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Mathieu Le Meur, Laurence Mansuy-Huault, Catherine Lorgeoux, Allan Bauer, Renaud Gley, et al.. Spatial and temporal variations of particulate organic matter from Moselle River and tributaries: A multimolecular investigation. *Organic Geochemistry*, 2017, 110, pp.45-56. 10.1016/j.orggeochem.2017.04.003 . hal-01939684

HAL Id: hal-01939684

<https://hal.science/hal-01939684>

Submitted on 29 Nov 2018

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Spatial and temporal variations of Particulate Organic Matter from Moselle

River and tributaries: A multimolecular investigation

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ABSTRACT

The spatial and temporal composition of organic matter (OM) was investigated in the Moselle watershed (Lorraine, France). The spatial composition was studied using different stations along the river and four tributaries. In addition, one anchor station was used in order to better understand the temporal OM composition during different hydrologic regimes and seasons. The first part of the organic characterization consisted of the extraction of the lipidic OM with an automatic extractor. The extracts were analyzed for their lipidic fatty acids (Lip-FAs), polycyclic aromatic hydrocarbons (PAHs) and sterols using gas chromatography-mass spectrometry (GC-MS). The insoluble fraction was also analyzed with thermochemolysis-GC-MS (TMH-GC-MS) using tetramethylammonium hydroxide (TMAH) and lignin phenols, permethylated deoxy aldonic acids and refractory fatty acids (Ref-FAs) were analyzed. The results showed that one station, (Florange station) on the small Fensch stream tributary displayed variations in the composition of the molecular OM with higher microbial markers (C_{16:1}, C_{18:1w7}, C_{18:1w9}, coprostanol) inputted to the highly industrialized and urbanized areas in this small sub-catchment. The other stations showed rather similar organic composition (Lip-

FAs, Ref-FAs, sterols, lignin compounds, PAHs) due to the size of the catchment (10,000 Km²) or the integrative state of the suspended particulate matter (SPM). The regime flow involved a decrease in SPM OM content as well as a decrease of the palmitoleic acid/palmitic acid ($C_{16:1}/C_{16:0}$) ratio and an increase of (stigmastanol+sitostanol+stigmasterol+sitosterol)/(cholesterol+cholestenol) ($C_{29}/C_{27(ST)}$) ratio revealing the presence of more allochthonous OM. The increase in regime flow was also correlated with a growing contribution of more degraded OM in the SPM that could be related to the leaching of subsurface soils from the watershed or to the remobilization of surface sediments. Seasonal variations were also observed, with a stronger contribution of autochthonous production during low flow level in summer. This work shows the importance of OM characterization in SPM in order to better assess to the spatial and temporal OM variations in the water column.

Keywords: Suspended Particulate Matter, Moselle River, Particulate Organic Matter, Molecular Characterization

1 Introduction

Rivers transport large amounts of organic matter (OM), from the terrestrial environment to the seas. In the river, OM can be transported in both dissolved (DOM or dissolved organic carbon, DOC) and particulate forms (POC or POM). It is estimated that 0.4 Gt/yr is exported by rivers to the oceans and the amount in particulate form is estimated to 0.17 Gt (Ludwig et al., 1996; Cole et al., 2007). The OM in aquatic systems is composed of a wide variety of complex compounds, resulting from the diversity of the natural processes of synthesis and degradation. One method used to classify OM is to separate the allochthonous OM from the autochthonous OM (Filella, 2009). The autochthonous OM is formed exclusively in the water column and is composed of the residues of phytoplankton, algae and aquatic bacteria (Wetzel,

2001). In natural aquatic media or in aquatic media with low anthropogenic input, the allochthonous OM results mainly from the degradation of higher plants by bacteria and fungi and is transferred from soils to rivers by rainwater (Filella, 2009). However, in most European rivers, the allochthonous OM might also result from human activity and could originate from domestic or industrial wastewater, via urban surface run-off (Micić et al., 2011). In rivers with high anthropogenic pressure, the industrial input and domestic input bring organic and mineral micropollutants from which polycyclic aromatic hydrocarbons (PAHs) are an important and commonly studied family (Jeanneau et al., 2006; Qiao et al., 2014). Because the PAHs are sorbed on suspended particulate matter (SPM) and due to their low water solubility, they are rather well preserved in aquatic media (Punning et al., 2008). Then, they constitute relevant organic markers, particularly for an anthropogenic input.

One way to investigate the composition of OM in aquatic media and distinguish between the sources is the use of pyrolysis in combination with gas chromatography and mass spectrometry (Py-GC-MS). This technique, based on separation, has the advantage to identify the pyrolysis products of molecular markers, such as lignins, carbohydrates and fatty acids (FAs), permitting characterization of different organic contributions to soils, sediments, suspended matter and water (Grasset et al., 2009; Micic et al., 2011; Bertrand et al., 2013; Jeanneau et al., 2014). A classical analysis for deciphering the different inputs of OM to the water column consists of measurements of molecular-level lignin, either by extraction using cupric acid oxidation or by thermochemolysis-GC-MS (TMH-GC-MS) (e.g. Hernes et al., 2008; Frazier et al., 2003). The characteristics of these compounds can inform on the land use, and nature of crops or on the OM degradation and can also permit the differentiation between allochthonous and autochthonous sources (Dalzell et al., 2005; Hernes et al., 2008). In particular cases, especially for small watersheds (a few km²), such studies of lignin can decipher contributions from soil erosion and from river bank erosion (Jeanneau et al., 2014).

Most studies of lignin phenols concern DOM and some others deal with the molecular analysis of lignin compounds within suspended matter (POM; Ward et al., 2015; Bianchi et al., 2007). Other compounds can also be studied in order to unravel the composition of the OM. For example, carbohydrates such as fucose can be used to reveal a microbial contribution as fucose is rarely encountered in vascular plant (Jeanneau et al., 2014, Grasset et al., 2009). The analysis of the lipid extract by way of GC-MS is a second means of performing source apportionment. Boëchat et al. (2014) used lipidic fatty acids (Lip-FAs) in order to evaluate the influence of human activity and land use on OM composition. They found that, downstream of large cities, the Lip-FAs distribution was dominated by palmitic (C_{16:0}) and stearic (C_{18:0}) acids. These compounds were described as FAs from treated and raw sewage (Quéméneur and Marty, 1994; Réveillé et al., 2003). In a more extended study of POM composition, Medeiros et al. (2012) showed the variation along the Mullica River (NJ, USA). Upstream, terrestrial markers from higher plants were predominant and sharply decreased downstream and were replaced by microbial markers. During high flow, significant amounts of upstream markers were found downstream, revealing the downstream transport of terrestrial material. Most studies concerning molecular scale investigation of OM in rivers focus on DOM. However, in aquatic media, POM acts as a carrier of pollutants, such as metals (Bibby et Webster-Brown, 2006; Hua et al., 2012) or organic chemicals (Ni et al., 2008), especially hydrophobic contaminants (Luo et al., 2009). POM also regulates aquatic metabolism (Cole, 2013) and can act as a ligand for particle aggregation (Lartiges et al., 2001). The few studies about POM generally focus on one single molecular group and most of the time deal with spatial considerations rather than temporal variations. Furthermore, the multi-molecular investigation of OM composition is performed mainly on small streams. For example, Medeiros et al. (2008) studied rivers with seasonal mean discharge ranging between 0.5 and 38 m³/s.

