RESEARCH ARTICLE

Fluorescence spectroscopy to study dissolved organic matter interactions with agrochemicals applied in Swiss vineyards

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Abstract UV/Vis fluorescence spectroscopy was used to study the possible interactions of dissolved organic matter (DOM) with the herbicide glyphosate and copper-based fungicide used in vineyards. The study focused on the role of DOM in the transport of these micropollutants from parcels to surface waters (river, lake). Soil solution and river water samples were collected in the Lavaux vineyard area, western Switzerland. Their fluorescence excitation emission matrices (EEM) were decomposed using parallel factor (PARAFAC) analysis, and compared to their content in glyphosate and copper. PARAFAC analysis of EEM of both types of samples showed the contribution of protein-like and humic-like fluorophores. In soil water samples, complexes between fulvic-like and humic-like fluorophores of DOM, copper, and glyphosate were likely formed. In surface water, DOM-copper and glyphosate-copper interactions were observed, but not between glyphosate and DOM.

Keywords Dissolved organic matter · Glyphosate · Copper · Fluorescence spectroscopy · Parallel factor analysis

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Introduction

The diffuse pollution of water bodies by herbicide molecules is determined by their mobility and their ability to be retained and degraded in agricultural soils. Glyphosate [N-(phosphonomethyl)glycine] is the most used herbicide-active ingredient in the world. The extent of glyphosate sorption in soils depends on different parameters, such as soil constituents and pedoclimatic conditions. Despite its affinity for soil mineral phases (Piccolo et al. 1992), glyphosate has been proved to bind also to soil organic constituents, such as humic substances (Dousset et al. 2004; Roy et al. 1989). Humic substances (HS) are constituted of relatively low-molecular mass moieties bound together mainly by H-bonding and hydrophobic links (Sutton and Sposito 2005). Their structure is sensitive to ambient conditions such as pH, ionic strength, and also to their own concentration (Aoustin et al. 2001). At high concentration of salts and/or HS themselves, they exhibit more compact sphero-colloidal structures, also linked with a decrease in intramolecular repulsive forces. Under these conditions, a decrease in the surface area and the disappearance of certain structural micropores are observed (Alvarez-Puebla and Garrido 2005), diminishing their binding potential for pollutants.

Dissolved organic matter (DOM) corresponds to the dissolved fraction of the soil organic matter (SOM) smaller than 0.45 μm, generally composed of molecules of relatively low molecular weight (Zsolnay 2003). Organic compounds, such as pesticides, can bind to DOM, which can increase their solubility and their availability for microorganisms (Franco 2001; Pennington et al. 1991). The potential enhanced leaching of pesticides in soils depends on the retention-mobilization dynamics, which can be influenced by the nature of DOM, e.g., its humification degree, as well as the soil properties that determine the nature of ionic species present in solution, and also by pesticide physicochemical properties

(Franco 2001; Haberhauer et al. 2002). However, retention of DOM can also occur on surfaces of the clay fraction (clay minerals and sesquioxides) and thus reducing the availability of active site for contaminants (Kaiser and Zech 2000; Zsolnay 2003).

According to Piccolo et al. (1996), glyphosate gets linked to humic substances (HS) mainly by H-bonding, which the extent depends on their molecular size and degree of aromaticity. The adsorption of glyphosate was more important in the presence of humic molecules with high molecular size and/or low aromatic content. A large molecular size induces a higher sorption potential because of a more important number of possible hydrogen bonding. Moreover, a lower abundance of aromatic rings in humic macromolecules enhances their stereochemical flexibility, leading for the small herbicide molecule to an easier access to their inner reactive sites. Ternary complexes between glyphosate and humus are also likely to be formed with the intermediate of di- and trivalent bridging metal cations, such as Cu^{2+}, Fe^{3+}, or Al^{3+} (Morillo et al. 1997; Barrett and McBride 2006; Borggaard and Gimsing 2008). Indeed, the presence of copper has been shown to lead to glyphosate desorption from the external sites (Al–OH groups) of montmorillonite and the formation of Cu-glyphosate complexes, which show a high stability and a lower sorption affinity than glyphosate alone (Morillo et al. 1997). Inversely, glyphosate may enhance copper mobility by chelating with Cu^{2+} previously sorbed on both mineral and organic surfaces (Barrett and McBride 2006). Thus, copper could have a significant influence on glyphosate mobility and potential transfer to ground and surface waters and vice versa. The role of SOM in glyphosate sorption remains controversial: SOM may either decrease glyphosate sorption by blocking sorption sites or increase it, as higher SOM content seems to enhance sorption ability of poorly ordered Al and Fe oxides (Borggaard and Gimsing 2008).

