Chemical composition of the fingermark residue: Assessment of the intravariability over one year using MALDI-MSI

Marie Gorka [a,*], Aurélien Thomas [b], Andy Bécue [a]

[a] School of Criminal Justice, Faculty of Law, Criminal Justice, and Public Administration, University of Lausanne, Switzerland
[b] Faculty Unit of Toxicology, University Center of Legal Medicine, Vulliette 04, 1000 Lausanne, Switzerland

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ABSTRACT

These past years, the chemical composition of fingermarks have attracted interest of researchers to meet multiple objectives like the determination of an individual's age, gender or lifestyle or the impact of some fingermark detection processes, to cite a few. These studies have highlighted the need to investigate the consistency of the fingermark composition over time. This research explores the evolution of the secretion residue composition of thirteen donors over one year, focusing on the intravariability. The dual use of Matrix-Assisted Laser Desorption/Ionisation Mass Spectrometry Imaging (MALDI-MSI) and chemometrics provided valuable data regarding the evolution of composition over time as well as the consistency of presence of hundreds of compounds.

1. Introduction

In the context of fingermark analysis, matrix-assisted laser desorption ionisation (MALDI) mass spectrometry is undoubtedly the most cited technique of the last decade for both profiling fingermark composition and imaging of the papillary ridges [1,2]. To date, MALDI mass spectrometry was successfully applied to the detection of (semi-)exogenous and endogenous compounds present in fingermarks [1,3–10], the reconstruction of the ridge pattern [7,10–21] and the differentiation of individuals [1,11,22,23].

Since 2014, MALDI-MSI is recognized as a class C fingermark recovery technique by the Home Office [24] and has proven its applicability on research projects and casework but also in sequence with other visualisation techniques [1,25,26]. These findings support that MALDI-MSI could become an essential asset when it comes to the analysis of fingermarks for both imaging and profiling purposes.

Overall, the development of this method for forensic science, especially fingermarks analysis, is promising. In this work, we propose to consider MALDI mass spectrometry as a way to gather fundamental knowledge regarding the intravariability of composition of fingermarks. Intravariability has to do with the modifications and changes that occur over time for a given individual, whereas intervariability relates to the differences that are monitored between individuals.

Gaining knowledge about the intravariability of the chemical composition of the fingermarks could be of valuable information to better understand the global composition of fingermarks itself but also to help refining the concept of donorship, which consists in categorizing donors when it comes to the development of new fingermarks detection reagents [27,28].

In an attempt to provide original and relevant data about the intravariability of the fingermark composition, the present study aims at investigating the composition of the fingermarks collected from thirteen donors over one year, using MALDI mass spectrometry. The chemical composition was analysed through several statistical treatments to assess the variations that occur during a year, their possible cause, as well as the qualitative and quantitative consistency. It is expected that this research will provide new fundamental knowledge about the composition of the fingermarks and hence bring a possible line of approach for creating representative group of donors for research purposes.

2. Experimentals

2.1. Materials

Acetonitrile (ACN), trifluoroacetic acid (TFA) and ultrapure water (H₂O) were purchased from Biosolve.

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* Corresponding author.
E-mail addresses: marie.gorka@unil.ch (M. Gorka),
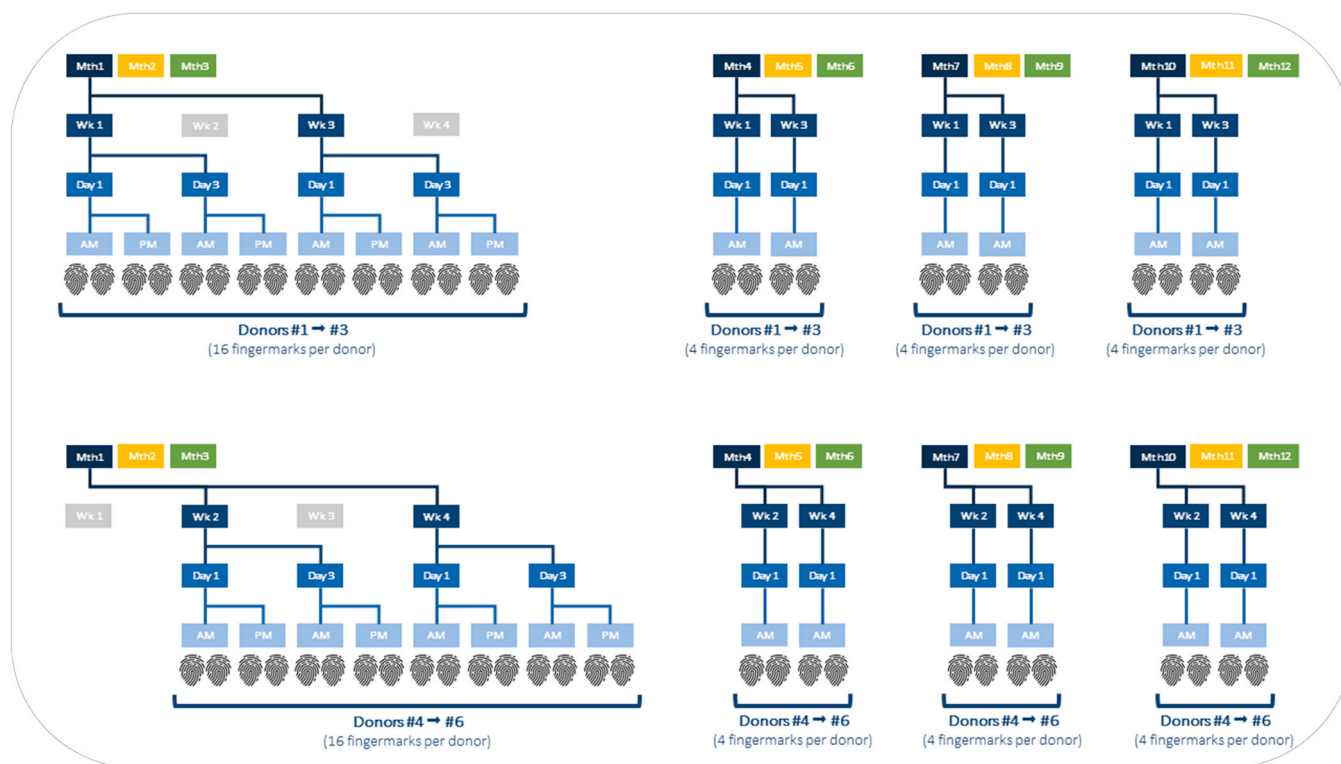aurelien.thomas@chuv.ch (A. Thomas), andy.becue@unil.ch (A. Bécue).

