products.

The Distribution of PEG in the Vasa

The PEG in the Vasa was analysed using core samples from three different positions in the ship. The samples were taken from areas where the condition of the wood was judged as good ($\text{Vasa}_{\text{Good}}$), average ($\text{Vasa}_{\text{Mid}}$) or poor ($\text{Vasa}_{\text{Poor}}$). For comparison a sample was taken from one of the Danish Viking Ships (Skuldelev II), in which the sample wood was judged as being in good condition. The cores were cut in 5 mm slices and exhaustively extracted using Soxhlet, according to[8], see Figure 1. Our results showed that the cores all contained PEG but that the distribution was dependent on the condition of the wood, see Figure 2. The wood, which was described as degraded ($\text{Vasa}_{\text{Poor}}$) or in "medium" ($\text{Vasa}_{\text{Mid}}$) condition was found to have an open structure that allows a uniform distribution of PEG in the wood up to a molecular weight to at least 1500. In sound wood the structure does not allow the diffusion of PEG into the core, as illustrated in the Figure 2, $\text{Vasa}_{\text{Good}}$ and Skuldelev, in which both samples represent wood classified as in good condition. In this respect, it is interesting to note that the Skuldelev sample is approximately 1000 years old, whereas the Vasa sample is only approximately 350 years old. The condition of the wood is therefore not directly related to its age, but just as much to the condition it has reached because of the microbial conditions that existed in the wood during its burial[9].

In $\text{Vasa}_{\text{Poor}}$ and Vasa_{Mid} there seems to be a tendency towards a lower content of PEG in the outer layers. However, these two samples are known to have suffered acid attack, and the areas from where they were taken have both been washed with an aqueous sodium bicarbonate solution ($NaHCO_3$). The reason for the lower PEG content in the wood may therefore be a partial washing out of the PEG during the water solution treatment. This treatment has recently been stopped because it led to a marked reduction of the quality of

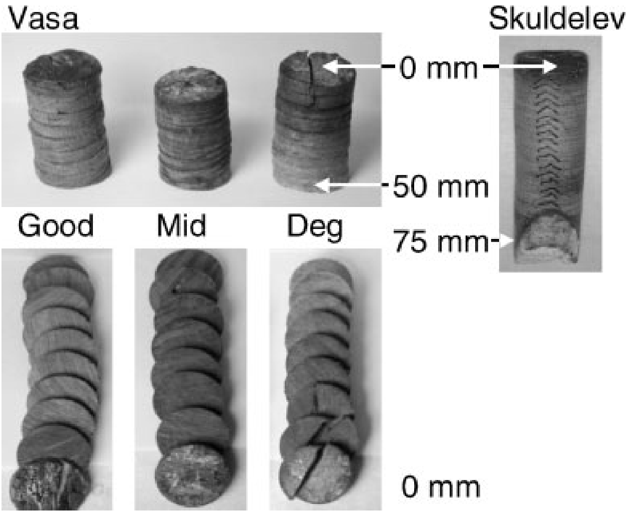

Figure 1.
Slices of samples taken from the Vasa warship and from the Skuldelev ship. Because of a crack in the Skuldelev sample, PEG had penetrated to the interior of the sample. Therefore the sample was only extracted and analysed in the outermost 50 mm.

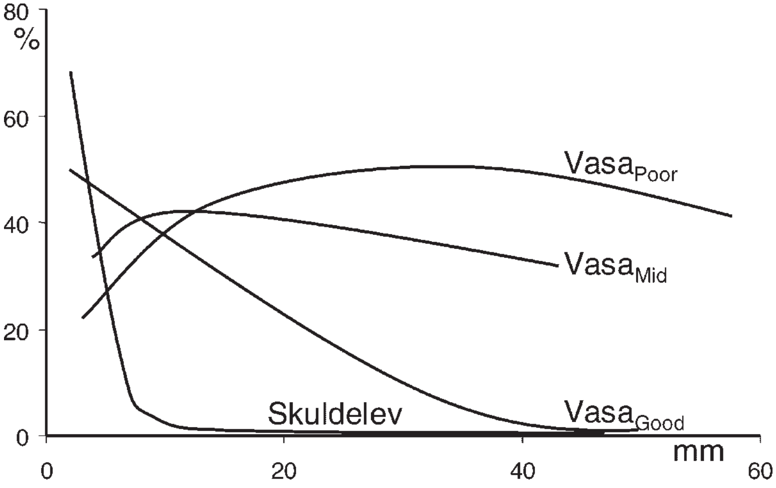

Figure 2.
A scematic drawing of the distribution of the total amount of PEG in the three samples analysed from $\text{Vasa}_{\text{Good}}$, Vasa_{Mid} and $\text{Vasa}_{\text{Poor}}$, together with the sample from Skuldelev, all shown in Figure 1. X-axis is the distance from the surface, Y-axis is the total amount of PEG in percent of the total weight of the sample. Data from [8].