To our knowledge, DOM has been little investigated as a possible carrier for glyphosate, especially in field studies. Recently, Mazzei and Piccolo (2012) studied the interactions of glyphosate with dissolved humic acids (HA) and fulvic acids (FA) at pH 5.2 and 7 by NMR spectroscopy. They confirmed the formation of H bonds between glyphosate carboxyl and phosphonate moieties and protonated oxygen functions in dissolved humic substances, with a larger binding for FA at pH 5.2 than for HA and for pH 7. Other spectroscopic techniques can be used to study the interactions of pollutants with DOM, such as UV/Vis fluorescence spectroscopy (Larrivee et al. 2003; Fu et al. 2007). This latter is largely used to characterize DOM (Kalbitz et al. 2000; Hudson et al. 2007; Nebbioso and Piccolo 2012). Furthermore, when combined with multivariate analysis, such as parallel factor (PARAFAC) analysis, a qualitative and quantitative discrimination of fluorophores present in complex samples of different origin and nature is

possible (Nebbioso and Piccolo 2012; Christensen et al. 2006).

The objective of this work was to study the role of DOM in the transport of glyphosate and copper from vineyard parcels to surface waters. To do so, the characterization of DOM by fluorescence spectroscopy of natural samples, soil water, and river samples was done using parallel factor analysis. In a second time, a principal component analysis was performed to assess possible interactions between fluorescence signatures of DOM and concentrations of these agrochemicals largely used in the studied vineyard area.

Material and methods

Natural samples

Soil solution samples from two vineyard parcels were collected in 2011 with porous ceramic suction cups (SDEC SPS200, Ø63 mm, porosity=1 μm) at four different depths at the bottom of each of the two parcels: 20, 40, 60, and 80 cm (Fig. 1). The applied tension was 0.6 bars, and the recovery of samples was done every week or more frequently during intense rainfall periods. Precipitation data were obtained from the Pully meteorological station (source: MeteoSwiss), located at 1.8 km from the two parcels (Fig. 1). More information about the soil properties of the studied area and the chemical composition of the soil solution samples can be found in a previous study (Daouk et al. 2013b). The Lutrive River was sampled during the year 2011 upstream and downstream the vineyard area, with two automatic samplers (ISCO 6712, Teledyne Inc.), equipped with polyethylene bottles and ultrasonic flow modules (Fig. 1). River mean discharge data and water chemical composition can be found in a previous study (Daouk et al. 2013c). It is worth to stress that sampling of soil solution and river was done during the same period, but not exactly at the same time. Indeed, soil solution-retrieved volumes depended on rainfall and for some sampling days and some depths no samples could be retrieved, whereas river water was always available.

Fluorescence spectroscopy and parallel factor analysis

Thirty-seven samples of both types were filtrated at 0.45 μm with nylon syringe filters and then analyzed by UV/Vis fluorescence spectroscopy. 3D excitation-emission matrices (EEM) were obtained with a spectrofluorometer (FluoroLog®-3, Horiba). Excitation wavelengths varied between 240 and 450 nm with a 5-nm increment and emission ones between 290 and 550 nm with a 2.5-nm increment. The relative intensities of the different fluorophores were calculated by dividing their fluorescence intensities by the DOC
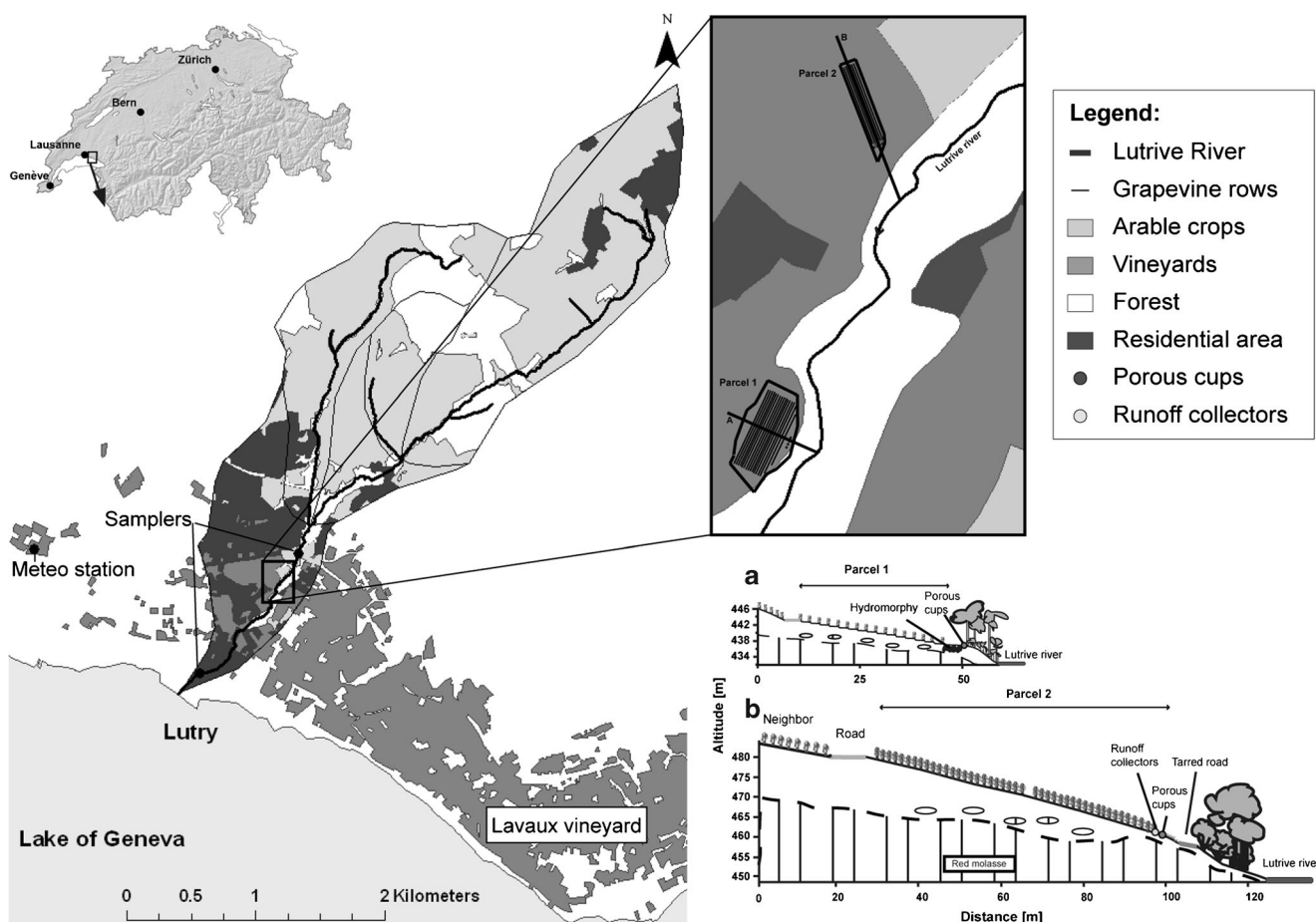
Fig. 1 Lutrive watershed in western Switzerland with its different land use, the location of the Pully meteorological station and of the two automatic samplers, as well as the one of the two investigated vineyard parcels and their transects with four porous cups located at their bottom at 20-, 40-, 60-, and 80-cm depth

