**Supplementary material**

Table S1. Seasonally averaged values for air temperature (Temp.), relative humidity of air (Rel. Hum.), wind velocity (Wind. vel.) and pollutant gases (ozone, nitrogen dioxide, ammonia and nitric acid vapour), and seasonally accumated value for rain, measured at Sanabria Lake during the sampling period (June 2016 - December 2017).

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Season** | **Temp. (°C)** | **Rel. Hum. (%)** | **Rain (mm)** | **Wind (m/s)** | **O3 (µg/m3)** | **NO2 (µg/m3)** | **NH3 (µg/m3)** | **HNO3 (µg/m3)** |
| **winter** | 6,5 | 64,6 | 348 | 2,1 | 71,9 | 0,8 | 0,2 | 1,0 |
| **spring** | 14,2 | 55,0 | 187 | 2,1 | 95,0 | 0,8 | 0,7 | 1,4 |
| **summer** | 19,8 | 52,3 | 35 | 2,2 | 77,4 | 1,5 | 0,7 | 1,8 |
| **autumn** | 10,3 | 67,0 | 226 | 1,5 | 69,5 | 1,0 | 0,2 | 1,0 |

Table S2. Individual polar compounds concentrations in PM10 of Sanabria.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Compound | mean(ng m-3) | min(ng m-3) | max(ng m-3) | SD |
| Diacids | Succinic acid C4 | 5.4 | <0.7 | 13.6 | 3.4 |
| Glutaric acid C5 | 1.3 | <0.3 | 6.3 | 1.0 |
| Adipic acid C6 | 1.1 | <0.1 | 2.8 | 0.7 |
| Pimelic acid C7 | 0.6 | <0.2 | 1.5 | 0.4 |
| Suberic acid C8 | 0.5 | <0.2 | 1.9 | 0.6 |
| Azelaic acid C9 | 1.5 | <0.4 | 4.7 | 1.1 |
| Pthalic acid | 3.0 | <0.4 | 8.9 | 2.3 |
| Terepthalic acid | 0.6 | <0.2 | 1.8 | 0.4 |
| Hydroxy/polyacids | Malic acid | 8.6 | <0.4 | 38.5 | 9.4 |
| Glyceric acid | 1.6 | <0.3 | 5.8 | 1.4 |
| SOA tracers(α-pinene) | Cis-pinonic acid | 4.6 | 0.4 | 25.0 | 4.4 |
| Pinic acid | 3.7 | 0.4 | 11.5 | 3.0 |
| 3-hydroxyglutaric acid | 2.4 | <0.8 | 10.1 | 2.6 |
| (MBTCA)\* | 2.3 | <0.5 | 9.5 | 2.4 |
| SOA tracers(isoprene) | C5-alkene triol (1) \*\*C5-alkene triol (2)C5-alkene triol (3) | 2.3 | <0.2 | 9.3 | 2.9 |
| 1.2 | <0.2 | 4.8 | 1.5 |
| 4.9 | <0.2 | 22.1 | 6.5 |
| 2-methylglyceric acid | 4.1 | <0.2 | 18.2 | 4.2 |
| 2-methylerythritol | 8.5 | <0.1 | 30.7 | 9.2 |
| 2-methylthreitol | 18.0 | <0.1 | 94.5 | 22.6 |
| Biomass burning tracers | Levoglucosan | 27.4 | 1.4 | 164 | 38.5 |
| Mannosan | 2.7 | <0.5 | 16.9 | 3.8 |
| Galactosan | 1.8 | 0.2 | 10.0 | 2.2 |
| Dehydroabietic acid | 1.9 | 0.4 | 18.2 | 3.0 |
| Fatty acids | n-C14 | 4.0 | 1.2 | 10.2 | 2.0 |
| n-C15 | 2.7 | 0.6 | 8.1 | 1.3 |
| Palmitic acid n-C16 | 15.3 | 6.8 | 32.5 | 7.1 |
| Estearic acid n-C18 | 5.6 | 2.7 | 16.6 | 3.3 |
| n-C19 | 0.8 | <0.3 | 5.2 | 0.8 |
| n-C20 | 1.2 | <0.3 | 3.9 | 0.8 |
| n-C21 | 0.2 | <0.3 | 1.1 | 0.3 |
| Alkenoic acids | Oleic acid | 5.1 | 2.1 | 16.0 | 3.2 |
| Linoleic acid | 3.0 | 0.5 | 27.3 | 4.6 |
| Sugars  | α-glucose | 8.9 | 1.2 | 31.6 | 8.8 |
| β-Glucose | 10.8 | 1.6 | 38.4 | 10.9 |
| sucrose | 2.9 | <0.1 | 13.1 | 3.3 |
| trehalose | 2.6 | <0.2 | 7.9 | 2.3 |
| sugar alcohols | xylitol | 1.5 | <0.1 | 7.7 | 2.2 |
| mannitol | 20.5 | 1.6 | 79.1 | 19.8 |