Fig. 1. Calendar of fingermark deposition illustrated for 6 donors. The same process was applied to all the 13 donors. The deposition schedule is repeated for months 1–3 and for months 4–12. Abbreviations: Mth for months, Wk for week.

α-cyano-4-hydroxycinnamic acid matrix powder (α-CHCA) were obtained from Merck / Sigma-Aldrich.

Superfrost Plus glass microscope slides (75 ×25 x 1 mm) were obtained from Thermo Fisher Scientific.

2.2. Instrumentation

2.2.1. MALDI-MSI

The same instrument and parameters were used as in [22]: "All the analyses were conducted on a hybrid mass spectrometer MALDI Linear Trap Quadrupole (LTQ) Orbitrap XL from Thermo Fisher Scientific equipped with a linear trap and coupled to an Orbitrap [29]. The ion source was an azote (N_2) laser with a wavelength of 337 nm, a spot size of 50 × 60 μm and a laser repetition rate of 60 Hz with a pulse duration of 3 ns. The instrument was used in positive ionization mode. The number of laser shots was set to 4 with an energy of 4 μJ. The analysed masses ranged from 100 to 2000 *m/z*, hence encompassing many polar molecules including lipids, amino acids, proteins and peptides. The spatial and spectral resolutions were set to 100 μm and 60'000, respectively. The plate had a raster movement. Automatic gain control and automatic spectra filtering were disabled. The Tune Plus window from Thermo Fisher Scientific [29] was used to control the instrument and acquire the data. The instrument was used in imaging mode and set to acquire a square area of several mm^2 corresponding to 150–200 pixels. By doing so, it was possible to gather information over a portion of fingermark (including several ridges) in an acceptable scanning time, instead of considering a single spot which presuppose a homogeneity of composition over the whole fingermark."

2.3. Method

2.3.1. Matrix preparation and deposition

The matrix preparation and deposition was conducted similarly to [22]: "α-CHCA was chosen as the matrix for MALDI-MSI, mostly

for its successful application in fingermark analysis [30]. Its preparation was adapted from the literature: 5 mg/mL of α-CHCA in 70:30 ACN:H2O and 0.1% TFA [13]. The matrix was deposited on the samples by spraycoating using an automatic SunCollect sprayer from SunChrom. The spraying coordinates were introduced manually and the spray height (i.e., 25.32 mm) as well as the number of layers (i.e., 10) were set according to the literature [31,32]. The ten layers were sprayed as follows: first layer at 10 μL/min, second at 20 μL/min, third at 30 μL/min, and from the fourth to the tenth at 40 μL/min. Spraying the matrix instead of spotting it results in a better homogeneity of deposition as well as a better control of the quantity left. Therefore, it confers a better reproducibility and standardization of the protocol."

2.3.2. Fingermark sampling

In this study, natural fingermarks from thirteen donors were collected. The pool of donors was composed of 6 men and 7 women, aged from 25 to 59.

The preparation and the deposition protocols followed the recommendations published in the literature [27,33–35]. Before providing fingermarks, the donors were asked to act normally and to avoid hand washing during the 45 min preceding the fingermark collection. A few seconds before the fingermark deposition, the hands were gently rubbed together to ensure an even repartition of the residue between the fingertips. The donors were then asked to leave two natural fingermarks on a glass microscope slide, using two different fingers. No further controls were applied.

The fingermark collection was conducted in the same room for the whole study. The temperature in the laboratory was stable, varying between 19 and 21 °C.

Depending on their availability, each donor provided a total of 22–30 fingermarks between January and December 2020, following a strict calendar (Fig. 1).

Due to the COVID-19 crisis, no deposition session took place between the end of March and the beginning of July, explaining why

the number of fingermarks varied slightly between donors, especially for donors 02, 03 and 07.

All the fingermarks were aged for 24 h before being analysed by MALDI-MSI. Two analyses were performed on each fingermark, for a total of 44–60 analyses per donor and 714 analyses overall.

2.3.3. MALDI-MSI stability

Besides the usual calibration process for the MALDI-MSI instrument, the MALDI signal was checked twice a week with a printed test strip to ensure that the instrument was able to successfully detect compounds present in fingermarks. The test strip was made with artificial sweat and sebum solutions derived from Sisco et al. [36] and printed using a the Fujifilm Dimatix Materials Printer DMP-2850 [37,38].

2.3.4. Data processing

The data collected from the MALDI-MSI analyses were visualized using the XCalibur software (Thermo Fisher Scientific; version 3.1) to ensure that no problem occurred during the acquisition of the data. Then, the files were extracted and exported to an.imzML format [39] using ImageQuest software (Thermo Fisher Scientific; version 1.1.0).

Regarding the spectra analysis, the peak picking and the generation of intensity tables were performed for each donor separately using a homemade R-coded tool based on the MALDIquant and MALDIquantForeign packages. Peak picking is an approach that allows peak detection in one or several spectra. Only the peaks characterized by an intensity and width above the minimum values set were selected.

For each sample (i.e., fingermark analysis), the intensity of each m/z for each pixel were then gathered into a.csv file. The pixels were reduced by the mean for each variable. The resulting data frame was eventually saved in a new.csv file, into which each row corresponds to a unique sample of the donor of interest.