content of the sample (see "Chemical analysis"). The humification index (HIX) was calculated as the ratio between the area of 435–480 nm and the area of 300–345 nm emission wavelength with an excitation at 254 nm according to Zsolnay et al. (1999).

A three-way analysis of fluorescence EEM, parallel factor analysis (PARAFAC), was done using a MATLAB (MathWorks©) routine developed at the University of Copenhagen (Bro 1997; Bro and Vidal 2011), and was adapted for GNU Octave (GNU General Public License). In order to apply PARAFAC analysis, attention should be paid to some factors affecting the PARAFAC decomposition, such as quenching and scattering (Christensen et al. 2006), and some preprocessing steps have been done. First, the absorbance of samples was checked to be less than 0.1 with an excitation wavelength of 360 nm to avoid any inner filter effects (Vieyra et al. 2009). Second, the Rayleigh and Raman first- and second-order bands were corrected using a simple algorithm. Lastly, fluorescence EEM were cut using a matrix-cutting function to constitute a three-way data array X in which they have the same dimensions (Christensen et al. 2006). For soil water

samples spectra, due to the presence of an instrument artifact at 240–245 nm of excitation during their acquisition, their EEM were cut at 260 for PARAFAC decomposition. The appropriate number of contributing factors for the model is defined by the quality of the spectral contribution separation, which can be expressed as a percentage named corcondia, for core consistency diagnostic (Bro and Kiers 2003). A value of 50 % would be problematic, whereas a value above 90 % can be interpreted as "very trilinear". Zhao (2011) suggests that a corcondia value above 60 % is acceptable.

Chemical analysis

The herbicide glyphosate and its metabolite aminomethylphosphonic acid (AMPA) were quantified by high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS), after their derivatization with FMOC-Cl followed by solid-phase extraction (SPE). Previously, the method was adapted from Hanke et al. (2008) and validated for the matrix effect that can occur in surface water and soil solution (Daouk et al. 2013a). The

method showed a LOQ of 10 ng/L and a good performance with recoveries between 86 and 109 % in environmental matrices. In soil solution samples, concentrations of glyphosate ranged between 0.02 and 12 μg/L and those of AMPA between 0.02 and 8 μg/L (Daouk et al. 2013b). In river water samples, they were varying between 0.01 and 4.97 for glyphosate and 0.015 and 0.62 μg/L for AMPA (Daouk et al. 2013c). Dissolved organic carbon (DOC) concentrations were measured with a C-analyzer (Liquitoc Elementar©). Concentrations varied between 2 and 24 mg/L in soil water samples and between 0.9 and 3.8 mg/L in river water samples (Daouk et al. 2013b, c). Trace metallic ions (Fe^{3+} and Cu^{2+}) were quantified by ICP-MS (ELAN® 6100 DRC, Perkin Elmer©) on selected samples. They were previously diluted with ultra-pure water acidified with HNO_3 (65 %) until reaching 2 % of the total sample volume, and H_2O_2 (35 %) was added to avoid possible interference with organic matter. A multi-elements standard solution (VI, Merck©) was used to build calibration curve, and indium-115 was used as an internal standard. Concentrations in soil water samples varied between 3.1 and 61.1 μg/L for Cu^{2+} and between 105.5 and 1183.1 μg/L for Fe^{3+} and in river water samples between 0.1 and 7.7 μg/L for Cu^{2+} and between 5.6 and 157.2 μg/L for Fe^{3+}.