This work aims at better understand the spatial and temporal variations of molecular OM in SPM from a relatively large watershed (11,500 km²). The spatial OM composition was investigated using different stations along the Moselle River and four tributaries. The different stations have different land use and the goal was to better understand the effects of land use on OM composition. The temporal variations were investigated using an anchor station sampled several times during different seasons and regime flow. The aims were to test the influence of different hydrologic and climatic conditions on the molecular OM composition in SPM. This work complements a previous study (Le Meur et al., 2015) where the SPM was fully characterized in terms of mineralogy and grain size distribution. Mineralogical markers demonstrated that SPM were rather homogeneous along the Moselle River, with no drastic variations from one station to another, and suggested that soil erosion was the main source of particles. Hydrological conditions were shown to play a stronger influence on elemental composition of SPM.

2. Material and methods

2.1. Study site

The study is located in the Moselle catchment in the northeastern France (Fig. 1; see also Le Meur et al., 2015). The mean annual temperature is 10°C and the mean annual precipitation is 775 mm. The Moselle watershed land use is heterogeneous with urban, cultivated and natural areas (Fig. 1 and Table 1). In order to evaluate the land use effect on the POM composition, we selected 10 stations along the Moselle River and four of its tributaries. These stations were selected on the basis of the land use. Fig. 1 and Table 1 show the urbanized parts of the Moselle catchment, using the Corine Land Cover layer (Corine Land Cover, 2006) and more details about the stations are provided in Le Meur et al. (2015). Among the 10 stations, Frouard (FRO) was selected as the anchor station to follow the water flow (Appendix A1) and seasonal variations in SPM properties. This station was selected due to the proximity to the

laboratory and the easy access to the river. On the Moselle River, the urbanization area is rather uniform (Table 1), with values ranging from 4.2-4.9% from the most upstream station Flavigny (FLA) and the most downstream station Thionville (THI). Among the stations, we considered that the station on the Fensch River (FLO in Florange) was a reference for a highly urbanized stream, due to the high proportion of urbanized areas (33%). The high level of contamination of Fensch water was reported in previous studies (Jeanneau et al., 2006, 2008; Montarges-Pelletier et al., 2007) and is due to the past industrial activity on one part and to the occurrence of direct wastewater input on the other.

2.2. Sampling procedure

SPM samples were collected between October 2012 and March 2015 (Table 2). For the collection of SPM, river water was pumped and sent to a continuous flow field centrifuge (CEPA Z-41 20000 RPM, equivalent 17000 g). The flow rate was set to 600 l/h. In order to collect high amounts of SPM (between 7 and 70 g of dried sample, depending on water turbidity), the centrifuge was run between 2 and 4 h for a given sampling campaign. The performance was checked during the whole sampling operation by measuring turbidity and grain size distribution of the raw water entering the centrifuge bowl and the exiting waters. The size cut-off of retained particles was approximate 3 μm and was checked with laser diffraction analysis of the centrifuge input and output at different times during the sampling procedure (Laser diffractometer SYMPATEC).

SPM samples were gently recovered from the Teflon plates covering the internal surface of the centrifuge bowl, and immediately frozen and freeze dried. The SPM content of the water column (mg/l) was also determined by filtering river water (100 to 1000 ml) through 0.22 μm Millipore © nitrocellulose membranes (weighed before use). Filters were oven dried (40 °C) overnight. SPM content was determined from the difference in weight. Three filter membranes were prepared for each water sample. The samples were selectively measured on

the basis of the land use properties at the station or the regime flow during the sampling.

2.3. Thermal analysis, OM content, Thermogravimetry (TG) and differential scanning calorimetry (DSC)

Thermal analysis was performed using differential scanning calorimetry (TG-DSC; Setaram Labsys Evo 1600) at the SOLEIL facilities (Gif sur Yvette, France). Samples (30 mg) were placed in an alumina crucible with an identical and empty crucible used as the reference, and heated from ambient to 1000 °C at 5 °C/min under an oxidizing atmosphere (flow rate 20 ml/min) of synthetic air (20% O₂ and N₂ balance). The data heat flow was corrected from the data of the standard measurement (measurement without sample).

2.4 Organic molecular characterization

Lipidic OM was extracted using dichloromethane (DCM) with an automatic extractor (Dionex ASE 350) at 100 °C and 10⁶ Pa. In order to avoid spectrometer damage due to the presence of elemental S, it was removed by the addition of metallic Cu. The insoluble fraction was analyzed using TMH-GC-MS with tetramethylammonium hydroxide (TMAH). This method is suitable in order to investigate the molecular OM and, in particular, the tracers utilized to separate terrestrial versus aquatic inputs (Frasier et al., 2003; Jeanneau et al., 2014). The solvent-extracted SPM was mixed with solid TMAH in excess (1:5 % wt.; Hatcher and Clifford, 1994). An aliquot (10-15 mg) was placed into a quartz tube and TMH-GC-MS (Hewlett Packard 6890-Hewlett Packard 5972) analysis carried out using a split/splitless injector. On-line flash pyrolysis at 620 °C was performed with a CDS 2000 Pyroprobe for 15 s. Pyrolysis products were separated on a DB 5-MS 60 m x 0.25 mm x 0.1 µm column. Samples were injected in splitless mode at 300 °C. The oven was cooled to 0 °C (held 0.5

min) by injecting liquid CO₂ and was programmed to 40 °C (held 10 min) at 45 °C/min, then to 315 °C (held 10.5 min) at 5 °C/min. Pyrolysis products were identified from GC retention times and mass spectra from comparison with the Wiley mass spectral library. Assignments were also carried out from comparison with published mass spectra of pyrolysis products (Challinor, 1995; Mason et al., 2012). A semi-quantification was applied for each sample. The peak area of the selected m/z value for each compound was integrated and corrected via a correction factor. The proportion of each compound class was calculated by dividing the sum of the areas of the compounds in the class by the sum of the peak areas of all analyzed compounds multiplied by 100. Eight lignin phenols were selected to describe the lignin composition, and six permethylated deoxy aldonic acids (glucose, mannose, galactose, xylose, rhamnose and fucose) to describe oses. The distribution of the Fatty acids in the refractory fraction (Ref-FAs) was also used (from n-C₆ to n-C₂₆).

The extracts were also analyzed with GC-MS for Lip-FAs, PAHs and sterols. Only the PAHs were quantified using internal standards and were analyzed separately. Four perdeuterated PAHs were added to each extract (naphthalene D₈, acenaphthene D₁₀, chrysene D₁₂, perylene D₁₂). In addition, four oxygenated-PAHs (O-PAHs) and nitrogenous-PAHs (N-PACs) were added (quinolone D₇, anthraquinone D₈, dibenzofuran D, 9Hand fluorenone D₈). PAHs are expressed in µg/g dry SPM. PAHs quantification was performed using a Shimadzu-2010 plus-QP2010 Ultra. This apparatus is equipped with a DB 5-MS column (60 m x 0.25 mm x 0.1 µm) and operated in selected ion monitoring (SIM) mode. Samples were injected in split mode (split ratio 1:5) at 300 °C. The GC oven temperature was programmed from 70 °C (held 2 min) to 130 °C at 15 °C/min, then from 130 °C to 315 °C (held 2 min) at 4 °C/min.

Sterols and Lip-FAs were analyzed qualitatively after derivatization using N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA)/trimethylchlorosilane (TMCS). Sterols and Lip-FAs were characterized using an Agilent GC7820/MS75. This apparatus was equipped

with a DB 5–MS column (60 m x 0.25 mm x 0.25 μ m) and operated in selected ion monitoring (SIM) mode. Samples were injected in split mode (split ratio 1:5) at 300 °C. The GC oven temperature was programmed from 70 °C (held 2 min) to 130 °C at 15 °C/min, then from 130 °C to 315 °C (held 2 min) at 4 °C/min.