The variable selection was computed using R, and was based on the percentage of presence of the variable among all his·her samples over the year (i.e., no selection, 50%, 75%, 90% and 100%). The threshold value was eventually set to 90%.

The chemometric analysis and all the charts were performed replacing the intensity values of zero with the minimum intensity value detected in the donor's associated data frame and using median normalization followed by logarithm transformation.

The charts corresponding to all donors are available as supplementary data.

3. Results

3.1. Impact of the time of the day on the fingermark composition

3.1.1. Trends observed within a day and between days

In order to investigate the changes of composition of a given donor's fingermarks during a day, heatmap has been calculated using fingermarks that were deposited the same day (i.e., first month of the deposition agenda). The most remarkable trends among the thirteen donors are illustrated in Fig. 2. For readers not accustomed to heatmaps, some interpretation hints are provided: each column corresponds to an analysed fingermark and each row to a specific m/z; the color of each cell, ranging from dark blue to dark red, characterizes the intensity of the m/z values in the analysed fingermarks (i.e., higher the intensity, darker the red; lower the intensity, darker the blue); the top and left hierarchical cluster trees regroup fingermarks/depositions and m/z, respectively. These are discussed further in the results, below.

From Fig. 2, it can be observed that the m/z that are systematically present in all the fingermarks collected over a three week timeframe present somewhat some variations of intensity. The majority of the donors (i.e., 10 out of 13) present patterns similar to

donors 08. For these donors, the clustered fingermarks are regrouped by the day of deposition rather than by the time of the day (i.e., morning vs afternoon). Donor 01 is the only one presenting a major intensity variation for one day. Donor 2 is the only one whose clustering is more important between AM and PM rather than between days. These observations mean that the variations of composition tend to be slightly more important between the days of deposition rather than within a given day, as showed with donor 05. Overall, there is no m/z values that are over- or under-represented specifically for fingermarks deposited in the morning and in the afternoon.

The over-representation that can sometimes be observed for some fingermarks and some donors (i.e., darker red areas) is often specific to one day (e.g., DON 01) or to one fingermark. No reproducible trend has been observed otherwise. The same statement can be made for the under-representation of m/z (i.e., darker blue areas).

3.2. Evolution of the composition over the year

For each donor, heatmaps were calculated for all the fingermarks left during a 1-year-timeframe, in order to visualize if relevant clusters could be identified (Fig. 3).

For 77% of the donors (10 out of 13), the months are intertwined (see DON 04 and 12 in Fig. 3). Donor 03 is the only exception for whom the fingermarks are well separated according to their month of deposition. Donor 10 is the only one with a low mixing in its month clusters. The results for donors 02 and 07 (supplementary data) are less interpretable as they deposited fingermarks for three to four months only, due to the COVID-19 crisis.

Overall, the composition of the fingermarks provided by the 13 donors is quite consistent over the months and the year. Except for one or two months for which less fingermarks were collected, no cluster is specific to one month. Moreover there are no over- or under-representation of m/z specific to a whole month in the heatmaps (darker red and blue areas, respectively), even for donor 03.

These results highlight the links of the chemical composition of the fingermark residue over the months.

Also, months that are spaced in time (i.e., January vs July, February vs November) are closely linked in the heatmaps, therefore emphasizing that seasons have little impact on the composition of the fingermark residue. Visually, some m/z values are clearly over- or under-represented throughout the year, although they are not specifically in accordance with month or season changes. Overall, these preliminary observations indicate that a fraction of the secretion residue remains relatively constant over a year for a given donor.

These results are strengthened by the PCA and heatmap depicting a classification of the fingermarks of all the thirteen donors combined according to their month of deposition (Fig. 4). These charts were built on 90% of the m/z values present in all the analysed fingermarks. As expected, consecutive months are always overlapped and the PCA clearly displays this continuity with a bottom-up succession of months (e.g., January, February at the bottom of the PCA, March, May, July in the middle and August, September, October, November, December at the top). Although, the heatmap emphasizes the interconnection between all the months confirming that seasons have a limited impact on the fingermark composition. This impact is reflected with a constant evolution throughout the months with the bottom-up effect showed in Fig. 4.

Moreover, this result, as well as the mixing of the months in the clusters of the heatmap (Fig. 4) indicate that the observed results are not due to a batch effect that could occurred during the analysis and remain genuine and reliable.