Statistics

A principal component analysis (PCA) was performed using the R software (R Development Core Team 2009) and the ade4 package (Chessel et al. 2004). Prior to it, each of the parameters was normalized to zero mean and unit variance, by subtracting the mean value of the variable and by dividing by the standard variation, allowing them to have the same influence in the PCA. Pearson correlation coefficients (r) were obtained through the PCA, and signification level was 99 % ($\alpha = 0.01$). It is worth to stress that only 12 soil solution samples and 21 river downstream samples have been used for PCA. These were samples for which fluorescence analysis, ICP-MS, and HPLC-MS/MS analysis could have been performed.

Results and discussion

Soil water samples

Fluorescence excitation and emission matrices (EEM) of soil water samples exhibit mainly the presence of fulvic-like fluorophores, characterized by a peak A ($\lambda_{ex}:\lambda_{em} = 250:440$) and humic-like fluorophores, characterized by a peak C ($\lambda_{ex}:\lambda_{em} = 315:440$). Temporal dynamics of the relative intensities of these two fluorophores had the same tendency, with peak A showing, however, always

a higher relative intensity than peak C (Fig. 2). In a few samples, a peak B ($\lambda_{ex}:\lambda_{em} = 260:310$) was also observed, indicating a protein-like fluorophore (data not shown).

Parallel factor analysis (PARAFAC) applied to the soil solution samples showed the contribution of three components (Fig. 3). The two fluorophores representing fulvic- and humic-like substances (A and C) in EEM could not be discriminated with PARAFAC analysis, confirming the "new views" on humic substances (Sutton and Sposito 2005; Kelleher and Simpson 2006), i.e., low-molecular mass moieties bind together by interactions of relatively low energy, such as H bonds. However, PARAFAC decomposition discriminated two different peak couples (Fig. 3b, c): A1/C1 ($\lambda_{ex}:\lambda_{em} = 250:400/315:400$) and A2/C2 ($\lambda_{ex}:\lambda_{em} = 250:475/340:475$). This suggests that dissolved humic substances present in soil solution samples can be divided in low and high molecular weight (MW) compounds, A1/C1 and A2/C2, respectively, as the fluorescence signal of these latter is localized at longer wavelengths for both excitation and emission. Indeed, compounds with high MW were shown to fluoresce at longer wavelengths, in both excitation and emission, due to more important energy losses in their more complex structures (Kalbitz et al. 2000; Ohno et al. 2007). Furthermore, comparing fluorescence signals from the two different parcels, fluorophores C1 and C2 were of lower intensity in parcel 1 than in parcel 2 (data not shown). This could be explained by the steeper slope of this latter, inducing a more important role of throughflows in soil solution transport as previously shown (Daouk et al. 2013b). The component corresponding to the peak B was present in some of the samples in both parcels (Fig. 3a).

Lutrive River samples

PARAFAC analysis applied to EEM of samples taken in the Lutrive River revealed also the presence of three components linked to the presence of protein-like fluorophores (Fig. 4a) and humic-like ones (Fig. 4b, c). The first one is representative of the release coming from the urban area, whereas the two others are naturally occurring in freshwaters and linked to the breakdown of organic material (Hudson et al. 2007).

