Influence of dissolved organic carbon content on modelling natural organic matter acid–base properties

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Abstract

Natural organic matter (NOM) behaviour towards proton is an important parameter to understand NOM fate in the environment. Moreover, it is necessary to determine NOM acid–base properties before investigating trace metals complexation by natural organic matter. This work focuses on the possibility to determine these acid–base properties by accurate and simple titrations, even at low organic matter concentrations. So, the experiments were conducted on concentrated and diluted solutions of extracted humic and fulvic acid from Laurentian River, on concentrated and diluted model solutions of well-known simple molecules (acetic and phenolic acids), and on natural samples from the Seine river (France) which are not pre-concentrated. Titration experiments were modelled by a 6 acidic-sites discrete model, except for the model solutions. The modelling software used, called PROSECE (*Programme d'Optimisation et de SpEciation Chimique dans l'Environnement*), has been developed in our laboratory, is based on the mass balance equilibrium resolution. The results obtained on extracted organic matter and model solutions point out a threshold value for a confident determination of the studied organic matter acid–base properties. They also show an aberrant decreasing carboxylic/phenolic ratio with increasing sample dilution. This shift is neither due to any conformational effect, since it is also observed on model solutions, nor to ionic strength variations which is controlled during all experiments. On the other hand, it could be the result of an electrode troubleshooting occurring at basic pH values, which effect is amplified at low total concentration of acidic sites. So, in our conditions, the limit for a correct modelling of NOM acid–base properties is defined as 0.04 meq of total analysed acidic sites concentration. As for the analysed natural samples, due to their high acidic sites content, it is possible to model their behaviour despite the low organic carbon concentration.

1. Introduction

In natural systems, as an estuary, components of natural organic matter (NOM) have a predominant role towards complexation of trace metals, and so, on their speciation (Buffle, 1988; Byrne, 1996; Hart, 1981). Thus, in the environment, pollutant metals transport and reactivity are partially controlled by NOM, conditioning toxicity and/or bioavailability of trace metals towards micro-organisms (phytoplankton, zooplankton, macro-algae…) (Erk and Raspor, 2001; González-Dávila et al., 2000; Vasconcelos and Leal, 2001). NOM study to model these complexing properties and predict its behaviour in a given system is a major issue to apprehend trace metals and NOM impact on the environment. Thus, the characterization of NOM complexing and acidic parameters, using discrete or

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continuous models, has been and is yet the purpose of many studies (Kinniburgh et al., 1999; Kozelka and Bruland, 1998; Mantoura, 1981; Sposito, 1981; Tipping, 2002; Town and Filella, 2000).

NOM acid–base properties are part of the essential factors which influence its complexing ability towards trace metals (Buffle, 1988; Christensen and Christensen, 2000; Perdue and Lytle, 1983; Ramos et al., 2002; Robertson and Leckie, 1999; Smith and Kramer, 1999). All models applied to NOM aim at defining carboxylic- and phenolic-like sites density (Christensen et al., 1998; de Souza Sierra et al., 2001; Lu and Allen, 2002; Masini et al., 1998; Milne et al., 2001; Ritchie and Perdue, 2003). As a matter of fact, the monitoring of carboxylic/ phenolic ratio's modifications allows to map out NOM properties variability and, often, to determine NOM origin. Thus, it has been stated that NOM with anthropic or "terrigen" origins have more marked phenolic characteristics (Letizia and Gnudi, 1999). Moreover, NOM extraction and/or separation in fulvic (FA) and humic (HA) acids have shown recurrent differences between these two types of extracted NOM, in terms of acidic site densities as well as carboxylic/ phenolic ratios (de Souza Sierra et al., 2001; Milne et al., 2001; Ritchie and Perdue, 2003).