3. Results

3.1 Thermal analysis, OM content, Thermogravimetry (TG) and differential scanning calorimetry (DSC)

The OM content of SPM was estimated from differential scanning calorimetry curves and thermal gravimetry curves (Appendix A2). In the 180–460 °C range, weight loss is essentially due to the exothermic combustion of OM. The content of OM varied from 6% to 12.6%, except for SPM from the FLO station which contained 22% (Appendix A2). The values were plotted against water discharge (Fig. 2) and showed a slight decrease with increase of water level. The decrease could be explained by the relative increase in lithogenic contribution to the SPM (see also Le Meur et al., 2015). The Total Organic Carbon (TOC) was also measured and the detailed results are presented in Le Meur et al. (2015). TOC values at FRO station also showed relative decrease with increase of the regime flow except for the highest regime flow (Appendix A3).

3.2. Macromolecular investigations

3.2.1. Fatty acids in the refractory fraction (Ref-FAs)

Fig. 3 displays the fatty acids distribution in the refractory fraction (Ref-FAs) for four samples collected in the same time period (November 2012), with similar regime flow. From upstream to downstream, the selected stations were Flavigny (FLA), Frouard (FRO) and Pont-

à-Mousson (PAM). The distribution obtained for FLO sample (our urban reference) was also plotted. The Fig. 3 shows that the distributions in these SPM samples were similar from one sample to another. Indeed, n -C₆ to n -C₂₆ alkanoic acids were observed in all the samples and showed a strong even/odd carbon number predominance. The composition was clearly dominated by palmitic acid (C_{16:0}) and stearic acid (C_{18:0}). However, slight variation could be observed from one station to another. At the downstream station PAM, palmitic acid and stearic acid appeared relatively more abundant, whereas their respective contributions appeared weakened for the most upstream station at Flavigny. SPM sample collected in Florange (FLO, Fensch River), displayed a relatively higher contribution for C_{16:1}, C_{18:1ω7} and C_{18:1ω9} (oleic acid) (Fig. 3). Due to the highly urbanized context, and the occurrence of several dozen examples of direct wastewater input to the Fensch River¹, the Florange sample was expected to display a drastically different fingerprint. However, the distribution in Fig. 3 shows an FA profile rather close to those of the Moselle SPM. The main differences occurred for C_{16:1}, C_{18:1ω7} and C_{18:1ω9}. Sewage water or domestic water can be fingerprinted by the presence of branched iso (i) and anteiso (a) C_{15:0} – acids and also C_{16:1} (Jardé et al., 2007). Only C_{16:1} could be observed with a higher contribution reflecting the bacterial contribution in FLO sample. The FRO station was sampled several times with different regime flows and seasons. The FA distribution displayed the predominance of palmitic and stearic acids similar to other stations. The SPM sampled during the summer low flow season (FRO jun13 35 m³.s⁻¹ and FRO jul13 15 m³.s⁻¹) showed higher contribution of C_{16:1} (Table 3).

3.2.2. Permethylated deoxy aldonic acids derived from carbohydrates

¹ Personal communication from A. Fall, in charge of Hydrology department of the CAVF (Fensch Valley cities network, communauté d'agglomération du Val de Fensch)

Series of permethylated deoxy aldonic acids in the pyrolysis products of all samples from the Moselle catchment were assigned on the basis of the predominant m/z 129 fragment in the mass spectra. These compounds are derived from carbohydrates (Fabbri et al., 1996; Mason et al., 2012) and are formed from the degradation of the glucose, galactose, xylose, rhamnose and fucose during the pyrolysis with TMAH. In all the samples, the most abundant compound was glucose, followed by galactose, xylose, rhamnose and fucose. These five permethylated deoxy aldonic acids are present in different proportions in the living organisms and can be used to differentiate sources (Grasset et al., 2009). Glucose is present in most of living organisms and at a higher level in vascular plants (Grasset et al., 2009). Mannose is present in higher proportion in gymnosperms than angiosperms (Cowie and Hedges, 1984). Conversely, xylose is produced in higher proportion by angiosperms than by gymnosperms (Wicks et al., 1991). Fucose is rarely observed in vascular plants but is present in higher proportion in some bacteria (Cowie and Hedges, 1984). The deoxy C_6/C_5 ratio (rhamnose+fucose)/(xylose arabinose) was defined in order to detect any variation in carbohydrate variations with regime flow or seasons and with different stations (Table 3).

Concerning spatial variability, the ratio did not show a clear trend. At FRO, we observed a slight increase during the summer low flow period. Jeanneau et al. (2014) observed evolution of the ratio with DOC. They showed that DOC was clearly higher than observed for our SPM. They also showed that DOC was between 0.4 and 0.2 in the soils, which is close to the ratio in our SPM.

3.2.3. Lignin-derived compounds

Like the Ref-FAs and polysaccharides, the thermochemolysis of the SPM produced a series of lignin-derived methylated monomers. These phenol compounds were semi-quantified and were sorted in three groups, vanillyl, syringyl and cinnamyl. From these compounds we can

277 separate the different plant tissues. Gymnosperm woody tissue contains mainly V units (80%)
 278 with C units whereas angiosperm woody tissues are characterized by V and S units in the same
 279 proportion with C units (Clifford et al., 1995; Challinor, 2001). Non woody tissues (grass,
 280 leaves, needles, stems) have V, C and S units in the same proportion. Several studies using
 281 CuO oxidation showed that the use of ratios such as C/V and S/V can permit the identification
 282 of terrestrial inputs (Hedges and Mann, 1979; Hedges et al., 1982). However, Clifford et al.
 283 (1995) also showed that the TMAH thermochemolysis can provide similar results without
 284 quantification using robust ratios. The ratio cinnamyl/vanillyl (C/V) was calculated following
 285 Hedges and Mann (1979). C/V is consistently higher in macrophyte and grass-derived plant
 286 tissue relative to woody tissue, making it a useful ratio for differentiating between the
 287 different vegetation types in a watershed. Table 3 shows C/V for all the SPM samples in the
 288 Moselle watershed. For the samples Flavigny, Frouard NOV12 and Pont-à-Mousson NOV12,
 289 which were sampled in the same range of regime flow, C/V was higher at Flavigny (0.58)
 290 than at Frouard (0.44). The value at Pont-à-Mousson was 0.49. The Richemont station
 291 showed high C/V ratio (1.12). The values of C/V ratio also showed a slight decrease with
 292 increase in regime flow for Frouard samples except for FRO nov13 ($C/V = 0.68$).
 293 Supplementary ratios were used to investigate the oxidative diagenesis of lignin. Indeed, the
 294 degradation of lignin compounds can be inferred from an increase in total acid phenols
 295 relative to the total aldehyde phenols (syringic acid to syringaldehyde ($Ad/Al(s)$) and vanillic
 296 acid to vanillin ($Ad/Al(v)$) ratios). The work of Hedges et al. (1982) showed that high values
 297 of these ratios can be explained by a degradation of lignin. $Ad/Al(v)$ in the watershed varied
 298 between 1.36 and 2.96 (Table 3), indicating different states of lignin degradation. In the
 299 Moselle River, for SPM collected at Frouard, $Ad/Al(v)$ slightly increased with water discharge,
 300 suggesting a contribution from more degraded lignin during flood events. Looking at the
 301 spatial variability, the SPM collected from the Madon and Meurthe Rivers, respectively at the

PSV and BOU stations, displayed lower values for the ratio, suggesting that the lignin degradation could be influenced by the Strahler order of the stream and/or by the land use.