The two peaks representing humic substances could not be discriminated with the parallel factor analysis (peaks A and C, Fig. 4c). Indeed, relative intensities of these two fluorophores had the same temporal dynamics for both upstream and downstream sites (Fig. 5a, b). Like in soil solutions, peak A showed always a higher relative intensity than peak C (Fig. 5a, b). Though peak C2 was present (Fig. 4c), the peak C1 was absent (Fig. 4b). This could mean that low MW humic acid-like compounds did not reach the freshwater system, but high MW ones did, suggesting the transfer of these from soil surface layers to the Lutrive River by surface runoff during rainfall events.
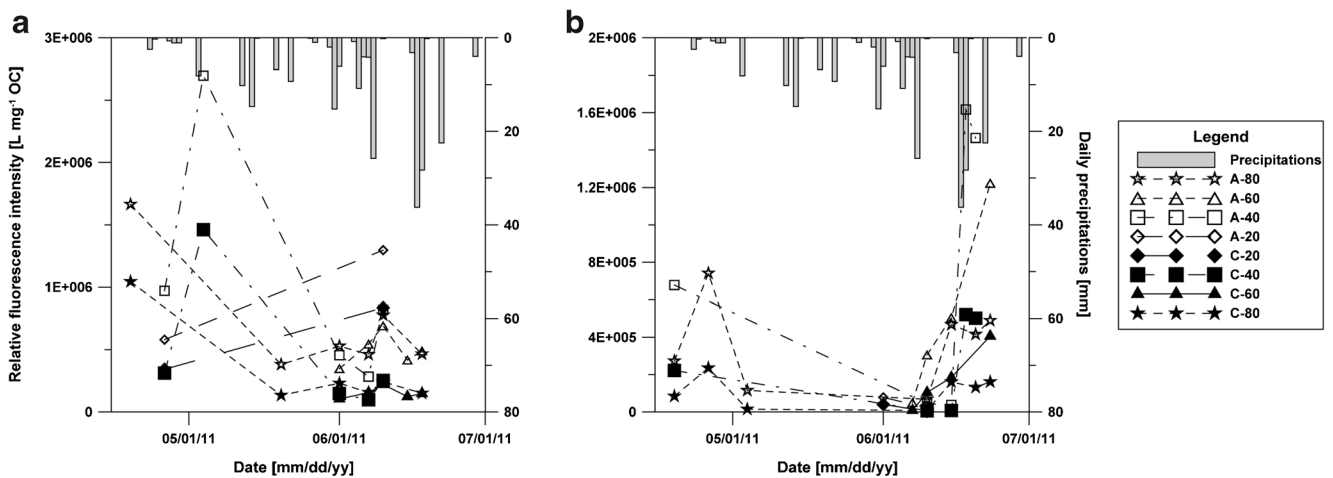
Fig. 2 Relative fluorescence intensities of peak A (*white symbols*) and C (*black symbols*) of soil water samples of **a** parcel 1 and **b** parcel 2 at different depths (20, 40, 60, 80 cm) from April to July 2011. Daily precipitations are represented with the second y-axis (source: MeteoSwiss)

Protein-like fluorophore (peak B) relative intensity shows a similar behavior than humic-like ones (peaks A and C) and increased likewise with the important precipitation of June (Fig. 5).

Humification index (HIX)

For soil water samples, the average values of the humification index (HIX) was higher in parcel 1 (3.7) than in parcel 2 (2.1), but variation of the humification index at different depths with time and precipitations was more important in parcel 2 (0.1–7)

than in parcel 1 (2.2–4.7) (Fig. 6a, b). The higher variability of HIX values in parcel 2 is certainly due to the steepness of the slope (Fig. 1). In general, HIX values were higher in superior layers (20 and 40 cm) than in deeper layers (60 and 80 cm), which could suggest the higher solubility and mobility of less humified compounds (fulvic-like compounds) reaching deep layers (Kalbitz et al. 2000). However, the presence of throughflows and/or temporal hydromorphy at 80-cm depth may also explain the mobility of colloidal more humified compounds in parcels and therefore the slightly higher HIX values at 80 cm than at 60 cm in parcel 1 (Daouk et al. 2013b).