Most studies concerning NOM acid–base properties characterisation have been carried out on isolated NOM, using different experimental protocols (IHSS protocol, ultrafiltration, reverse osmosis, evaporation, XAD-8 and XAD-4 resins…), as IHSS standard NOM (Kinniburgh et al., 1999; Christensen et al., 1998; de Souza Sierra et al., 2001; Lu and Allen, 2002; Masini et al., 1998; Ritchie and Perdue, 2003; Takács et al., 1999). Experiments consist in potentiometric titrations of isolated NOM solutions, usually realised at high dissolved organic carbon (DOC) contents (40 to more than $1000 \, \text{mg} \, l^{-1}$ of DOC), which are very different from natural sample concentrations (0.1–$10 \, \text{mg} \, l^{-1}$) obtained for low-eutrophised waters (Mounier et al., 1999). In addition to the possible modifications of NOM properties during these isolation protocols, it seems interesting to know if the characterisation of NOM behaviour towards proton is feasible with the lowest possible errors, at lower or even at natural DOC contents, without any isolation treatment.

The aim of this work was to analyse the effect of DOC content on the ability to determine NOM acid–base properties with a discrete model using a new software called PROSECE (Garnier et al., 2004). Thus, potentiometric titrations have been carried out on solutions of extracted Laurentian River fulvic and humic acid (LRFA and LRHA) at different DOC concentrations (2–$100 \, \text{mg} \, l^{-1}$). This study was first based on the estimation of DOC content effect on carboxylic/ phenolic ratios evolution, and more precisely on acidic parameters of some defined sites. Moreover, various

sampling, conducted on the Seine river (France) (Garnier, 2004), and analysed without any isolation protocol (i.e. 2.1–$7.5 \, \text{mg} \, l^{-1}$ of DOC), allowed to observe possible differences between these natural solutions and the extracted LRFA and LRHA. Finally, this work was completed with potentiometric titrations of model mixtures of phenol and natrium acetate, at concentrations close to carboxylic and phenolic contents of LRFA and LRHA solutions, to prevent interferences due to NOM structural and behaviour complexity.

2. Experimental

2.1. Natural organic matter and reagents

From LRFA and LRHA parent solutions, respectively, at 226.8 and $205.0 \, \text{mg} \, l^{-1}$ of organic matter (i.e. 117.9 and $106.6 \, \text{mg} \, l^{-1}$ of DOC), diluted solutions of extracted organic matter were realised, according to different dilution factors: 2, 10, 20 and 50.

Natural organic matters were sampled on the Seine river, within the SeineAval2 research program framework. Seventeen samples were collected on 5 upstream to downstream sampling sites (Poses, La Bouille, Caudebec, Tancarville and Honfleur) between April 2002 and December 2002, and completed by two marine-estuary sampling (March and September 2002) of different depths. All these samples have been analysed in detail elsewhere (Garnier, 2004).

A model solution, mixture of natrium acetate ($10.14 \, \text{mmol} \, l^{-1}$ CH_3COONa Labosi analypur) and phenol ($9.91 \, \text{mmol} \, l^{-1}$, from C_6H_5OH Merck for analysis), was diluted according to different dilution factors: 2, 5, 10, 20, 50, 100, and 200.

LRFA, LRHA and natrium acetate–phenol solutions ionic strength was maintained at $0.10 \, \text{M}$ by adding $NaNO_3$ (J.T. Baker) and all solutions were stored in the dark at $4 \, ^\circ C$.

2.2. Potentiometric titrations

Titrations experiments have been carried out in thermostated cells at $25 \pm 0.2 \, ^\circ C$, using KOH ($0.10 \, \text{M}$, from KOH $0.5033 \, \text{M}$ Sigma-Aldrich) and HNO_3 ($0.20 \, \text{M}$, from HNO_3 69% J.T. Baker) standardised CO_2-free solutions, under stirring and streamed by an ultra-pur nitrogen flow (water saturated and decarbonated using $1 \, \text{M}$ KOH solution). $NaNO_3$ concentration in KOH and HNO_3 standard solutions was $0.10 \, \text{M}$. The KOH solution was titrated using potassium hydrogen phthalat, then the HNO_3 solution was titrated using this KOH solution.