the surface layers overall appearance and rigidity; probably because of the washing out of PEG. The content of PEG in the wood can easily be qualitatively estimated using Attenuated Total Reflectance/Fourier Transform Infrared Spectroscopy (ATR/FT-IR) which enables spectra to be collected from otherwise difficult-to-analyse brownish/blackish surfaces such as PEG treated wood. An example of a series of spectra from PEG impregnated wood is seen in Figure 3, which shows the IR spectra collected from chosen slices of the $\text{Vasa}_{\text{Good}}$ sample. Of special interest are the peaks at 1594 cm^{-1} (6.27 μm), originating from the aromatic structure of the lignin, in the fresh oak sample and at 841/842 cm^{-1} (11.89 μm), originating from the $-CH_2\text{-}O\text{-}CH_2-$ structure in the pure PEG 4000 sample. These peaks are only represented in the wood and in the PEG respectively, and can therefore be used as an evaluation of the presence of PEG in the sample. It is seen that in the outermost layer ($\text{Vasa}_{\text{Good}}$ 0mm), the presence of a prominent peak at 842 cm^{-1} and an almost vanishing peak at 1594 cm^{-1} shows the presence of a large amount of PEG in the outer layer of the wood. In the inner sample at 37 mm the situation is reversed, the peak at 1594 cm^{-1} is now prominent, whereas the peak at 842 cm^{-1} is now hardly visible.

The Fate of PEG in Impregnated Wood

The stability of PEG in a preserved piece of wood is of utmost importance. The stability of a microbially degraded piece of wood depends partly on the rigidity of the PEG polymer as it is imparting strength to the entire structure. Thus, if the PEG softens, its rigidity is lowered and the physical stability of the decomposed wood will be lowered. Furthermore, the smaller the average molecular weight of the PEG, the higher is the hygroscopicity, and the impregnated wood will therefore have an increased tendency to absorb water from the air. This is not a problem in relation to microorganisms, as the water activity, which determines their growth limit, is only related to the relative humidity (RH) of the surrounding air. However, an increased amount of water in the wood may lead to an increased solubilisation of salts embedded in the hull, and in turn, an increased mobility of these together with a risk of recrystallisation if the RH is lowered, or worse, is fluctuating.