Fig. 3 Parallel factor analysis of 37 soil water samples with three contributing components: **a** protein-like, **b** humic-like, and **c** fulvic-like, and **d** their relative weight in samples with components (**a**) in *blue*, (**b**) in *green*, and (**c**) in *red*. Core consistency was of 80.2 %
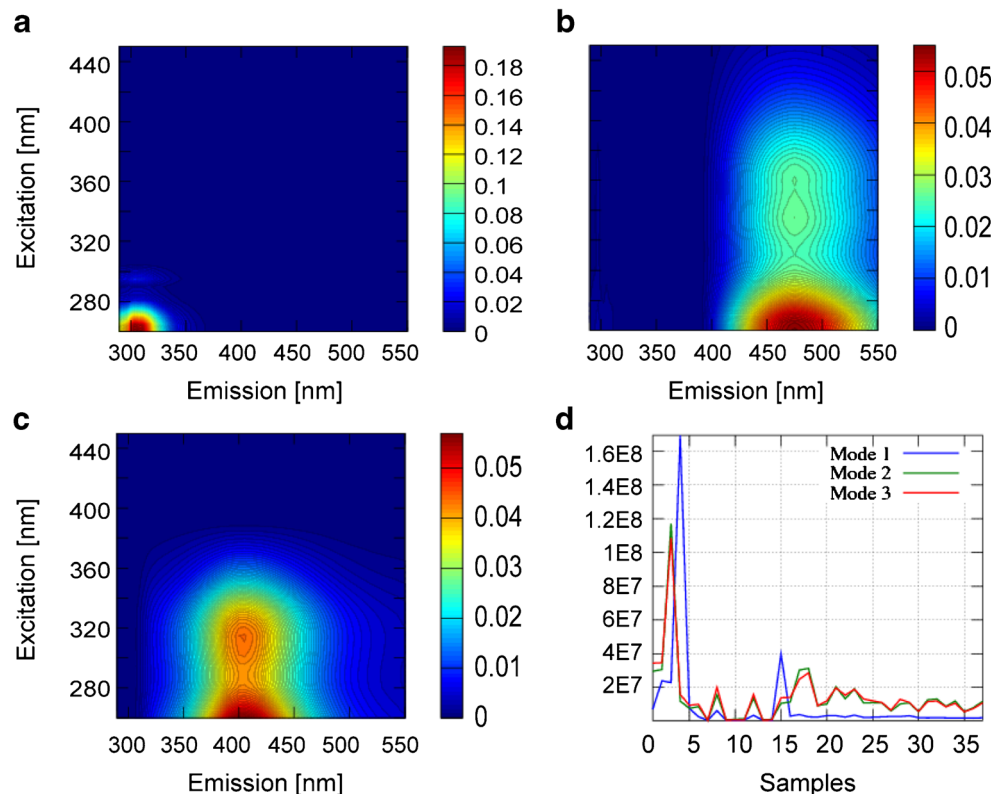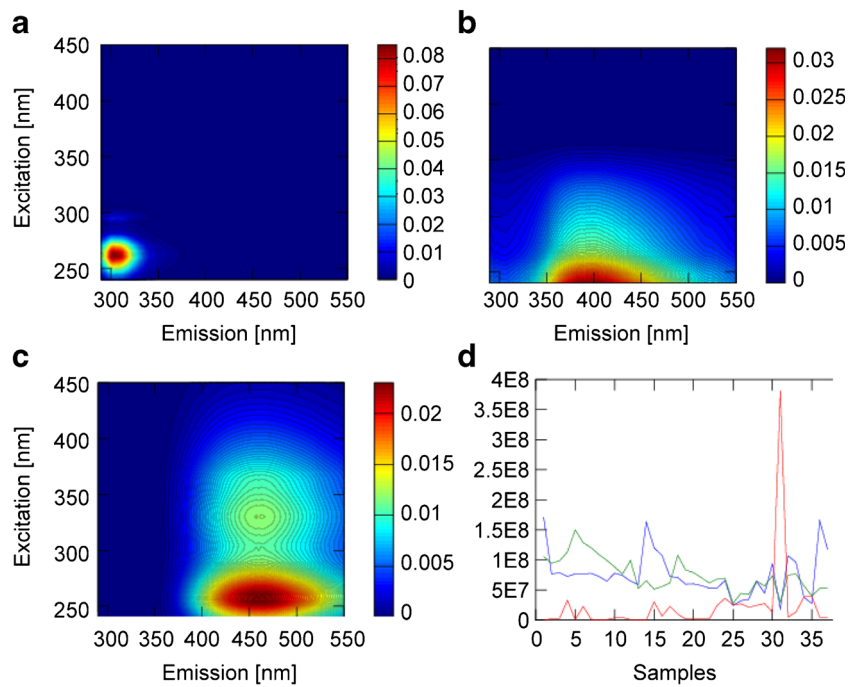
Fig. 4 Parallel factor analysis of 37 river water samples with the three contributing components: **a** protein-like, **b** fulvic-like, and **c** humic-like, and **d** their relative weight in samples with component (**a**) in *red*, (**b**) in *blue*, and (**c**) in *green*. Core consistency was of 90.7 %

Though no general relation between precipitations and HIX values could be pointed out, in parcel 1 these latter seem to increase with rainfall and decrease during dry periods, which is clear at 60-cm depth. In parcel 2, however, this tendency is not very clear. This absence of tendency is certainly due to the more important influence of preferential pathways taken by soil solution in this parcel, as previously observed (Daouk et al. 2013b). The significant increase of HIX values in the subsoil (80 cm) during the intense rainfall of mid-June following a dry period reveals this phenomenon. Indeed, the presence of preferential flow paths, combined with the