Seasonal changes, physiological changes, emotions, diet and lifestyle habits do have an impact on the composition of fingermarks. However, overall, some consistency in the fingermark
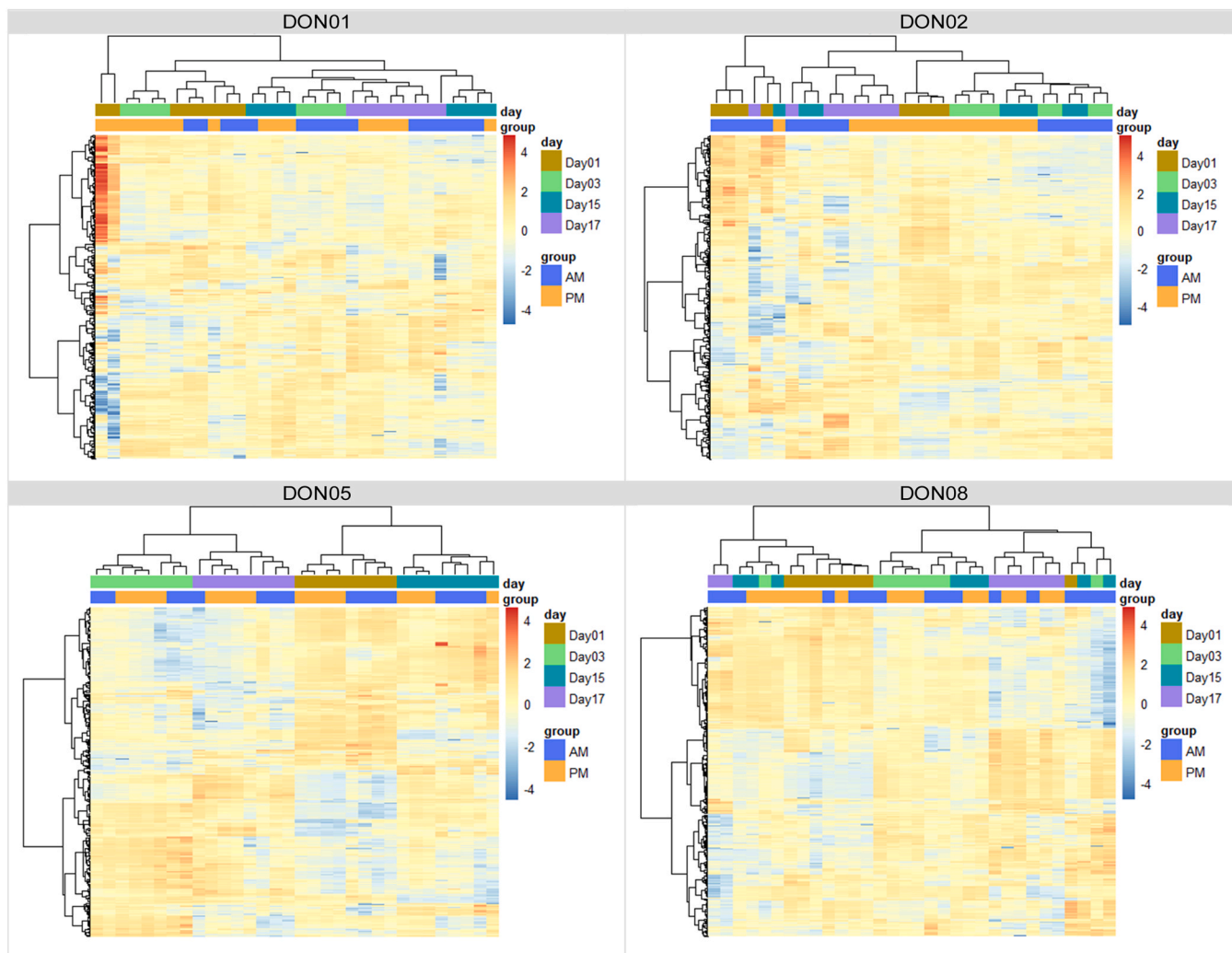
Fig. 2. Heatmaps corresponding to four donors (i.e., 01, 02, 05 and 08), built on 90% of the *m/z* values present in all the fingermarks provided by a given donor and showing the difference in composition between morning (AM) and afternoon (PM) and between days of deposition. *m/z* are represented in the left hierarchical clustering.

composition along the year has been emphasized for each of the thirteen donors of this study.

To investigate more in depth the variations that occur over months and year, boxplots of the intensity of 6 *m/z* equally distributed from the 25% variables with the most stable interquartile range over the year were generated. The most remarkable trends are depicted in Fig. 5.

For more than 85% (11 donors out of 13), the variations are similar to the ones observed in Fig. 5. Two exceptions can be pointed out in supplementary data for donors 07 and 09. In these two cases, there is an unexpected variation of one compound for the month of September (month09). Regarding the class of compounds stable throughout the year, approximately one third to half of them can be characterized as triglycerides in the human metabolome database [40]. Such compounds can be either from endogenous or (semi-) exogenous origin.

Overall, for a same *m/z*, some intensity variations occur throughout the months, sometimes higher for some isolated months (i.e., longer boxplot for DON05 *m/z* 1296.08), but these variations remain small when comparing *m/z* between them. Moreover, they do not highlight any pattern that could be specific to a seasonal evolution.

Below the 25% of variables with the most stable interquartile range, wider variations are observed (data not shown), meaning that a small fraction of the secretion residue remains quantitatively consistent throughout the months.

Overall, the results emphasize a qualitative stability as well as a quantitative consistency of the secretion residue throughout the year for at least one quarter of the detected *m/z*.

3.3. Consistency of the composition over the year

To further investigate the consistency of composition of the fingermark residue, the number of detected *m/z* values was determined for each donor of this study, and further selected according to their percentage of presence among the fingermarks (see Figs. 6 and 7). The peak picking process was performed individually for the thirteen donors.

Overall, without any prior selection, an average of 971 *m/z* were extracted after the peak picking process for all the donors. Moreover, 96% of these *m/z* features are present in at least 50% of the fingermarks collected from all the donors over the year. Between 45% and 26% of all the detected *m/z* are also present in the composition of 90% and 100% of the fingermarks collected, respectively.