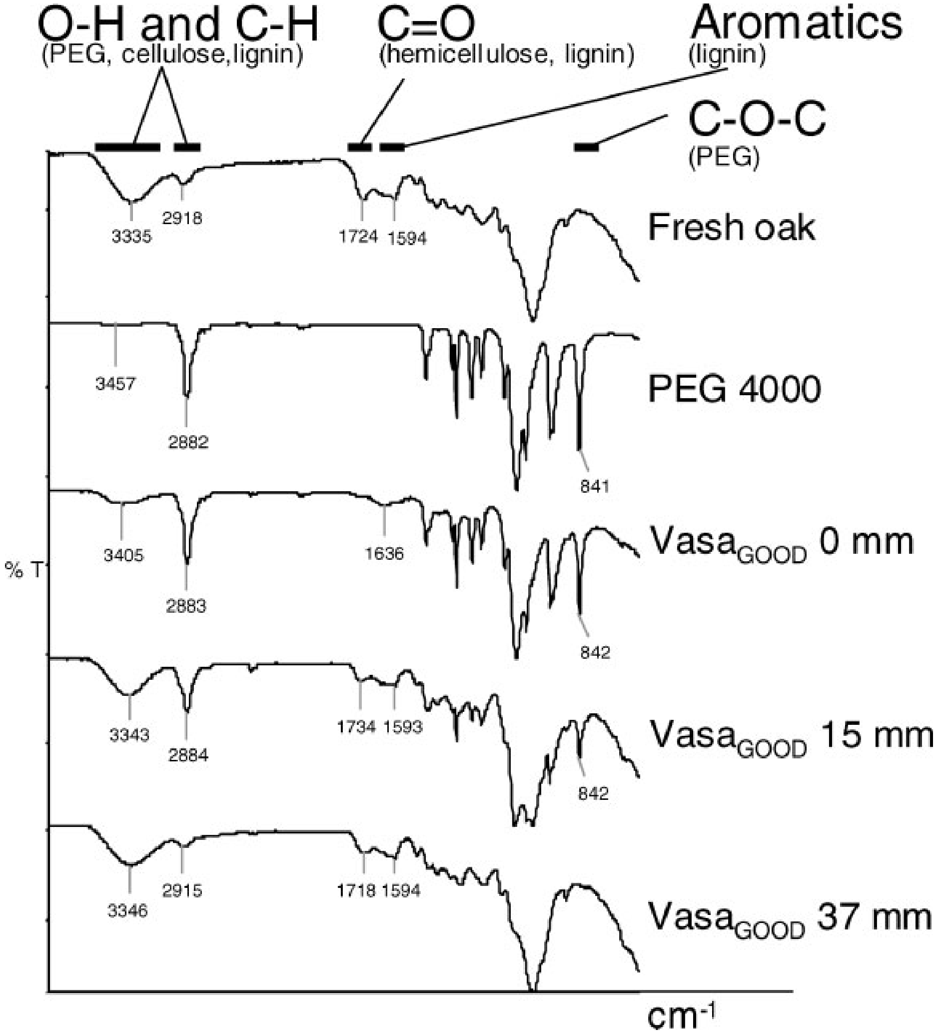

Figure 3.
ATR-FT/IR spectra of Fresh oak and pure PEG 4000, together with selected samples from The Vasa$_{Good}$ extraction. The wavelengths are written at the apex of selected peaks.

The Vasa was impregnated over a period of 17 years, and three different molecular weights were used, PEG 600, 1500 and 4000. In Figure 4 is seen a Matrix-Assisted-Laser-Desorption-Ionisation Time-of-Flight (MALDI-ToF) spectrum of the PEG found in the analysis of the outer layer of the Vasa$_{Good}$ sample. The spectrum shows the presence of all three types of PEG (600, 1500 and 4000) and the characteristic bell shape profile of the PEG's are still present. The average molecular weights of the three different fractions are still around the originally specified molecular weights. Similar spectra, showing the PEG in an overall good condition, can on a general basis be seen in the other slices from the samples (not shown). This indicates that the overall condition of the polymer is still satisfactory even though the polymer is on average 30 years old.

There are, however, indications that PEG may suffer minor decomposition. According to the theory[5], these degradation products

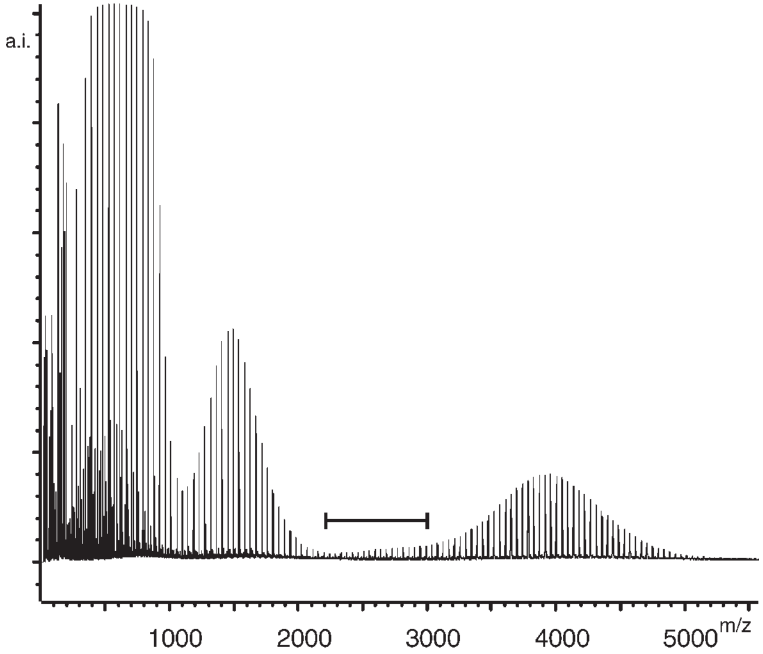

Figure 4.
A MALDI-ToF spectrum of the extracted PEG from the outer five mm layer from the $\text{Vasa}_{\text{Good}}$ sample. X-axis is the molecular weight of the polymer and Y-axis is the relative intensity of the peak. In the region from 2200 to 3000 m/z (indicated) is seen a slightly elevated PEG oligomer level. Data from [8].

should only appear as smaller homologoues. In the Vasa sample in Figure 4, minor amounts of degradation products were seen, these were, however, not quantified. The inner fraction of the core sample from the Skuldelev ship, which was only treated with PEG 4000, show that small PEG units are indeed present in this sample, but only in small concentrations; less than two percent of the total weight of the wood (results not shown).