\*MBTCA: 3-methyl-1.2.3-butanetricarboxylic acid

\*\*C5-alkene triols: cis-2-methyl.1.3.4-trihydroxy-1-butene (1). trans-2-methyl.1.3.4-trihydroxy-1-butene (2) and 3-methyl-2.3.4-trihydroxy-1-butene (3).

Table S3. Compounds analyzed in Fraction 2 and concentrations in Sanabria.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Compound | mean(ng m-3) | Min(ng m-3) | Max(ng m-3) | SD  |
| Aliphatics | n-C20  | 0.9 | 0.3 | 4.9 | 0.8 |
| n-C21 | 0.7 | 0.0 | 1.9 | 0.4 |
| n-C22 | 0.6 | 0.0 | 2.6 | 0.5 |
| n-C23 | 1.3 | 0.3 | 5.4 | 1.0 |
| n-C24 | 1.1 | 0.3 | 4.1 | 0.7 |
| n-C25 | 1.6 | 0.4 | 4.0 | 0.9 |
| n-C26 | 1.0 | 0.3 | 2.0 | 0.4 |
| n-C27 | 1.8 | 0.3 | 4.0 | 1.0 |
| n-C28 | 0.7 | 0.3 | 1.4 | 0.3 |
| n-C29 | 1.8 | 0.3 | 5.0 | 1.2 |
| n-C30 | 0.6 | 0.1 | 1.4 | 0.3 |
| n-C31 | 1.3 | 0.2 | 4.2 | 0.9 |
| n-C32 | 0.5 | 0.1 | 1.5 | 0.3 |
| n-C33 | 0.6 | 0.1 | 1.6 | 0.4 |
| n-C34 | 0.5 | 0.1 | 1.7 | 0.4 |
| PAHs | Phenanthrene | 0.042 | <0.002 | 0.470 | 0.078 |
| Anthracene | 0.001 | <0.005 | 0.021 | 0.004 |
| Fluorantene | 0.032 | <0.002 | 0.127 | 0.025 |
| Pyrene | 0.028 | <0.003 | 0.114 | 0.022 |
| Benzo(a)Anthracene | 0.009 | <0.003 | 0.039 | 0.010 |
| Crysene | 0.035 | <0.003 | 0.133 | 0.035 |
| Benzo(b+j)Fluoranthenes | 0.035 | <0.004 | 0.168 | 0.039 |
| Benzo(k)Fluoranthene | 0.023 | <0.004 | 0.149 | 0.033 |
| Benzo(e)Pyrene | 0.022 | <0.002 | 0.144 | 0.034 |
| Benzo(a)Pyrene | 0.010 | <0.008 | 0.070 | 0.020 |
| Indene(1.2.3-cd)pyrene | 0.023 | <0.004 | 0.166 | 0.039 |
| Dibenzo(a.h)anthracene | 0.003 | <0.003 | 0.021 | 0.005 |
| Benzo(g.h.i)perylene | 0.027 | <0.003 | 0.154 | 0.034 |
| Coronene | 0.008 | <0.007 | 0.056 | 0.013 |
| Retene | <0.002 |  |  |  |
| Quinones | 9-fluorenone  | 0.006 | <0.002 | 0.074 | 0.019 |
| Antraquinone | 0.045 | <0.001 | 0.503 | 0.092 |
| Benzo(a)Fluorenone | 0.002 | <0.002 | 0.015 | 0.003 |
| Benzo(b)Fluorenone | 0.002 | <0.002 | 0.009 | 0.002 |
| Benzanthrone | 0.002 | <0.002 | 0.018 | 0.004 |
| Hopanes | 17(H)α-21(H)β-29-norhopane | 0.005 | <0.002 | 0.059 | 0.014 |
| 17(H) α -21(H)β-hopane | 0.006 | <0.002 | 0.065 | 0.016 |

**Analytical method**

After spiking with surrogate standards, filter was extracted in triplicate for 15 minutes with dichloromethane:methanol (2:1; v/v) under ultrasonication. Each extract was filtered and concentrated to 1 mL.