The consistency of composition observed over the year is also reproducible between the thirteen donors, as the percentage of the *m/z* retained between each selection is similar for everyone (Fig. 6).
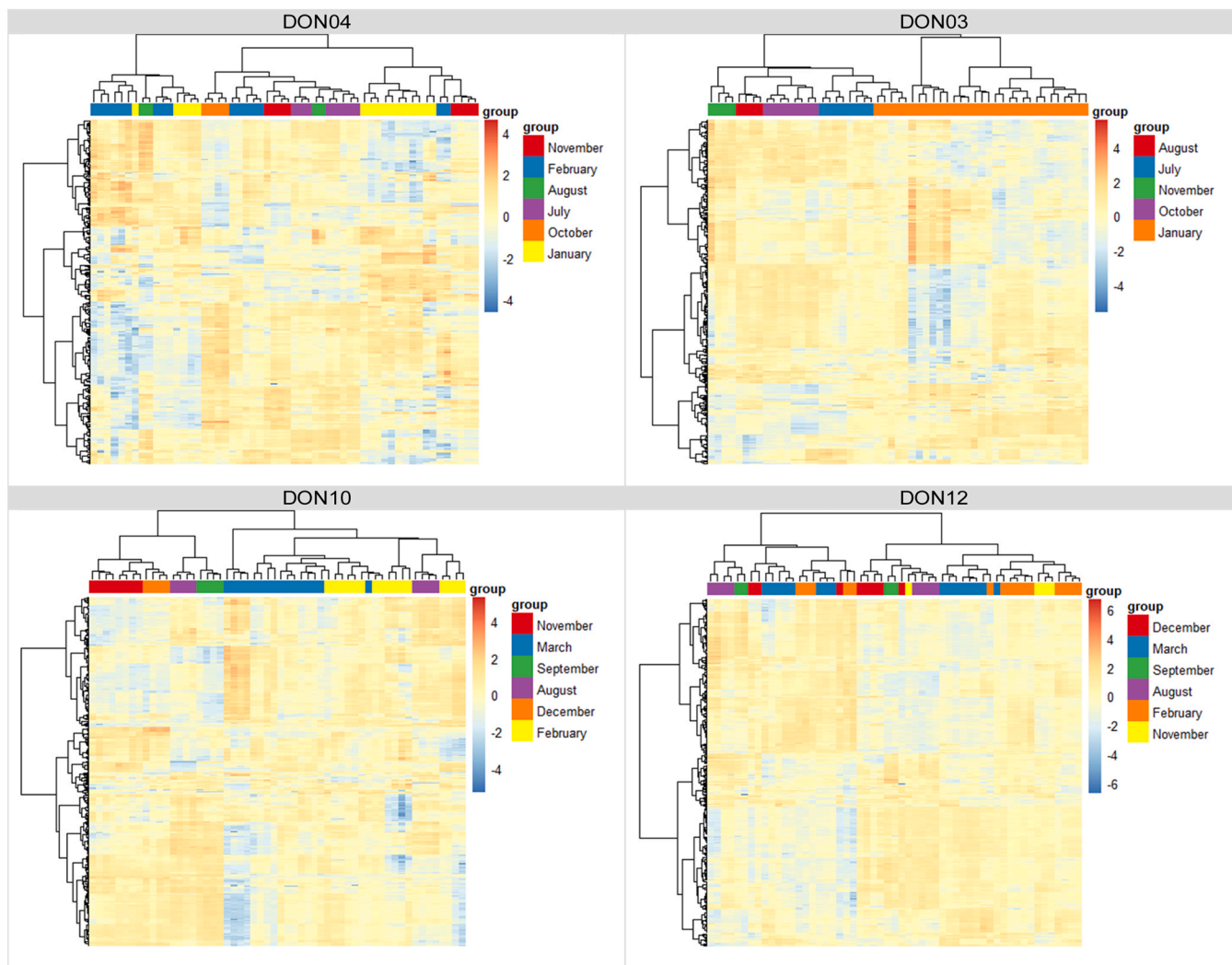
Fig. 3. Heatmap of four donors built on 90% of the *m/z* values present in every fingermark for each donor and showing the different months of the year when the fingermarks were deposited. *m/z* are represented with the left hierarchical clustering.

The same conclusions can be drawn from Fig. 7, depicting the consistency of composition of the fingermarks collected during the first month (including the morning and afternoon deposition sessions). A new peak picking process was applied on these fingermarks to determine the number of *m/z* detected during one month. The number of variables detected is almost equal that those presented in Fig. 6. Therefore, it supports the consistency of the chemical composition of the fingermarks along the year.

Overall, these results emphasize, that for each donor, it may be possible to build a set of *m/z* values that are representative of the composition of their fingermark residue (Figs. 6 and 7).

In Fig. 8, a common peak picking for all the donors was considered, meaning that the *m/z* detected are present in at least 30% of all the fingermarks among all the donors at a specific percentage, due to the arbitrary cut-off set in the peak-picking R code. This process allows determining which fraction of the *m/z* values is common to the thirteen donors.

Regarding a qualitative aspect, the number of common *m/z* detected is usually smaller than for each single individual but remains close to the values presented in Fig. 6.

When it comes to quantitative aspects, according to Girod et al. [27], it is expected to observe an intensity variation that is lower for the intravariability than for the intervariability for some variables.

The exploration of the intervariability was not a purpose in this study, but will be investigated in further research.

Overall, considering the *m/z* consistent for the thirteen donors, 34% of the detected *m/z* values are present common to the thirteen donors over a one-year timespan. In other words, a hundred of *m/z* are present in all the fingermarks provided by the 13 donors combined.

4. Discussion

4.1. Variation of composition between individuals and over varying timespans

The results presented in this study highlight that a fraction of the chemical composition of the fingermark tend to be consistent throughout the year qualitatively but also quantitatively to some extent.

Regarding the variations observed, no external factors like the seasons or the time of day seem to impact this consistency as shown in Figs. 2 to 5. The gender of the donors does not explain these variations either.