3.3 Lipid fraction

3.3.1 Fatty acids in the lipid fraction (Lip-FAs)

Fig. 4 shows the fatty acid distributions in the lipid fraction (Lip-FAs) for samples collected in November 2012 (FLA, FRO and PAM), and also for FLO. The distributions in the selected SPM samples were very similar to those in the refractory fraction. In this fraction again, the FAs were dominated by palmitic acid ($C_{16:0}$) and stearic acid ($C_{18:0}$). However, we could observe n - C_6 to n - C_{32} alkanolic acids with a strong even predominance. Slight variation in distribution could also be observed from one station to another. $C_{18:1\omega7}$ was observed for the three stations on Moselle River but was not detected at FLO station. For the FLA and PAM stations, the $C_{20:0}$ to $C_{32:0}$ compounds were more represented than for the FRO and FLO stations. In addition, the Terrigenous/Aquatic Ratio (TAR) $(C_{28}+C_{26}+C_{24})/(C_{18}+C_{16}+C_{14})$ was higher for PAM (0.23) and FLA (0.24) than for FRO (0.01) and FLO (0.03), reflecting the higher contribution of terrestrial compounds at FLA and PAM. FLA station also displayed higher $C_{16:1}$ contribution (Table 4). FRO jul13 also shows higher $C_{16:1}/C_{16:0}$ ratio.

3.3.2 Sterol composition

The sterol family was composed of 5β -Cholestan- 3β -ol (coprostanol), cholest-5-en- 3β -ol (cholesterol), 24-ethylcholest-5-en- 3β -ol (sitosterol), 24-ethyl- 5β cholestan- 3α -ol (24-ethylepicoprostanol), 24-ethyl- 5β -cholestan- 3β -ol (24-ethylcoprostanol), 24-ethylcholesta-5,22E-dien- 3β -ol (stigmasterol), 24-Methylcholest-5-en- 3β -ol (campesterol), 24-ethyl-5 α -

cholestan-3 β -ol (sitostanol), 24-ethyl-5 α -cholesta-22E-dien-3 β -ol (stigmastanol), 24-methyl-5 α -cholestan-3 β -ol (campestanol), 5 α -cholestan-3 β -ol (cholestanol), 5 β -cholestan-3 α -ol (epicoprostanol). Fig. 5 shows the sterol distribution in the Moselle and Fensch samples. Among the twelve sterols in the SPM samples, coprostanol and cholesterol dominated. Coprostanol comes mainly from the degradation of cholesterol by bacterial activity in the digestive system of sheep, cattle, pigs, cats and humans (Leeming et al., 1996) and is the main sterol in human feces (60% of the steroids, MacDonald et al., 1983) and so is often used as a waste water treatment plant (WWTP) marker (Hatcher and McGillivray, 1979). Cholesterol is a ubiquitous compound and can be encountered in both plant and animal kingdoms. Different ratios can be used to identify any contamination in river waters. For example, values of coprostanol/cholesterol (Cop/Chol) > 0.5 are characteristic of human feces (Grimalt et al., 1990; Fattore et al., 1996; Reeves and Patton, 2005). In the Moselle catchment, the values obtained varied between 0.2 and 2.94. In most cases, the value was > 0.5, indicating the high contribution of coprostanol (Table 4). During summer and low flow regime (FRO JUN13, FRO JUL13, 35 m³.s⁻¹ and 15 m³.s⁻¹ respectively), Cop/Chol ratio was low, showing a strong terrestrial and/or an autochthonous contribution of sterols. Cop/Chol increased with flow regime, indicating that waste water was directly discharged into the Moselle River or the lower autochthonous OM contribution. Only two samples (FRO-jun13 and FRO-jul13) showed values of 0.2. FLO station displayed the highest Cop/Chol ratio (2.9). This value could be related to the WWTP located upstream of the sampling site on the Fensch River. The ratio was also high at BOU (2.4), PAM (2.9) and FRO (2.58 for November 12). BOU and PAM stations are downstream of the WWTP of Nancy and Pont-à-Mousson cities respectively.

The (stigmastanol+sitostanol+stigmasterol+sitosterol)/(cholesterol+cholestenol) ratio ($C_{29}/C_{27} (ST)$) can also be used in order to evaluate the proportion of allochthonous and

autochthonous OM (Nishimura and Koyama, 1977). Higher plants synthesize a C_{29} sterol, β -sitosterol (Huang and Meinschein, 1976). This compound can also be encountered in phytoplankton and notably in diatoms (Volkman, 1986, 2003). In contrast, C_{27} sterols have essentially an aquatic origin (Huang and Meinschein, 1976). The values of C_{29}/C_{27} (ST) increased with regime flow, indicating higher C_{29} contribution or lower C_{27} contribution (Table 4) and inform on the higher autochthonous OM during high flow regime. The high flow regimes SPM were sampled during the winter. In these winter samples, few diatoms were observed (Le Meur et al., 2015). In addition, brassicasterol and 24-methylenecholesterol were not observed in our samples. These sterols are typical sterols encountered in diatoms. The C_{29} should have a terrestrial origin in our SPM during the winter storm event samples or at least the decrease of autochthonous OM contribution.

3.2.3 PAHs composition

The 16 PAHs listed by the US Environmental Protection Agency (EPA) were quantified and some ratios calculated to provide an overview of the PAHs contamination through the catchment (Table 5). The sum of 8 PAHs concentrations in the SPM from Moselle catchment ranged between 2.3 and 7.7 $\mu\text{g/g}$. All the samples displayed lower 8 PAHs concentrations than the regulatory value of 8.649 $\mu\text{g/g}$ defined by the European legislation (recommended concentration to evaluate the quality of sediments and SPM in continental waters). The PAHs in SPM were dominated by heavy aromatic hydrocarbons (HMW-PAHs) from fluoranthene (Flt) to benzo(ghi)perylene (Bghi) (Table 5 and supplementary information 4). Indeed, the contribution of 4 to 6 ring PAHs accounted for 69 to 91% of the total PAHs concentration. The dominant PAHs at all the stations was fluoranthene. The sum of 16 PAHs quantified in the SPM did not show clear spatial trends in the Moselle catchment. No clear increase in PAHs content could be observed for samples collected in the vicinity of highly urbanized areas (FLO station for example) and also for FRO samples collected during different regime

flow (2.9 to 5.1 $\mu\text{g/g}$). Several ratios were tested to evaluate their variation in the catchment. The An/178 ratio (anthracene/(anthracene+phenanthrene)) (Budzinski et al. 1997), the BaA/228 ratio (benzo(a)anthracene/(benzo(a)anthracene+chrysene)) and the Fl/202 ratio (fluoranthene/(fluoranthene+pyrene)) (Yunker et al., 2002) are usually used to distinguish between petrogenic and pyrogenic inputs. Through the Moselle catchment BaA/228 varied between 0.53 and 0.58 (except for MIL 0.40 and FRO oct13 1.00) and was constant spatially and temporally. Fl/202 ratio also showed constancy, with values ranging from 0.54 to 0.59, except for FRO oct13 for which the value was 0.43 and for MIL (0.75). An/178 showed wider variation, with values ranging from 0.29 to 0.55. However, the variations did not show clear trend. The three ratios were rather stable along the Moselle catchment and with regime flow and highlighted the idea that PAH content in the SPM did not vary spatially and temporally. Thus, the quantification of PAHs in SPM is a useful tool for evaluating the anthropogenic pollution and for comparing catchments with a surface area of similar order. The Oxygenated-PACs (O-PACs) and nitrogenous-PACs (N-PACs) were also quantified in the SPM and the results are presented in the supplementary data (Appendix A4) as there was no clear trend between the stations, regime flow or seasons.