The micro-titration stand (Metrohm) was equipped with two titrators Titrino 716 controlled by Tinet2.4 software. The combined pH-micro-electrode used

(Mettler, Inlab422, reference: Ag/AgCl/KCl 3.0 M) was calibrated weekly by pH-buffer solutions (HANNA 4.01, 7.01 and 10.01).

Titrations were conducted on 50 ml of LRFA, LRHA and model solutions, and 100 ml of natural samples, these volumes were chosen to increase the analysed acidic sites number. Titrations were carried out with HNO_3 additions until pH 2 was reached. After 20 min of stirring, the solution was free from carbonates, and the pH was increased to a value of 11.9 by addition of KOH. To increase the accuracy of the curves (pH = $f(V_{KOH})$), experiments consisted on dividing titration into four pH sections (2–2.5, 2.5–3.5, 3.5–10.5 and 10.5–11.9), in which the added volume was adjusted from 5–250 µl. pH was measured with stable conditions of 0.5 mV/min or 120 s. one hundred and fifty to 250 data points (pH, added KOH volume) per analysis arise from these conditions, the average time per experiment was about 12 h. To determine acid–base properties of these solutions, only the data points corresponding to pH values between 2.5 and 11.5 were used in order to minimize the effect of pH micro-electrode non-linearity at extreme pH values.

2.3. Modelling of experimental data: PROSECE

In this study, the model used to apprehend acid–base properties of natural and isolated organic matters is based on the definition of a discrete distribution of acidic sites, whose acidic constants ($pK_{H,i}$) and concentrations ($L_{T,i}$) have to be determined. Determination of these parameters, by experimental curves fitting, has been realised using a new software, PROSECE, developed in our laboratory in cooperation with Pr. P. Seppecher (ANLA laboratory). This software, available on request, has been written on the basis of the numeric calculation program Octave (freeware) and consists of a speciation calculation integrated in a module that optimises the complexing parameters, as explained elsewhere (Garnier et al., 2004).

The modelling of NOM behaviour towards proton has often been realised using a set of acidic sites. The number of defined sites varies according to the analysed NOM and the optimisation program used. Thus, de Souza Sierra et al. (2001) have modelled extracted NOM potentiometric titrations by 2 sites (one carboxylic and one phenolic), Takacs et al. (1999) by 3 sites, Lu and Allen (2002) by 4 sites and Masini et al. (1998) have reached 6 different sites. Smith and Kramer (1999), using a slightly different model (DISI), defined 4 groups of sites according to the obtained pK_a values.

So, due to these differences, the first step of this study consists in the optimisation of the sites number leading to the best experiments modelling with the simplest system.

3. Results and discussion

3.1. Titrations of LRFA and LRHA concentrated solutions

Experimental curves of potentiometric titrations of LRFA and LRHA concentrated solutions are presented in Fig. 1. As expected, these curves did not show well-defined equivalent points, which emphasises the great heterogeneity of acidic functions carried by these isolated NOM. With regard to the KOH quantity necessary to neutralise all these NOM acidic sites, FA presents a higher sites density than humic acid. These results compares well with those obtained on standard organic matters by Milne et al. (2001) and Ritchie and Perdue (2003).

LRFA and LRHA potentiometric titrations have been modelled using discrete distributions of 2, 3, 4, 5, 6 and 7 different sites to determine the number of discrete sites necessary to correctly model these titrations curves. The errors on titration pH values, calculated from differences between experimental and calculated pH values and optimised by PROSECE, as a function of the number of defined sites are presented in Fig. 2. According to the given results, a 6 sites discrete distribution has been considered for LRFA, LRHA and natural samples analysis.