accumulation of water-soluble organic compounds in the soil caused, for example, by elevated temperature or dry periods without soil leaching, leads to elevated concentrations and fluxes of DOM in subsoil horizons at the beginning of intense rainfall (Kalbitz et al. 2000). Thus, precipitations and soil structure are likely to be driving forces for the solubilization and the mobilization of humic substances, principally localized in the top soil layer, and their leaching and horizontal transport throughout the parcels. This could be of importance for the transport of copper and glyphosate. Indeed, DOM export from the top soil during intense rainfall events via rapid
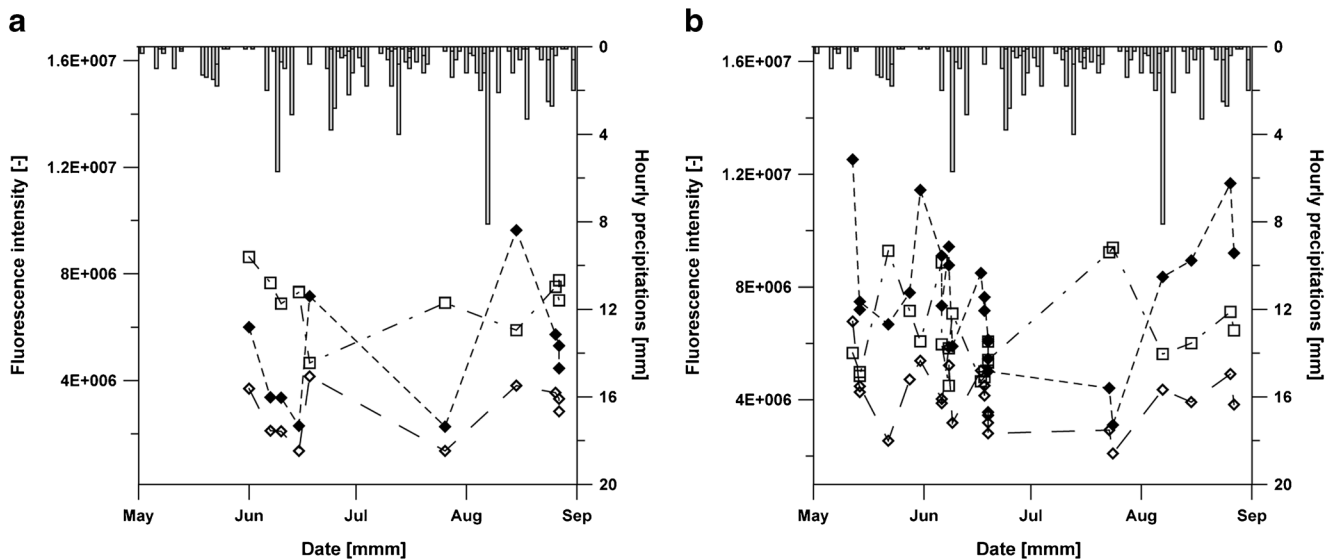

Fig. 5 Variations of the relative fluorescence intensities of peaks A (♦), B (□), and C (◇) in Lutrive River samples at **a** the upstream and **b** the downstream site for the period May–August 2011. Hourly precipitations are represented with the second y-axis (source: MeteoSwiss)
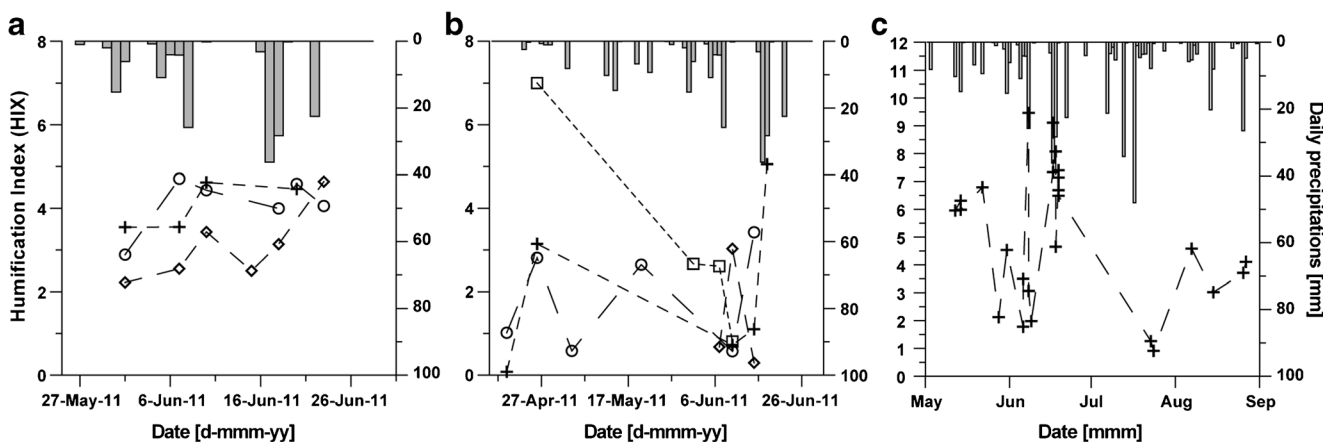
Fig. 6 Humification index (HIX; Zsolnay et al. 1999) temporal dynamics in soil water samples from **a** parcel 1 and **b** parcel 2 from April to June 2011 (□, 20 cm; +, 40 cm; ◊, 60 cm; and ○, 80 cm), as well as **c** in the Lutrive River from May to September 2011

water flow, e.g., through macropores, is likely more reactive towards metals and organic xenobiotics, than during rainfall of low intensity via matrix flow (Kaiser and Guggenberger 2005).

HIX values of downstream river samples varied between 0.9 and 9, with a mean value of 5, and high values were observed during the high rainfall events of June (Fig. 6c). This confirms the transfer of more humified organic compounds from the top soil layer to the river by surface runoff during these events.