Also, it has previously been demonstrated that PEG suffers fast decomposition when heated, leading to the formation of formic acid[5,10]. Furthermore, as suggested by Westermark[4], there may be a risk of solvolysis of the wood as the result of the presence of sulphuric acid, wood and PEG[11–13], leading to the formation of levulinic and formic acid.

The concentrations of the formic and acetic acid have been measured in 40 samples taken from different positions from five different shipwrecks, the Batavia (375 years old), the Vasa (375 years old), the Bremen cog (650 years old), the Oberländer boat and the Danish Viking Ships from Skuldelev (both around 1000 years old). The average of the formic acid concentrations in different positions and depths in samples from the five ships are shown in Figure 5. The individual samples show concentrations from 0.006% in samples from the Skuldelev ships and up to 0.15% in one of the Batavia samples. Notably, the average concentration in the Vasa does not exceed the average concentration in the other ships analysed, where the Viking ships and the Batavia also have high concentrations of sulphur in the hull, up to 1%, whereas the Bremen Cog only show low concentrations[14]. The Bremen Cog, however, shows the highest average concentration of formic acid. This therefore contradicts the thesis that PEG, sulphuric acid and wood should lead to the solvolysis of the wood and formation of formic acid. Also in Figure 5 is the average of a sub-set

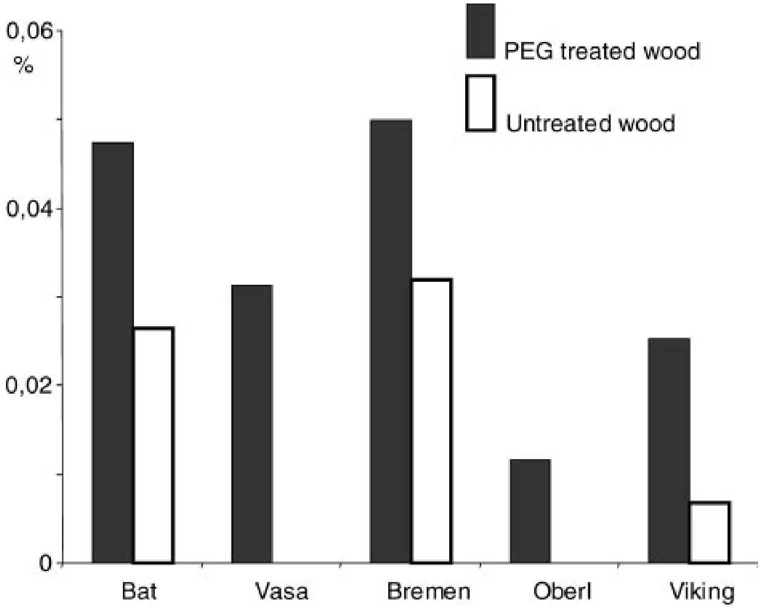

Figure 5.
The averages of the concentration of formic acid in samples taken from different positions and depths of the ships, black/white bars show the average concentrations of the samples with a content of PEG/without PEG in the wood. Number of analysed samples are: the Batavia (Bat, 10/1 samples) the Vasa (Vasa, 10 samples), the Bremen cog (Bremen, 4/3 samples), the Oberländer boat (Oberl, 2 samples) and the Danish Viking Ships (Viking, 8/2 samples). Data partly from[15]

of samples (6 samples) from the ships, the concentration of formic acid in dry, non-conserved wood. It is noticeable that the concentrations in these samples seem to be consistently lower than in the samples treated with PEG, even though the conserved wood has been through an exhaustive and lengthy aqueous treatment during the conservation of the wood. This therefore strongly suggests that the increased amounts of formic acid in the samples are related to the PEG content.

One specific sample, a long core (25 cm) from the Batavia, was cut into smaller parts and the formic acid content measured for each 2 cm. The results are seen in Figure 6, and show a tendency towards a concentration increase with depth. The explanation for this may well be that the formic acid was evenly distributed during the impregnation process. However, during the many years of exhibition of the wreck in a dry state, the formic acid slowly evaporates and the concentration in the surface layers slowly decreases. We have previously measured the concentration of formic acid in air in the Vasa museum and found that the concentration of formic acid in the air in enclosures aboard the ship was approximately double the air concentration on the upper deck (Glastrup unpublished).

The acetic acid concentration follows a different pattern. The averages of the samples from the five ships are shown in Figure 7. In these, the average acetic acid contents of the dried wood samples are at the same level as the conserved samples (data not shown). Fresh oak easily exceeds an acetic acid content of 2%[3], but in these ships the content is now reduced to between 0.35 and 0.05%. Nevertheless, there are still measurable acetic acid concentrations after 1000 years.

In general, the acetic acid concentration seems to decrease with the age of the ships, with the Batavia samples as an exception.