For LRFA and LRHA, this 6 sites model combined to the use of PROSECE allowed the acid–base properties ($pK_{H,i}$, $L_{T,i}$) optimisation of 3 carboxylic-like ($pK_{H,i} < 7$) and 3 phenolic-like ($pK_{H,i} > 7$) sites. This is in agreement with Masini et al. (1998) previous results. Calculated values for defined acidic parameters are summarised in Table 1. Carboxylic/Phenolic ratios are calculated by dividing the sum of the 3 carboxylic-like sites concentrations by the sum of the 3 phenolic-like ones. The obtained carboxylic/phenolic ratios, respectively, 1.32 and 0.54 for LRFA and LRHA (Table 2),
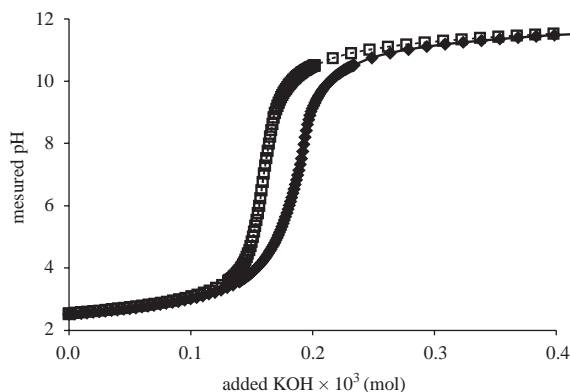

Fig. 1. LRFA (♦) and LRHA (□) solutions potentiometric titration curves.

are in the range of those analysed by Ritchie and Perdue (2003), and obviously show differences between the behaviour towards pH of a FA and a HA isolated from the same NOM. It has to be pointed out that LRFA and LRHA phenolic sites densities are almost the same (respectively, 2.55 and 2.49 meq g^{-1} NOM), while FA carboxylic sites density (3.37 meq g^{-1} NOM) is 2.5 times higher than the HA one (1.34 meq g^{-1} NOM).

For LRFA and LRHA concentrated solutions titrations, PROSECE-optimised errors are, respectively, of 2.86 and 3.76 (sum of absolute differences between measured and PROSECE-calculated pH values), for the 6 sites model, which corresponds to mean errors on scanned pH values of 0.29% (i.e. 0.009 pH unity) and 0.38% (i.e. 0.012 unity of pH).

3.2. Titrations of LRFA- and LRHA- diluted solutions

In this case, PROSECE calculations consist in optimising the 6 sites concentrations only, the sites being defined by their acidic constants optimised by concentrated solutions modelling. The obtained sites concentrations for potentiometric titrations of LRFA and LRHA diluted according to dilutions factors of 2, 10, 20 and 50 are given in Table 2.

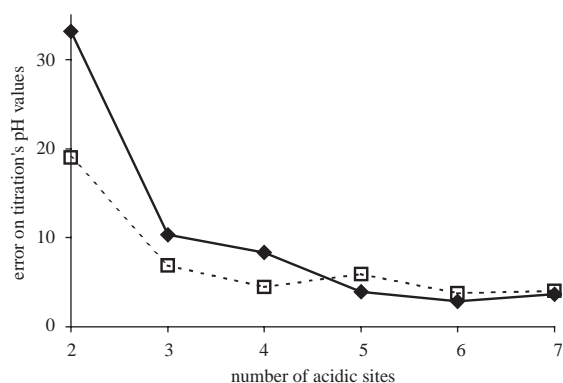Carboxylic and phenolic sites densities (meq g^{-1} NOM) evolutions as a function of NOM concentration,

Fig. 2. Error evolution on PROSECE optimisation of LRFA (♦) and LRHA (□) titrations, as a function of the defined acidic sites number.

i.e. the LRFA and LRHA quantities in concentrated and diluted solutions, are presented in Fig. 3. Theoretically, there should not be any differences in terms of sites densities when NOM concentration decreases, i.e. the obtained results at 20 mg$_{NOM}$ l^{-1} should be the same than those obtained at 200 mg$_{NOM}$ l^{-1}.