4. Discussion

4.1. Spatial Variability in OM composition, influence of land use

One of the goals of this study was to evaluate the sensitivity of OM markers in order to trace variations along the Moselle River. The Moselle watershed is characterized by the evolution of land use through the catchment (Table 1). Consequently, the OM markers were expected to vary through the catchment. One station, FLO station, showed variations of the molecular OM composition. This station showed higher relative contribution of $\text{C}_{16:1}$, $\text{C}_{18:1w7}$, $\text{C}_{18:1w9}$ for the Ref-FAs and $\text{C}_{16:1}$ is one of the compounds characteristic of sewage water (Jarde et al., 2007).

Other compounds such as coprostanol was also higher. Such higher contribution was expected, as this station on the Fensch River is characterized by high anthropogenic pressure in this small watershed (Jeanneau et al., 2006, 2008; Montarges-Pelletier et al., 2007, 2014). The mineral composition at Florange station is also impacted by the anthropogenic pressure with, in particular, the presence in high proportion of iron oxyhydroxides and trace metals such as lead and Zinc (Le Meur et al., 2015). The FLA station, which is the most upstream station sampled, also showed a significant contribution of anthropogenic markers such as $C_{16:1}$ and coprostanol besides the low urban area (6%). A domestic water contribution was also expected at this station, located in the Flavigny city. However, the Lip-FAs showed a high contribution from $C_{24:0}$ to $C_{30:0}$ and TAR ratio was also low. These observations reflect a relatively high terrestrial contribution as these compounds are believed to be components of higher plants wax (Rieley et al., 1991; Meyers, 2003).

The family of compounds corresponding to lignin derivatives also did not show a clear evolution along the course of the Moselle except for Richemont station. SPM from RIC station displayed C/V values higher than for the other samples (Table 3). This higher ratio could be related to the higher proportion of cultivated areas for the Orne watershed (67%). Some other studies have reported variation of C/V for the Mississippi River (Bianchi et al., 2007) and the Amazon River (Ward et al., 2015). However, in these large rivers, the quantity of exported OM is high and explains the variation in lignin composition. In order to decipher any variation in C/V through the Moselle watershed, it would be necessary to take into account the regime flow of the river and also report on the OM productivity and exportation.

The degradation state of lignin, observed through the $Ad/Al_{(v)}$ ratio showed more preserved lignin in the Madon and Meurthe Rivers. The lignin degradation could thus be affected by the Strahler order of the stream or the land use.

Other compounds such as PAHs did not show a clear trend in the Moselle catchment, with relatively low variation in the sum of the 8 PAHs and low variation in the different ratios calculated (An/178; BaA/228; Fl/202). This relative homogeneity could be a result of the global atmospheric pollution and its deposition as particles in the river. For Tianjin River, the absence of a trend between upstream and downstream stations was also reported by Shi et al. (2005). They found better spatial relationships in sediments with greater contamination close to industrialized areas. SPM from Tianjin River were also enriched in HMW PAHs (32% of total PAHs; Shi et al., 2005). Because they are more hydrophobic, HMW PAHs would more likely enter in the river in particulate form from soil run off or atmospheric deposition (Countway et al., 2003).

The characteristics of POM did not vary through the catchment and only smaller sub-catchments (e.g. Fensch) showed variation in relation with the extensive industrialization and urbanization. This similarity in composition could be the result of the size of the Moselle catchment, as it drains $> 10,000 \text{ km}^2$. The other explanation could come from the POM itself that appears to be more integrative than DOM. The mineral characterization of Moselle SPM also showed a relative homogeneity, with variations only encountered at Florange and Richemont (Le Meur et al., 2015).

4.2. Temporal variability of OM composition, influence of season and hydrological conditions

The other aim of this study was to decipher any variation in the OM composition with seasonality (mainly driven by temperature) and/or regime flow of the Moselle River. During low flow regimes at the FRO station, where the temperature was high, the samples were characterized by a higher deoxy C6/C5 ratio which indicates microbial contribution (Rumpel and Dignac, 2006). In addition, the number of diatoms during summer low flow regime is high (Le Meur et al., 2015). The C_{16:1}/C_{16:0} ratio is also high and monounsaturated FAs are major components of freshwater algae and bacteria (Cranwell, 1974, 1982; Volkman et al.,

1980). In addition the total OM content is high and the OM is relatively unaltered (low Ad/Al_(v) ratio). All these markers encountered in the extract and in the macromolecular OM are in accordance with an enhancement of autochthonous OM during the summer low flow level with high temperatures.

The increase in regime flow, sampled during the winter storm period involved a decrease in the markers cited above, which can be assigned to a greater contribution of allochthonous OM and/or by rapid degradation of OM. A clear decrease in POM content was also observed (Fig. 2). This can be assigned on one hand to the decrease in autochthonous OM as its production is high in warm seasons and its contribution to POM dominates at low flow periods. On the other hand, during high flow periods, allochthonous POM dominates. It can be assumed, that intense rain events provoke the contribution from subsurface soil horizons (a few cm), containing a lower amount of OM, or displaying higher degree of mineralization of OM (also see Le Meur et al., 2015). In addition, C/V ratio and Ad/Al_(v) indicated more degraded lignin during high flow level (Fig. 6). Another explanation could be the remobilization of sediments in the water column. Other studies have shown variation in DOM composition, with less degraded lignin mobilized during high flow level in small catchments (few km²; Dalzell et al., 2005; Hernes et al., 2008; Jeanneau et al., 2014). In their review, Marin-Spiotta et al. (2014) show that, during low flow, the DOM in the water column resembles deep OM from soil, whereas, during high flow, the DOM resembles surface soil DOM, suggesting different pathways during high and low water flow. Our results suggest that POM transfer from soil to river in a large catchment would not follow the same path as DOM. As for the spatial distribution, the PAHs content of SPM ($\Sigma 16$ PAHs and $\Sigma 8$ PAHs) does not show a clear trend with regime flow or with temperatures.

5 Conclusions

Molecular analyses of POM were performed in the Moselle catchment at different stations and during different flow regimes and seasons. Due to contrasted land use from upstream to downstream the Moselle watershed, SPM OM composition was expected to evolve. However, the OM composition was rather similar at the Moselle, Meurthe and Madon stations. Only one station, the FLO station, displayed variations in the POM chemistry with higher relative contribution of $C_{16:1}$ and coprostanol which are indicators of microbial contribution and sewage water. The Meurthe and Madon tributaries showed more preserved lignin through the $Ad/Al_{(v)}$ ratio. This observation suggest that the Strahler order of the stream or the land use can affect the lignin degradation. The PAHs showed slight variation through the catchment, highlighting the fact that a catchment of this size is integrative. This similarity can also come from the integrative status of the POM itself. SPM OM composition was also followed as a function of flow regime and seasons at FRO station. The increase of the limb of the hydrograph resulted in a decrease of OM content in SPM. In addition, the different lignin indicators (C/V and $Ad/Al_{(v)}$ ratios) revealed the presence of more degraded lignin at FRO station during high flow regime. These results could be explained by the higher contribution of allochthonous OM coming from the subsurface soil leaching or by the surface sediments remobilization. Seasonal variations were also observed with higher total OM content in SPM and high deoxy C_6/C_5 and $C_{16:1}/C_{16:0}$ ratios during low flow level in summer. These markers traduce the enhancement of autochthonous OM at FRO station during low flow level in summer

These results showed relative similarity of OM composition in SPM through the Moselle catchment with the exception of FLO station. However, we expected more contrasted OM composition because of the heterogeneous land use. The use of other markers such as Zn isotopic measurements could permit to better separate the different sources of SPM in the

watershed (SPM from urban, forest or farm areas). In addition, the regime flow sampling in this study was realized during different days and additional sampling during one storm event should be performed in order to better characterize the OM composition variations in relation with regime flow.