One hypothesis is that changes in the composition of fingermarks might be explained by some physiological modifications like stress
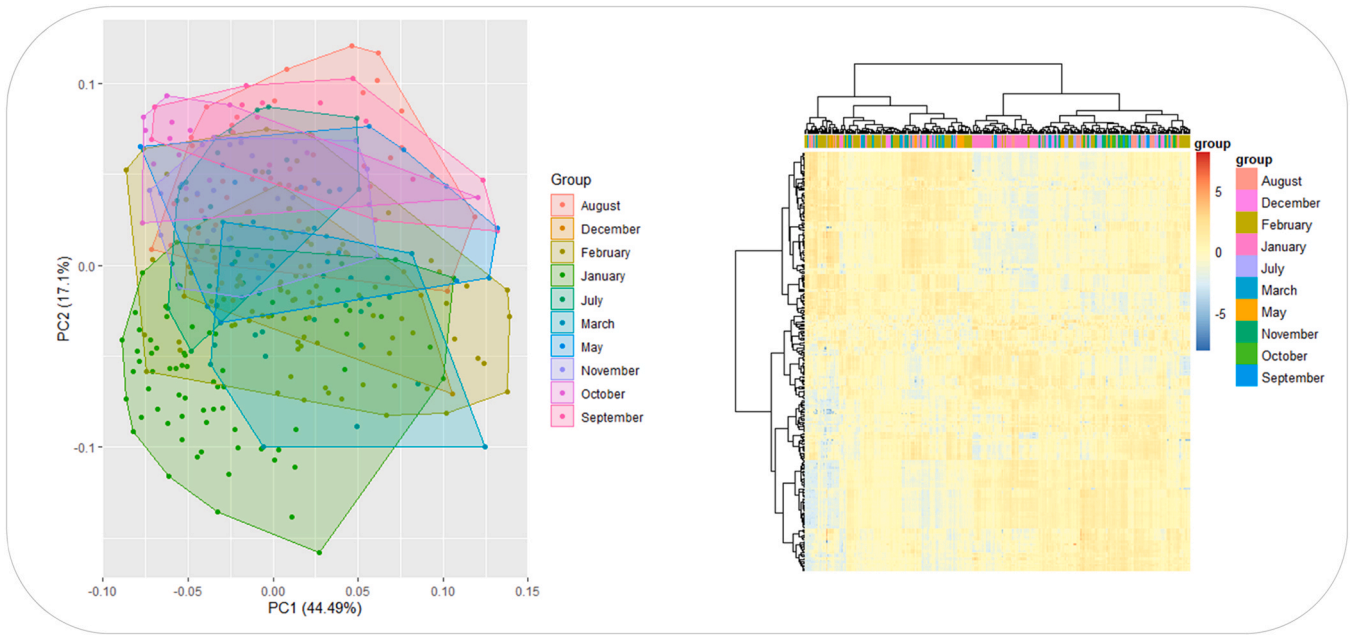
Fig. 4. PCA (on the left) and heatmap (on the right) built on 90% of the *m/z* values present in all the fingermarks provided by the 13 donors and classified according to their month of deposition.

levels, emotions, alimentation, lifestyle, habits or pathologies that can affect the composition of sweat [41–43]. Indeed, it is long time proven that concentrations of metabolites present in the human sweat are controlled by metabolic processes and evolve regularly depending on many factors like diet or activity levels [43–48]. The fact that natural fingermarks were collected in this study means that the donors were allowed to naturally touch their face and other parts of their body before depositing fingermarks. As a result, sebaceous- or apocrine-originating components may be present on the fingertips and induce some variability compared to sebum-rich or eccrine-rich fingermarks [2,49,50]. Overall, various factors can induce non-linear changes in the fingermark composition. These factors tend to explain why no specific pattern could be identified based on weeks, months or seasons.
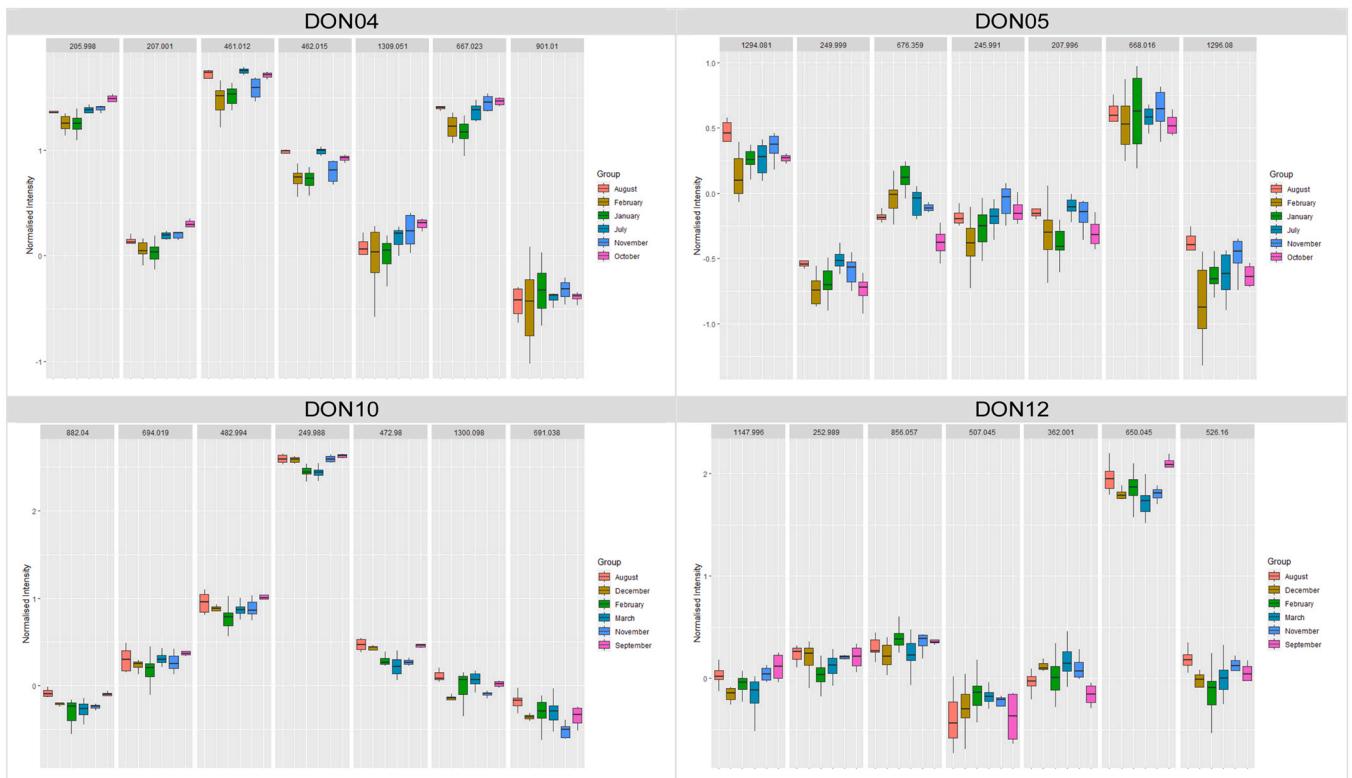