Concerning carboxylic sites, until a dilution factor of 10 corresponding to 22.7 and 20.5 mg l^{-1} of LRFA and LRHA respectively, density is almost constant. Below this dilution factor, sites densities widely increase to reach 7.32 meq g^{-1} LRFA (+118%) and 8.92 meq g^{-1} LRHA (+563%), respectively.

This phenomenon is widely amplified for phenolic sites. Indeed, for solutions diluted by a factor 2 (i.e. 113.4 and 102.5 mg$_{LRHA}$ l^{-1}), densities respectively increase of 25 and 55%. For dilution factors above 2, phenolic sites densities reach 50.85 meq g^{-1} LRFA (+1892%) and 59.62 meq g^{-1} LRHA (+2288%). So, the calculated carboxylic/phenolic ratio decreases with decreasing NOM content (see Table 2) to reach 0.14 and 0.15, respectively, for LRFA and LRHA solutions diluted by 50.

A more precise study of each site density variations shows a major increase for sites number 3 (p$K_{H,3}$ ~ 6.5) and number 6 (p$K_{H,6}$ ~ 10) only, and in the case of the most diluted solution, an increase for almost all sites.

So, LRFA and LRHA diluted solutions analysis draw attention to an over-estimation of the acidic sites concentrations when NOM concentration decreases. This phenomenon, especially noticeable for phenolic-like sites, leads to important variations of carboxylic/phenolic ratio values during dilution. Thus, it seems quite difficult to correctly determine acid–base properties of extracted NOM at low DOC content (i.e. below 10 or even 50 mg l^{-1} of DOC), and so, it seems impossible to analyse natural samples which are not treated according to a NOM isolation protocol.

3.3. Titration of natrium acetate and phenol model solutions

To validate or not the obtained results on extracted organic matter, the titration/modelling protocol has been applied to a well-known natrium acetate and phenol model solution, whose sites concentrations are

Table 1
Acidic parameters (p$K_{H,i}$ and $L_{T,i}$ meq g-1NOM) modelling potentiometric titrations of LRFA and LRHA concentrated solutions (226.8 and 205.0 mg$_{NOM}$ l^{-1})

		1	2	3	4	5	6	Carboxylic	Phenolic
start_posLRFA	$L_{T,i}$	1.69	0.89	0.79	0.32	0.47	1.76	3.37	2.55
	p$K_{H,I}$	4.18	5.33	6.58	7.61	8.93	9.99		
LRHA	$L_{T,I}$	0.72	0.40	0.22	0.55	0.55	1.39	1.34	2.49
	p$K_{H,i}$	4.71	5.90	6.67	7.74	9.2	10.08		

Table 2
Optimised sites densities for potentiometric titrations of LRFA and LRHA- diluted solutions

| (NOM) mg l^{-1}	$L_{T,I}$ (meq g$_{NOM}^{-1}$)								
	1	2	3	4	5	6	Carboxylic	Phenolic	Ratio
LRFA									
226.8	1.69	0.89	0.79	0.32	0.47	1.76	3.36	2.55	1.32
113.4	1.39	0.95	0.80	0.37	0.44	2.39	3.14	3.20	0.98
22.7	0.37	1.35	1.38	0.50	0.82	10.82	3.10	12.15	0.25
11.3	1.87	0.75	2.47	0.63	1.26	19.49	5.09	21.38	0.24
4.5	0.74	1.06	5.53	0.00	4.01	46.85	7.32	50.85	0.14
LRHA									
205.0	0.72	0.40	0.22	0.55	0.55	1.39	1.35	2.50	0.54
102.5	0.63	0.51	0.33	0.59	0.77	2.51	1.47	3.87	0.38
20.5	0.00	0.94	0.95	0.48	0.88	11.76	1.89	13.13	0.14
10.3	0.00	2.02	1.04	0.55	1.91	20.13	3.06	22.59	0.14
4.1	3.28	2.39	3.25	2.69	9.88	47.05	8.92	59.62	0.15
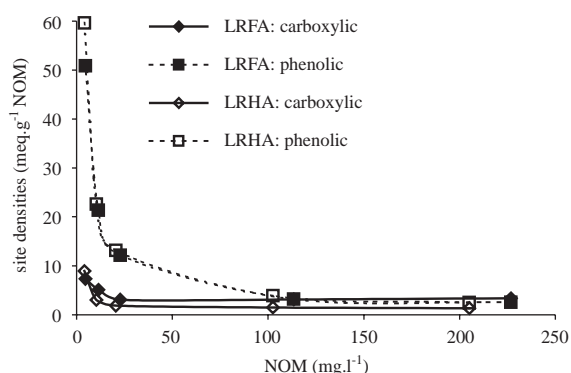
Fig. 3. Carboxylic- and phenolic-like sites densities optimised for LRFA and LRHA concentrated and diluted solutions.