6 Acknowledgments

This study was performed in the context of the Zone Atelier Moselle (ZAM), which belongs to the French LTER network, and was financially supported by the French CNRS-INEE and Region Lorraine (CPER). The authors thank E. Rotureau and F. Fraysse for their contributions to manuscript reading. In addition, the authors would like to thank SARM-CRPG for chemical analyses. The authors also would like to thanks the two anonymous reviewers for their constructive comments.

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Table 1

A. Background data for the different stations (Corine Land Cover, 2006)

Code	Town	Sample site	Watershed surface area (km ²)	GPS coordinates	Urbanized area (%) ^a	Cultivated area (%)	Forest (%)
FLA	Flavigny	Residential area	2013	6°11'19.5''E 48°34'11.7''N	6.0	38.3	55.3
PSV ^b	Pont Saint Vincent	Agricultural catchment	1036	6°06'21.6''E 48°36'02.1''N	3.0	77.2	19.8
FRO	Frouard	Upstream of junction with Moselle	3768	6°08'11.8''E 48°46'30.4''N	6.1	49.1	43.6
BOU ^b	Bouxières aux dames	Downstream of Nancy city	3055	6°08'58.5''E 48°45'22.7''N	6.7	43.7	49.3
MIL	Millery	Residential area	6830	6°07'37.0''E 48°48'53.1''N	6.2	47.1	46.5
PAM	Pont à Mousson	Downstream the city limits	7209	6°02'39.0''E 48°56'06.1''N	6.1	47.6	45.9
ARG	Argancy	Downstream of Metz city	9213	6°11'59.9''E 49°08'38.6''N	6.0	52.5	40.9
RIC ^b	Richemont	Downstream of city limit	1276	6°10'23.5''E 49°16'48.6''N	6.0	67.0	26.5
FLO ^b	Florange	Industrial catchment	59	6°08'05.4''E 49°19'55.2''N	33.0	22.2	44.9
THI	Thionville	In Thionville city	10882	6°10'26.4''E 49°21'30.6''N	6.7	53.9	38.7

^a $\frac{\text{Urbanized surface (\%)}}{\text{Catchment surface (\%)}}$

^b Station on a Moselle tributary: PSV, Madon; BOU, Meurthe; RIC, Orne; FLO, Fensch.

Table 2 Water data for Moselle catchment (Hydro Eau France, 2015).

Station	Date	Water discharge (m ³ /s)		Water temperature (°C)	Turb. (NTU)	SPM (mg/l)
FLA	16/10/2012	71		6.6	3.5	2.9*
PSV (Ma)	29/11/2012	7		6.8	7.7±0.2	8.8±1.7
PSV (Ma)	20/12/2012	28		5.4	43.5±1.0	46.4±5.0
FRO	27/11/2012	82		7.8	2.8±0.2	2.1*
FRO	17/12/2012	397	(storm)	6.6	85.0±3.6	90.2±6.4
FRO	19/06/2013	35	(low water)	25.4	5.2±0.8	6.2±0.3
FRO	17/07/2013	15	(low water)	23.5	3.7±0.6	3.1±0.7
FRO	16/10/2013	394	(storm)	11	27.5±3	29.6*
FRO	8/11/2013	198		-	20.9±0.2	22.3*
FRO	18/12/2013	36	(low water)	4.8	3±0.3	5.6±1.7
FRO	15/01/2014	104		6	6.17±0.05	3.65±0.82
FRO	19/02/2014	124		6	32.9±1.8	16±3.9
FRO	16/10/2014	44	(low water)	-	-	-
BOU (Me)	15/05/2015	35		11.4	6	5.9±1.7
MIL	16/10/2012	136		9.9	4.6	4.1 ^b
PAM	20/11/2012	81		7.7	3.8	3.2 ^b
PAM	6/2/2013	475		4.8	37.2±1.2	36.2±6.0
ARG	13/11/2012	171		8.9	19.2	20.4 ^b
RIC (O)	30/04/2013	8		9.6	1.4	3.0±0.7
FLO (F)	9/10/2012	1		14.9	4.7	4.2 ^b
THI	6/12/2012	200		5.5	7.1±0.6	7.5±0.1

^a River water discharge data taken from the hydrometric station in Toul for FLA and FRO, in Pulligny for PSV, in Custine for MIL, PAM and ARG, in Rosselange for RIC, in Knutange for FLO, and in Hagondange for THI; Ma refers to Madon River, Me to Meurthe River, O to Orne River, and F to Fensch River. ^b SPM concentration extrapolated from turbidity values

Table 3 Data for the different samples from Moselle River watershed: regime flow (Q , $m^3 \cdot s^{-1}$); $C_{16:1}/C_{16:0}$ ratio; Deoxy C6/C5 ratio, C/V ratio; Ad/Al_(v) ratio

Station	Q (m^3/s)	$C_{16:1}/C_{16:0}$	Deoxy C6/C5	C/V	Ad/Al (v)
FLA	71	0.22	0.52	0.58	2.12
PSV* nov12	7	0.15	0.46	0.49	1.45
PSV* dec12	28	0.10	0.42	0.33	1.59
FRO jul13	15	0.36	0.57	0.50	1.38
FRO jun13	35	0.17	0.48	0.65	1.77
FRO dec13	36	0.24	-	0.42	1.44
FRO oct14	44	0.46	-	0.51	1.87
FRO nov12	82	0.16	0.55	0.44	1.86
FRO feb14	124	0.14	0.55	0.40	1.86
FRO nov13	198	0.61	-	0.68	2.96
FRO dec12	397	0.06	0.54	0.36	2.04
BOU	35	0.60	0.65	0.47	1.72
MIL	136	0.44	0.65	0.52	1.77
PAM nov12	81	0.10	0.55	0.49	2.24
PAM fev13	475	0.08	0.45	0.92	2.7
ARG	171	0.25	0.54	0.42	1.36
FLO	1	0.36	0.56	0.38	1.87
RIC	8	0.63	0.77	1.12	2.5
THI	200	0.34	0.54	0.34	1.76

Table 4

Coprostanol/Cholesterol, $C_{29}/C_{27(ST)}$ and $C_{16:1}/C_{16:0}$ from peak area of each product for the different Moselle catchment SPM samples in the lipidic fraction