Fig. 5. Boxplots of 6 *m/z* from the top 25% variables with most stable interquartile range for each donor separately. Each colour corresponds to a month of deposition of the corresponding analysed fingermarks.
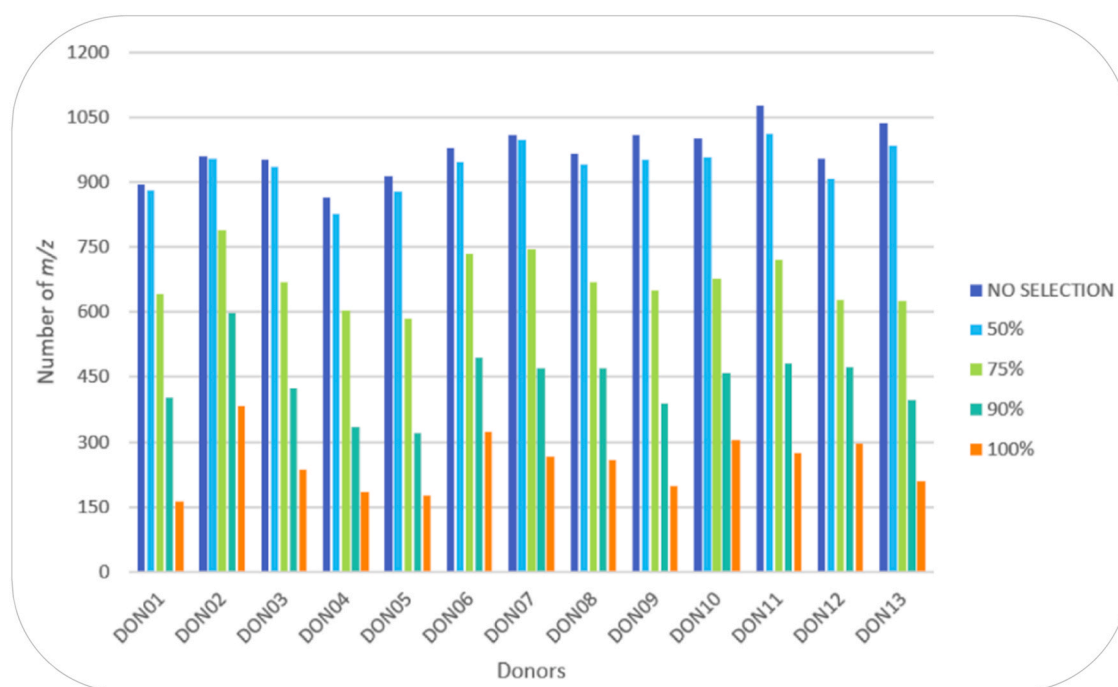
Fig. 6. Number of *m/z* (variables) present in the fingermarks of the 13 donors over a one-year timespan according to their ratio of presence among the analysed fingermarks (coloured labels). For example, light green bars indicate the number of *m/z* (compounds) that have been detected in 75% of the analysed fingermarks.

Despite these changes, consistency was observed along the weeks and the year (Figs. 7 and 8). These results highlight the presence of 25–45% of the *m/z* detected for the fingermarks of each donor. Also, up to 34% of these *m/z* are common to all the donors throughout the year, which emphasizes the importance of endogenous and (semi-)exogenous compounds into the consistency of composition of the fingermarks.

Overall, there is an undeniable qualitative consistency over the year for each donor. There is also a certain signal stability as see in Fig. 5 but only for a certain fraction of the detected *m/z*, emphasizing the fact that there are some variations in terms of intensity that are

occurring monthly. This statement is in accordance with the results published by Chadwick et al. [28] and based on the observation of processed fingermarks. An attempt to characterize the 25% most systematically present *m/z* was carried out by using the HMDB database. Most of these compounds were lipids, followed by metabolites, benzoids, and amino acids fragments. Overall, these results emphasize the possibility to create representative group of donors as already highlighted by Girod et al. [27] and further suggest that the chemical composition of fingermarks could be of valuable interest in the development and optimisation of new detection reagents (e.g., targeting specific compounds).
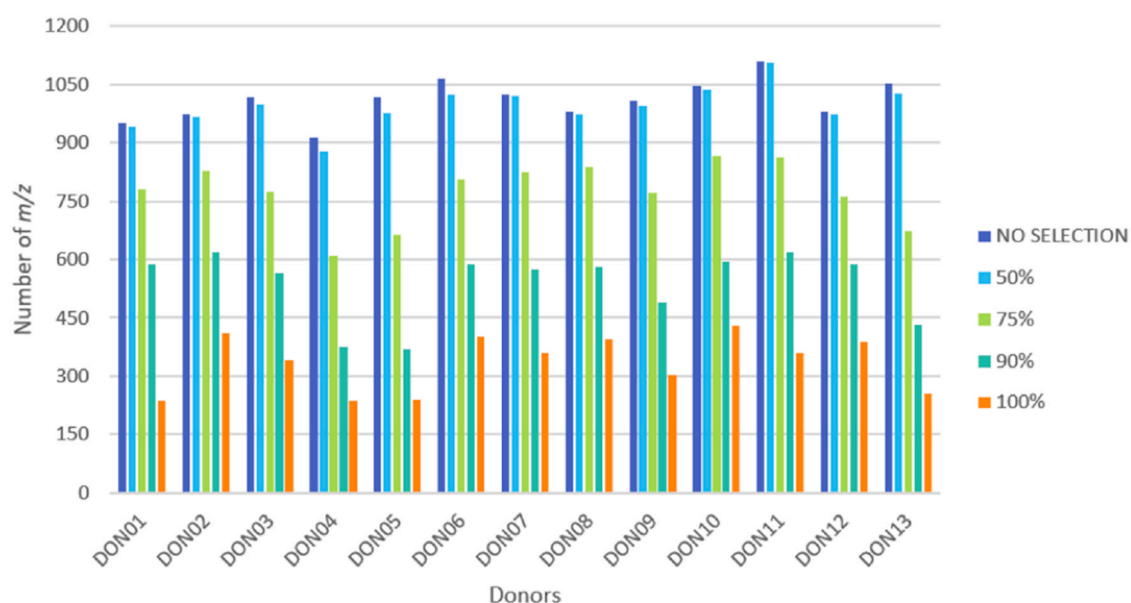