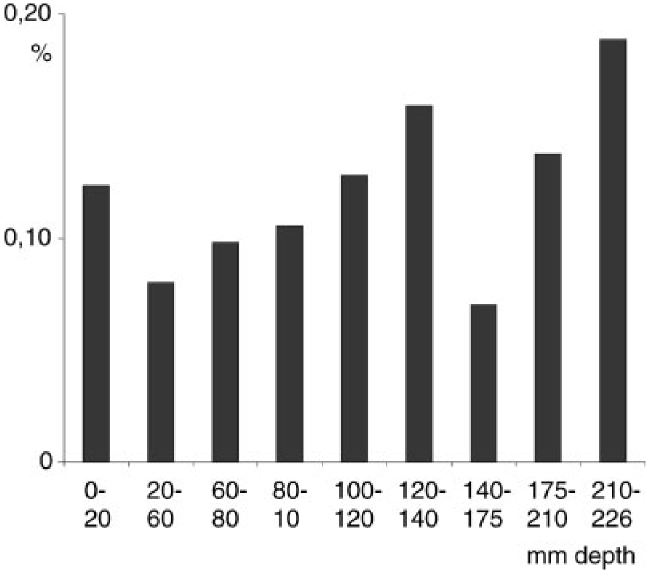

Figure 6.
The concentration of formic acid in a single sample from Batavia at different depths of the wood.

This is probably due to out washing and evaporation from the wood. The low average concentration in Batavia may be explained by the conditions at the site of burial. The Vasa, the Bremen Cog, the Oberländer boat and the Danish Viking ships all sank in protected areas and were covered with silt. The Batavia sank near the western Australian coastal line, in an exposed sandy area. It therefore seems that the residual acetic acid in ancient shipwrecks not only depends on their age, but also on the burial conditions.

Conclusion

We have analysed three wooden cores from the Vasa and measured the PEG content in these as a function of the depth of the wood.

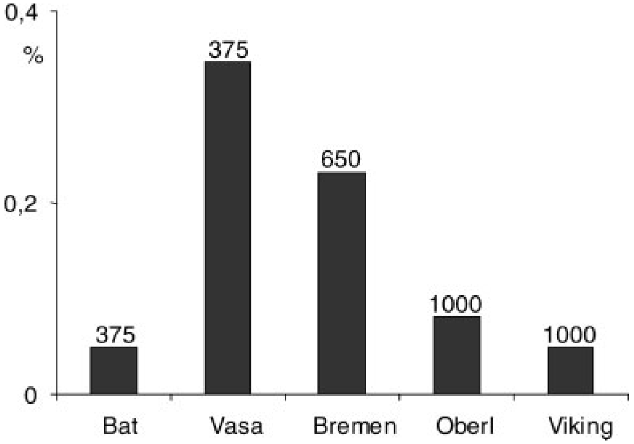

Figure 7.
The average concentrations of acetic acid in the five different ships analysed. The denominations of the ships are as in Figure 5, the approximate age of the wreck is given above the bars. Data partly from [15]

We have also characterized the PEG using MALDI-ToF on the extracted PEG. In general the PEG still seems to be in good condition, which more specifically means that the PEG analysed still has approximately the average molecular weight which was specified when it was applied. Minor amounts of PEG's were found, which could not be attributed to either PEG 600, 1500 or 4000. However, in Skuldelev the concentrations did not exceed 2% of the total wood weight and in the Vasa they were also judged to be of minor importance. There seems to be a somewhat increased level of formic acid in wood treated with PEG, the average concentration is at the same level as in other ships treated with PEG but in which sulphuric acid is not recognised as a problem. Therefore, this effect is probably attributed to a PEG degradation mechanism previously described[5]. The formic acid, together with the residual acetic acid, may however represent an additional threat to especially metallic and calcareous objects in the surroundings, as they tend to evaporate and lead to corrosion.

All in all it must be concluded that the PEG, after thirty years, is still in a satisfactory state, with the ability to stabilise the archaeological artefacts for many years to come. Whether PEG is an ultimate conservation agent for objects that are expected to last hundreds of years is still an open question.

Acknowledgements: This work was performed within the National Maritime Museums of Sweden research project "Save the VASA" sponsored by The Bank of Sweden Tercentenary Foundation, The Swedish National Heritage Board, The Swedish Foundation for Strategic Research (SSF), The Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS), and The Swedish Agency for Innovation Systems (Vinnova). The authors wish to thank Emma Hocker, Gunnar Almkvist, Per Hoffmann and Vicki Richards for providing samples. Also a thank to the Augustinus foundation for the donation of the SPME-GC/MS equipment.

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