Station date	Coprostanol/Cholesterol	$C_{29}/C_{27(ST)}$	$C_{16:1}/C_{16:0}$	Flow regime m ³ /s
FLA nov12	2.05	1.29	0.18	71
PSV nov 12	1.47	1.22	0.13	7
FRO nov 12	2.58	0.79	0.01	82
FRO jun13	0.21	0.28	0.43	35
FRO jul13	0.24	0.69	0.52	15
FRO oct 13	0.92	1.39	0.07	394
FRO feb14	1.14	1.49	0.32	124
MIL oct12	1.97	0.91	0.18	136
BOU mar15	2.41	0.99	0.19	35
PAM nov12	1.26	0.72	0.06	81
PAM fev 13	2.90	1.12	0	475
ARG nov12	1.03	1.22	0.13	171
FLO oct12	2.90	0.46	0.04	1
THI dec12	2.06	1.02	0.05	200

Table 5 PAHs in the Moselle SPM ($\mu\text{g}\cdot\text{g}^{-1}$)

Station	$\Sigma 16\text{PAHs}$	$\Sigma 8\text{PAHs}$	An/178	BaA/228	Fl/202	% of LMW	% of HMW
FLA	4.69	2.8	0	0.54	0.54	9.11	90.89
PSV nov 12	5.33	3.3	0.42	0.54	0.56	12.04	87.96
PSV dec12	4.95	3.07	0.37	0.55	0.58	10.91	89.09
FRO juil13	3.67	2.28	0.36	0.53	0.54	11.33	88.67
FRO jun13	4.71	2.98	0.36	0.53	0.56	10.43	89.57
FRO dec13	3.33	1.73	0.36	0.58	0.59	28.67	71.33
FRO jan14	5.12	2.59	0.39	0.57	0.59	30.26	69.74
FRO oct14	4.98	3.08	0.48	0.55	0.55	12.11	87.89
FRO feb14	2.96	1.87	0.39	0.54	0.54	8.52	91.48
FRO nov13	4.88	2.78	0.5	0.56	0.54	28.2	71.8
FRO oct 13	3.95	2.21	0	1	0.43	22.88	77.12
BOU	5.79	3.96	0.41	0.55	0.56	27.94	72.06
MIL	7.66	4.74	0.55	0.4	0.75	17.64	82.36
PAM nov 12	4.47	2.78	0.3	0.55	0.55	12.01	87.99
PAM fev13	4.66	2.94	0.29	0.51	0.59	10.22	89.78
ARG	3.61	2.17	0.3	0.57	0.58	12.19	87.81
RIC	3.97	2.48	0.46	0.53	0.55	21.42	78.58
FLO	4.36	2.59	0.31	0.54	0.56	11.95	88.05
THI	2.29	1.35	0	0.53	0.59	11.99	88.01

^aThe European Union guideline for the evaluation of contamination in sediments (Directive No. 2000/60/CE – circular DCE 2005/12) takes into account the sum of 8 PAHs for which the regulatory content values are (in $\mu\text{g/g}$): naphthalene (Na, 0.048), anthracene (A, 0.034), fluoranthene (Fl, 0.083), indeno(1.2.3-cd)perylene (IP, 0.560), benzo(b)fluoranthene (BbF, 0.170), benzo(k)fluoranthene (BkF, 0.140), benzo(a)pyrene (BaP, 7.600) and benzo(g,h,i)perylene (BgHi, 0.140); An/178: anthracene/(anthracene+phenanthrene); BaA/228, benzo(a)anthracene/(benzo(a)anthracene+chrysene); Fl/202, fluoranthene/fluoranthene+pyrene; HMW: 4 to 6 rings; LMW: 2-3 rings;

Figure captions

Fig. 1. Moselle River catchment showing the main rivers (blue); urbanized areas (grey), cultivated areas (yellow), and forest (green) (Corine Land Cover, 2006). This figure also shows sampling stations (red points). On Moselle River, from upstream to downstream: Flavigny (FLA), Frouard (FRO), Millery (MIL), Pont à Mousson (PAM), Argancy (ARG), Thionville (THI), on Madon River, Pont-Saint-Vincent (PSV), on Meurthe River, Bouxières aux dames (BOU), on Orne River, Richemont (RIC), and on Fensch River, Florange (FLO).

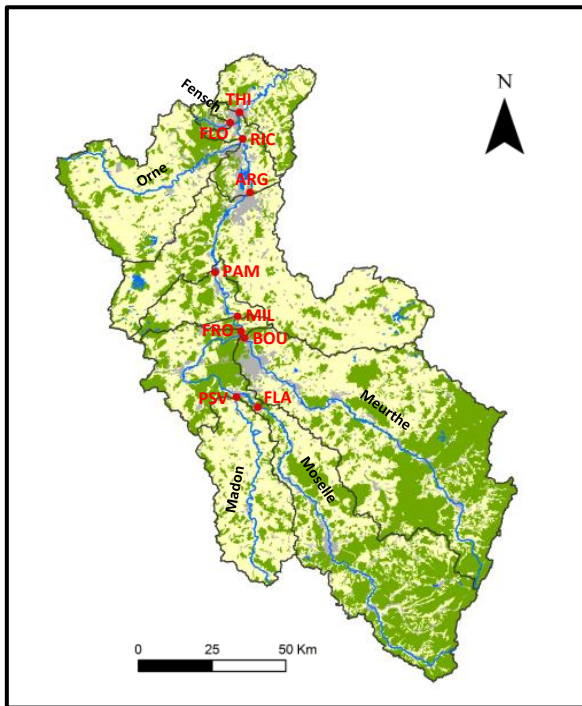
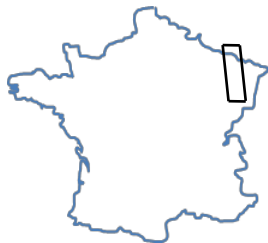
Fig. 2. Evolution of OM content of Moselle SPM (estimated from DSC and TG curves (see Supplementary material A2); black squares: all SPM samples; grey diamonds: SPM samples from Frouard station.

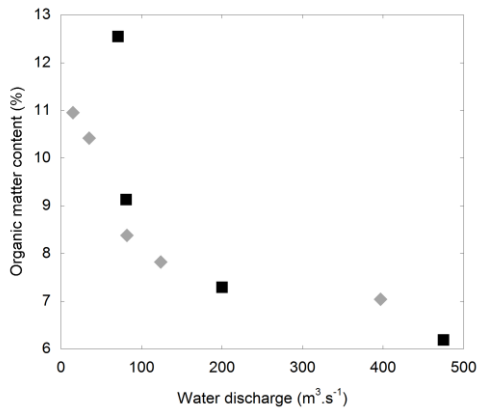
Fig. 3. Composition of Ref-FAs in Moselle SPM for samples collected in November 2012 from four different stations; Flavigny (FLA), Frouard (FRO), Pont-a-Mousson (PAM) and for Florange sample (FLO).