Polar compounds (Fraction 1) were derivatized to their trimethylsilyl esters as follows:

25 µL of the extract were evaporated until dryness under nitrogen, then 25 µL of BSTFA/TMCS, 25 µl of isooctane, 10 µl of pyridine and 5 µl of internal standard, palmitic acid-d31 were added, and then kept at 70°C during 1 hour.

2 µL of this solution were splitless injected into a GC/MS Agilent 7890/5977A, equipped with a DB5MS column (60m, 0.25 mm x 0.25 µm). MS detector operated in electronic impact ionization mode at 70eV and SIM.

Following fragment ions were used for the quantification of compounds: *m/z* 247 for succinic acid, *m/z* 251 for succinic-d4 (surrogate standard), *m/z* 261 for glutaric acid, *m/z* 275 for adipic acid, *m/z* 289 for pimelic acid, *m/z* 309 for suberic acid, *m/z* 295 for azelaic acid, *m/z* 295 for pthalic and terepthalic acids, *m/z* 245 for malic acid, *m/z* 292 for glyceric acid, *m/z* 171 for cis-pinonic and pinic acids, *m/z* 349 for 3-hydroxyglutaric acid, *m/z* 405 for MBTCA, *m/z* 231 for C-5 alkene triols, *m/z* 219 for 2-methylglyceric acid and tetrols, *m/z* 204 for levoglucosan, mannosan, α- and β-glucose, *m/z* 217 for galactosan, xylitol and sedoheptulosan (surrogate standard), *m/z* 239 for deydroabietic acid, *m/z* 285 for n-C14 acid, *m/z* 299 for n-C15 acid, *m/z* 313 for n-C16 acid, *m/z* 327 for n-C17 acid, *m/z* 341 for n-C18 acid, *m/z* 355 for n-C19 acid, *m/z* 369 for n-C20 acid, *m/z* 389 for n-C21 acid, *m/z* 344 for palmitic acid-d10 (IS), , *m/z* 319 for mannitol, *m/z* 337 for linoleic acid, *m/z* 339 for oleic acid, and *m/z* 361 for sucrose and trehalose.

Peak identification was done by comparison of retention times with those of authentic standards when available, comparison of mass spectra with literature and library data.

Calibration curves (internal standard method) were constructed by analyzing aliquots of a stock solution of authentic standards in methanol, evaporated and derivatized in the way shown above. Results were corrected by the recovery of surrogate standards succinic acid-D4 and sedoheptulosan.

No standards were available for 2-methyl glyceric, glyceric acids, 3-hydroxyglutaric acid, MBTCA, xylitol, mannitol, dehydrabietic acid, C5 alkene triols, 2-methylthreitol, 2-methylerytritol, sucrose and trehalose that were tentatively identified by their mass spectra and comparison with literature data.

For those compounds whose standards were not available, succinic or α-glucose curves were applied for semi-quantification.

The remaining extract was concentrated under nitrogen and re-dissolved in 0.5 mL of hexane:dichloromethane (9:1 v/v) for aliphatics, hopanes, quinones and PAHs analysis (Fraction 2).

A clean-up procedure on 1 g of activated alumina was applied. Apolar compounds were eluted with 4 ml of hexane:dichloromethane (9:1 v/v), then 4 ml of hexane:dichloromethane (1:2 v/v).

The obtained fraction was concentrated to 50 µL, internal standard (pyrene-d10) was added and then splitless injected into a GC/MS Agilent 6890/5975B, equipped with a DB5MS column (30m, 0.25 mm x 0.25 µm), operanting in SIM mode.

Following fragment ions were used for the quantification of compounds: *m/z* 85 for aliphatics n-C20 to n-C34, *m/z* 66 for n-C24-d50 (surrogate standard), *m/z* 178 for phenanthrene and anthracene, *m/z* 202 for fluoranthene and pyrene, *m/z* 228 for benzo(a)anthracene and pyrene, *m/z* 252 for benzo(b+j)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene and benzo(a)pyrene, *m/z* 276 for indene(1,2,3-cd)pyrene and benzo(g,h,i)perylene, *m/z* 278 for dibenzo(a,h)anthracene, *m/z* 300 for coronene, *m/z* 219 for retene, *m/z* 188 for anthracene-d10 (surrogate standard), *m/z* 212 por pyrene-d10 (internal standard), *m/z* 240 for benzo(a)anthracene-d12 (surrogate standard), *m/z* 264 for benzo(k)fluoranthene-d12 (surrogate standard), *m/z* 288 for benzo(g,h,i)perylene-d12(surrogate standard), *m/z* 180 for 9-fluorenone, *m/z* 208 for anthraquinone, *m/z* 230 for benzo(a)fluorenone, benzo(b)fluorenone and benzanthrone, *m/z* 191 for hopanes.