Fig. 7. Summary of the number of *m/z* (variables) present in the fingermarks of the 13 donors over a one-month timespan according to their percentage of stability among the analysed fingermarks (colour labels). For example, light green bars indicate the number of *m/z* (compounds) that have been detected in 75% of the analysed fingermarks.
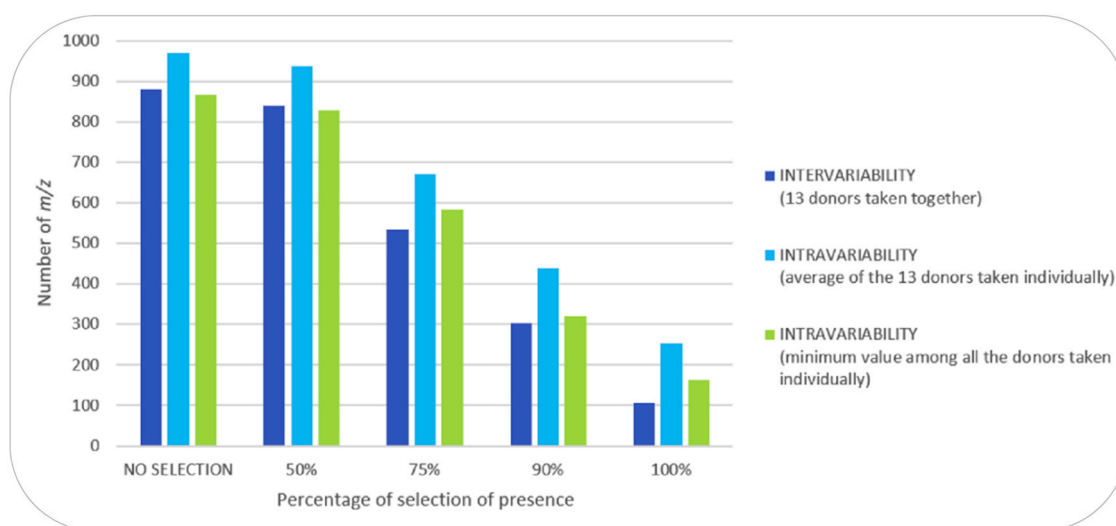
Fig. 8. Number of *m/z* (compounds) present in a systematic manner in the collected fingermarks of all the donors (intervariability) vs the average number of *m/z* (compounds) detected for each specific donor (intravariability) and the minimum value of *m/z* detected among the intravariability.

4.2. Impact and outcomes for the forensic and the medical fields

This study has demonstrated that there is a significant percentage of *m/z* values that can be specific to the fingermarks provided by one donor or common to several individuals. Metaphorically, this may be considered as a molecular signature. For each individual, it is possible to isolate hundreds of *m/z* whose presence is verified in the majority of his·her fingermarks along the year. If one considers these compounds as representative of the individual (incl. its lifestyle and metabolism), therefore, two types of molecular signature can be drawn: an individual one, specific to a donor and his·her fingermarks; and a collective one, composed of *m/z* variables that are detected in the fingermarks of a pool of donors.

For the forensic field, these results offer original scientific knowledge about the intravariability of composition of fingermarks collected from several donors over a one-year timespan. It also offers outcomes for the researchers involved in the development of fingermark detection techniques. Indeed, in this field, it is often asked to characterize the capacity of donors to provide fingermarks reacting more or less with a specific detection technique, and classified according to their donorship (e.g., good, average or bad donor) [27]. Using the concept of collective molecular signature, it may be possible to form representative groups of donors whose fingermarks would react in a comparable manner to fingermark detection techniques, which is still a challenge today [22,27,34,35,51].

Finally, the consistency of the composition of the fingermarks over the year also open doors in the investigative field of forensic science. It is reasonable to assume that the chemical composition of fingermarks could help differentiating donors based on the molecular signature [22]. Further data treatments are currently conducted in that regard.

The results of this research could also be extrapolated to the biomedical field. Indeed, the changes in composition highlighted for each donor open up prospects for the use of fingerprints for diagnostic purposes. Further research investigating more in depth the cause of the changes observed in the fingermark composition could help establishing links between a molecular signature (restricted or not) and a pathology of interest [41,43], as it has been seen that there is a consistency of composition during the year. One can suppose that abnormal changes in this composition could help detecting pathologies.

5. Conclusion

The aim of this study was to investigate the intravariability of the composition of fingermarks among a pool of thirteen donors composed of men and women of varying ages, over one year, and using MALDI-MSI.

Overall, a qualitative and quantitative degree of consistency was observed for each donor. On average, 25–45% of the detected components (*m/z*) are found in all the fingermarks left by a given individual over the year.

Also, the results showed no evidence of the impact of seasonal change or the time of the day the fingermarks were deposited, on the composition of the papillary residue. Other factors are more likely at the origin of these variations, such as physiological changes, emotions, and health or lifestyle habits.

When considering the compounds detected among all the donors, up to 34% of the *m/z* detected are common to all the deposited fingermarks.

These findings are of valuable interest for many fields. In forensic science, besides gaining additional fundamental knowledge about the composition of the papillary residue, this could help defining pools of donors for fingermark detection reagents research. In biomedicine, links could be established between fingermark composition and pathologies, providing hence original and non-invasive detection protocols.

Finally, further research is currently ongoing to determine if the set of *m/z* specific to the fingermarks left by a donor could help differentiating individuals, therefore bringing relevant information in an investigative context.

CRediT authorship contribution statement

Marie Gorka: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Aurélien Thomas:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Andy Bécue:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.forsciint.2022.111380.

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