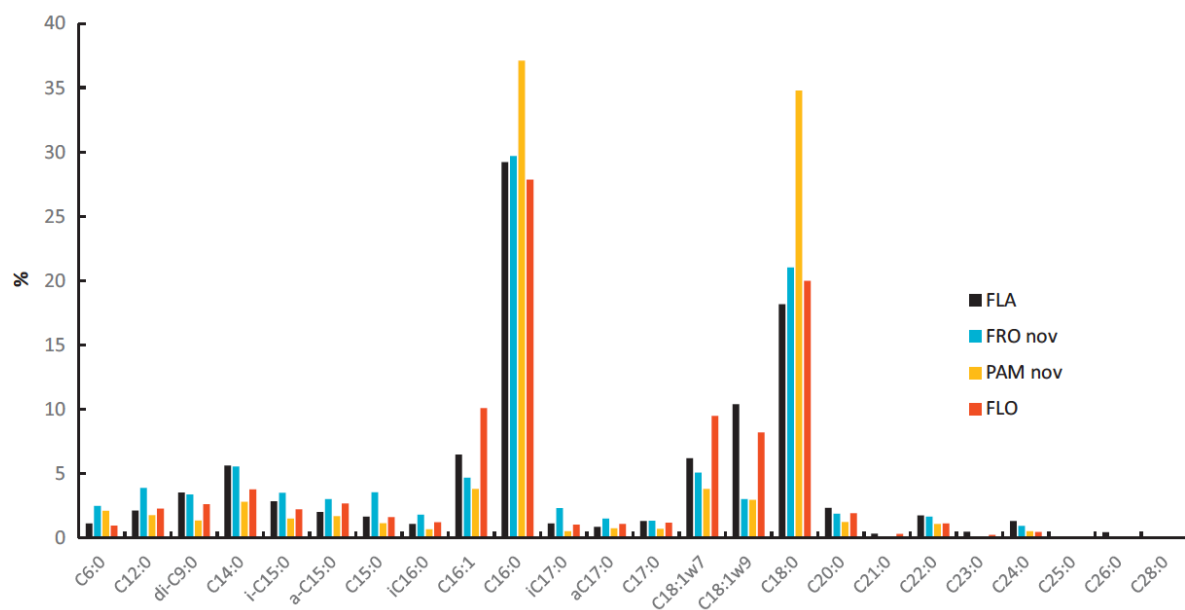
Fig. 4. Composition of Lip-FAs in Moselle SPM for samples collected in November 2012 from four stations: Flavigny (FLA), Pont-a-Mousson (PAM) Frouard (FRO) and Florange sample (FLO).

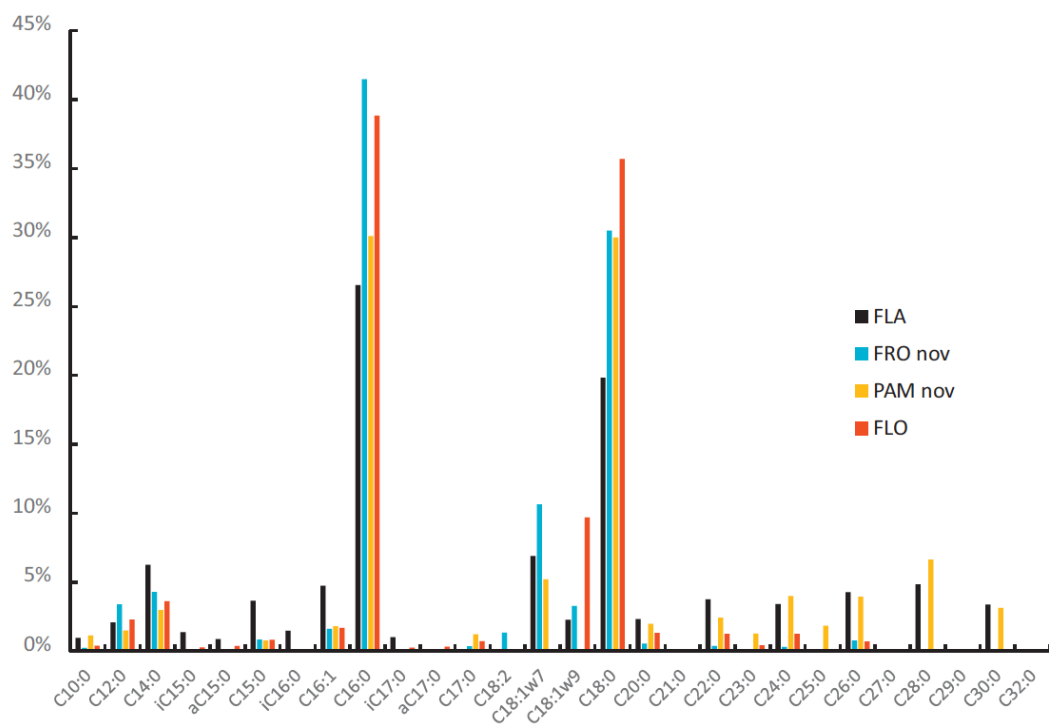
Fig. 5. Composition of sterols in Moselle SPM for samples collected from four stations: Flavigny (FLA), Pont-à-Mousson (PAM), Frouard (FRO) and for Florange (FLO).

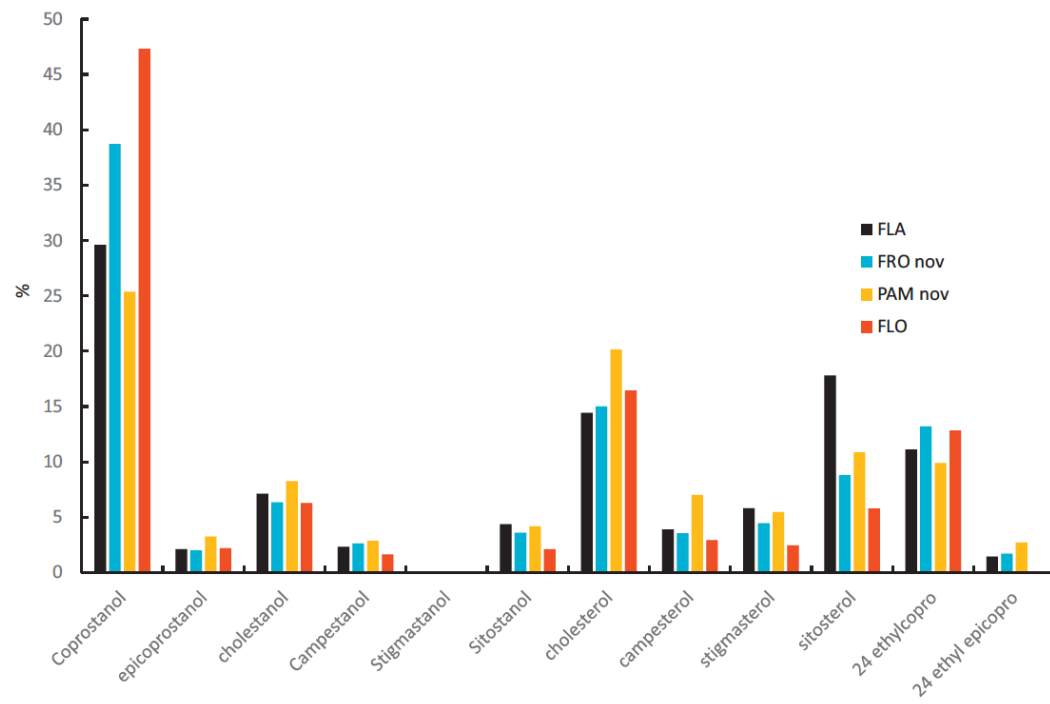
Fig. 6. SPM weight loss (%), C/V and Ad/Al_(v) ratios vs. water discharge (m³/s).

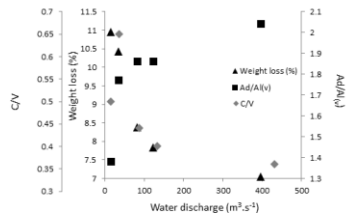












Highlights

SPM was collected along the Moselle River and for different regime flow and seasons.

SPM organic markers from the lipidic and the refractory fractions were characterized.

Fensch River showed higher microbial contribution, highlighting urbanized areas.

The Regime flow engendered OM content decrease and more degraded OM.

Seasonal variations were recorded with high autochthonous contribution during summer.