An internal standard method was used for quantification. No standards were available for benzo(b)fluorenone, benzanthrone and hopanes. Calibration curves of benzo(a)fluorenone and benzo(a)pyrene were used for semi-cuantification of quinones and hopanes respectively.

Analytical parameters of the method are summarized in Tables S3 and S4.

Table S3. Analytical parameters of identified polar compounds, and selected ions in MS detection.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Compound | Ions(m/z) | Linear range (ng mL-1) | r2 | LOD (ng m-3) | RSD (%) |
| Diacids | Succinic-D4 (Surrogate std) | 251 |  |  |  |  |
| Succinic acid C4 | 247 | 0.02-2 | 0.9988 | 0.70 | 6 |
| Glutaric acid C5 | 261 | 0.02-2 | 0,9997 | 0.31 | 14 |
| Adipic acid C6 | 275 | 0.01-1 | 0.9999 | 1.3 | 11 |
| Pimelic acid C7 | 289 | 0.05-5 | 0.9999 | 0.48 | 8 |
| Suberic acid C8 | 303 | 0.02-2 | 0.9972 | 0.50 | 14 |
| Azelaic acid C9 | 295 | 0.02-2 | 0.9929 | 0.42 | 16 |
| Pthalic acid | 295 | 0.02-2 | 0.9956 | 0.48 | 7 |
| Terepthalic acid | 295 | 0.01-1 | 0.9974 | 0.15 | 11 |
| Hydroxy/polyacids | Malic acid | 245 | 0.02-2 | 0.9930 | 0.48 | 14 |
| Glyceric acid | 292 | 0.02-2 | 0.9995 | 0.31 | 13 |
| SOA tracers(α-pinene) | Cis-pinonic acid | 171 | 0.02-2 | 0.9988 | 0.35 | 14 |
| Pinic acid | 171 | 0.02-2 | 0.9999 | 0.18 | 13 |
| 3-hydroxyglutaric acid | 349 | 0.02-2 | 0.9996 | 0.84 | 14 |
| (MBTCA)\* | 405 |  |  | 0.50 | 16 |
| SOA tracers(isoprene) | C5-alkene triol (1) \*\*C5-alkene triol (2)C5-alkene triol (3) | 231231231 |  |  | 0.260.130.82 | 132413  |
| 2-methylglyceric acid | 219 |  |  | 0.33 | 13 |
| 2-methylerythritol | 219 |  |  | 0.52 | 13 |
| 2-methylthreitol | 219 |  |  | 0.55 | 3 |
| Biomass burning tracers | Levoglucosan | 204 | 0.02-2 | 0.9996 | 0.27 | 13 |
| Mannosan | 204 | 0.02-2 | 0.9999 | 0.05 | 9 |
| Galactosan | 217 | 0.02-2 | 0.9997 | 0.01 | 8 |
| Dehydroabietic acid | 239 |  |  | 0.04 | 14 |
| Sedoheptulosan (surrogate standard) | 217 |  |  |  |  |
| Fatty acids | n-C14 | 285 | 0.01-1 | 0.9954 | 0.81 | 14 |
| n-C15 | 299 | 0.02-2 | 0.9994 | 0.51 | 5 |
| Palmitic acid n-C16 | 313 | 0.02-2 | 0.9950 | 5.3 | 5 |
| n-C17 | 327 | 0.01-1 | 0.9981 | 0.91 | 17 |
| Estearic acid n-C18 | 341 | 0.01-1 | 0.9908 | 2.6 | 16 |
| n-C19 | 355 | 0.02-2 | 0.9996 | 0.50 | 18 |
| n-C20 | 369 | 0.02-2 | 0.9990 | 0.94 | 9 |
| n-C21 | 383 | 0.01-1 | 0.9988 | 0.17 | 18 |
| Palmitic acid-D10 (Internal Standard) | 344 |  |  |  |  |
| Alkenoic acids | Oleic acid | 339 | 0.05-5 | 0.9990 | 1.5 | 3 |
| Linoleic acid | 337 | 0.03-3 | 0.9997 | 0.15 | 8 |
| Sugars  | α-glucose | 204 | 0.02-2 | 0.9960 | 0.42 | 17 |
| β-Glucose | 204 | 0.02-2 | 0.9960 | 0.64 | 14 |
| sucrose | 361 |  |  | 0.42 | 12 |
| trehalose | 361 |  |  | 0.42 | 12 |
| sugar alcohols | xylitol | 217 |  |  | 0.02 | 11 |
| mannitol | 319 |  |  | 0.06 | 14 |