Statistics

The PCA performed on the normalized matrix of different parameters for soil and river water samples showed 2 components with Eigenvalues above 1, which accounted for 72.8 % of the dataset variance (Fig. 7). The plan formed by component 1 (51.7 %) and component 2 (21.1 %) was able to discriminate between soil solution and river water samples. Soil solutions showed indeed a higher A/C ratio in average (2.8) compare with river samples (1.8). Glyphosate concentrations were high in R1 and R21 samples and decreased along the y-axis. They were well correlated to both copper ($r=0.79$) and iron ($r=0.68$) concentrations, suggesting its possible chelation which has been proved to happen and with a relatively high stability in solution (Subramaniam and Hoggard 1988; Barja and dos Santos Afonso 1998). This phenomenon can have some major implications in the facilitated transport of the studied herbicide, as previously observed in vineyard soils for copper (Dousset et al. 2007). Looking at the correlations between spectroscopic signatures of DOM and pollutants of interest, the relative fluorescence intensities of fulvic-like (peak A) fluorophore were poorly, but significantly (*p* value<0.01), correlated with

glyphosate ($r=0.48$), iron ($r=0.48$), and copper ($r=0.57$) concentrations. The relative fluorescence intensities of humic-like (peak C) fluorophore were significantly correlated with iron ($r=0.45$) and copper ($r=0.51$), but not with glyphosate ($r=0.41$). AMPA concentrations were only correlated to glyphosate ones and no significant correlation was observed between HIX values and glyphosate or copper concentrations. This means that DOM humification degree was not a determining factor in the transport of these pollutants. When analyzing separately soil solution and river water samples, copper concentrations were correlated to both fulvic-like and humic-like
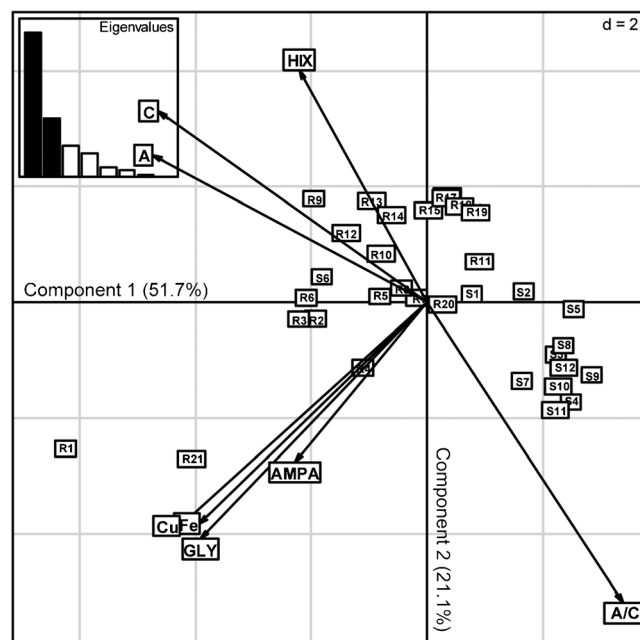

Fig. 7 Principal component analysis (*PCA*) applied to chemical and spectroscopic analysis of soil solution (S1–S12) and river water (R1–R21) samples made with the R software. The two first components showed Eigenvalues above 1 (*in black in the upper-left figure*) and explained 72.8 % of the dataset variance

signatures in soil solution, but only to fulvic-like ones in the river. The significant positive correlation between copper and DOM indicates that copper is likely transported as DOM-Cu complexes, but it is known that copper can quench the DOM fluorescence signal. As such, a quenching at a constant site density would result in a negative correlation between DOM signal and copper, a correlation remaining positive indicates that the signal quenching is likely compensated by an increase of the site density and therefore enhances the hypothesis of copper transport by DOM. Glyphosate concentrations were correlated to iron and copper ones in both types of samples, but not in a significant way to fulvic- and humic-like signatures in river samples. These results highlight the potential formation of complexes between dissolved humic substances and metals in freshwater environment as previously observed with fluorescence spectroscopy (Larrivee et al. 2003; Hudson et al. 2007). They also suggest the formation of ternary complexes between fulvic-like acids, glyphosate and copper in soil solution as previously observed (Maqueda et al. 1998). These considerations should, however, be taken with precaution because only the fluorescent part of DOM was considered to study its role in the fate of glyphosate and copper in vineyards and other binding mechanisms could be involved. Nevertheless, even if significant correlations do not imply causality, previous studies in laboratory conditions support these field observations (Piccolo et al. 1992; Maqueda et al. 1998).

Conclusions

UV/Vis fluorescence spectroscopy, combined with parallel factor (PARAFAC) analysis, allowed to characterize in a proper way DOM of soil and surface water samples from the studied vineyard area. Furthermore, with this technique, the multiple interactions between the herbicide glyphosate, its metabolite AMPA, copper and iron could be assessed in the collected natural samples. Results strongly suggest the formation of complexes between dissolved humic substances and copper in soil and river water samples from the studied vineyard area. They also suggest interactions between DOM, glyphosate, and copper in soil solution, but only between glyphosate and copper and iron in surface water.

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