Table S4. Analytical parameters of identified apolar compounds, and selected ions in MS detection.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Compound | Ions(m/z) | Linear range (ng mL-1) | r2 | LOD (ng/m-3) | RSD (%) |
| Aliphatics | n-C20  | 85 | 0.1-10 | 0,9999 | 0.023 | 16 |
| n-C21 | 85 | 0.1-10 | 0,9999 | 0.029 | 22 |
| n-C22 | 85 | 0.1-10 | 0,9998 | 0.045 | 12 |
| n-C23 | 85 | 0.1-10 | 0,9995 | 0.041 | 8 |
| n-C24 | 85 | 0.1-10 | 0,9994 | 0.046 | 10 |
| n-C25 | 85 | 0.1-10 | 0,9993 | 0.051 | 9 |
| n-C26 | 85 | 0.1-10 | 0,9994 | 0.050 | 8 |
| n-C27 | 85 | 0.1-10 | 0,9994 | 0.053 | 8 |
| n-C28 | 85 | 0.1-10 | 0,9994 | 0.045 | 10 |
| n-C29 | 85 | 0.1-10 | 0,9995 | 0.050 | 11 |
| n-C30 | 85 | 0.1-10 | 0,9995 | 0.054 | 12 |
| n-C31 | 85 | 0.1-10 | 0,9998 | 0.054 | 9 |
| n-C32 | 85 | 0.1-10 | 0,9994 | 0.067 | 22 |
| n-C33 | 85 | 0.1-10 | 0,9996 | 0.031 | 22 |
| n-C34 | 85 | 0.1-10 | 0,9992 | 0.050 | 22 |
| n-C24-d50 (surrogate standard) | 66 |  |  |  |  |
| PAHs | Phenanthrene | 178 | 0.01-1 | 0,9880 | 0.002 | 5 |
| Anthracene | 178 | 0.01-1 | 0,9930 | 0.005 | 7 |
| Fluorantene | 202 | 0.01-1 | 0,9993 | 0.002 | 8 |
| Pyrene | 202 | 0.01-1 | 0,9996 | 0.002 | 9 |
| Benzo(a)Anthracene | 228 | 0.01-1 | 0,9990 | 0.003 | 3 |
| Crysene | 228 | 0.01-1 | 0,9996 | 0.003 | 6 |
| Benzo(b+j)Fluoranthenes | 252 | 0.01-1 | 0,9988 | 0.004 | 2 |
| Benzo(k)Fluoranthene | 252 | 0.01-1 | 0,9992 | 0.004 | 6 |
| Benzo(e)Pyrene | 252 | 0.01-1 | 0,9917 | 0.002 | 4 |
| Benzo(a)Pyrene | 252 | 0.01-1 | 0,9990 | 0.008 | 2 |
| Indene(1,2,3-cd)pyrene | 276 | 0.01-1 | 0,9993 | 0.004 | 3 |
| Dibenzo(a,h)anthracene | 278 | 0.01-1 | 0,9996 | 0.003 | 13 |
| Benzo(g,h,i)perylene | 276 | 0.01-1 | 0,9997 | 0.003 | 4 |
| Coronene | 300 | 0.01-1 | 0,9952 | 0.007 | 17 |
| Retene | 219 | 0.01-1 | 0.9996 | 0.002 | 20 |
| Anthracene-d10 (surrogate std) | 188 |  |  |  |  |
| Pyrene-d10 (internal std) | 212 |  |  |  |  |
| Benzo(a)Anthracene-d12(surrogate std) | 240 |  |  |  |  |
| Benzo(k)Fluoranthene-d12(surrogate std) | 264 |  |  |  |  |
| Benzo(g,h,i)perylene-d12(surrogate std) | 288 |  |  |  |  |
| Quinones | 9-fluorenone  | 180 | 0.01-1 | 0.9990 | 0.010 | 8 |
| Antraquinone | 208 | 0.01-1 | 0.9996 | 0.010 | 14 |
| Benzo(a)Fluorenone | 230 | 0.01-1 | 0.9971 | 0.002 | 11 |
| Benzo(b)Fluorenone | 230 |  |  |  | 10 |
| Benzanthrone | 230 |  |  |  | 7 |
| Hopanes | 17(H)α-21(H)β-29-norhopane | 191 |  |  |  | 7 |
| 17(H) α -21(H)β-hopane | 191 |  |  |  | 11 |