close to those calculated for LRFA and LRHA concentrated solutions. So, this model solution has similar acid–base properties (p$K_{H,i}$ and $L_{T,i}$), without the conformational variations likely to occur on natural organic matter. Indeed, taking account of the highly heterogeneous structure and reactivity of the studied extracted and natural organic matters, sensible to many physico-chemical factors, it seems important to test simple and stable solutions with known thermodynamic acid–base properties.

PROSECE calculation, for the concentrated model solution, consists in the optimisation of acidic parameters (p$K_{H,i}$ and $L_{T,i}$) of two sites. Calculated acidic constants, respectively, 4.66 and 9.98 for natrium acetate and phenol, are close to the thermodynamic ones: 4.65 and 9.80 (Ringbom, 1967). Moreover, the obtained concentrations are, respectively 9.8 mmol l^{-1} and 10.3 mmol l^{-1}, which is quite closed to the expected values (10.14 mmol l^{-1} and 9.91 mmol l^{-1}).

Titrations of diluted model solutions have been modelled by PROSECE, using the obtained acidic constants for concentrated solutions and optimising the acidic site concentrations. Table 3 shows the obtained concentrations of acetate and phenol. In Fig. 4 is presented the evolution of the calculated total sites concentrations as a function of the expected total sites concentrations for model solutions, compared to LRFA and LRHA solutions. As shown previously on these extracted NOM solutions, modelling over-estimates acid–base sites concentrations at low organic matter content, as proven by the difference to the theoretical curve (see Fig. 4). Moreover, carboxylic/phenolic ratio values decrease, down to a value of 0.29 for the most diluted model solution, instead of 1.02 as expected (Table 3). Considering these results, it seems not possible to correctly determine acid–base properties when the calculated total sites amount is below 0.04 meq, (average value), which could be defined as the limit for a correct modelling (see dotted rectangle on Fig. 4).

So, the phenomenon consisting of an apparent increasing sites densities when the DOC content decreases, especially for phenolic-like sites, seems to be independent of the analysed chemical compounds nature. But, the exact origin of this phenomenon is not yet determinated. The only certitude is that it is neither due to ionic strength which is controlled during the titrations, nor to any conformational effect as the observed carboxylic/phenolic ratio shift also appears for simple molecules.

3.4. Titrations of natural samples

Considering the obtained results for LRFA and LRHA titrations modelled using PROSECE, a discrete distribution based on 6 different acidic sites has been used to analyse potentiometric titrations of natural

Table 3
Calculated and expected amounts (meq) of acetate and phenol in model solutions

| Solution	Factor	Acetate (meq)		Phenol (meq)		Ratio	
		Calculated	Expected	Calculated	Expected	Calculated	Expected
Concentrated		0.490	0.507	0.517	0.498	0.95	1.02
Diluted	2	0.249	0.254	0.271	0.249	0.92	1.02
Diluted	5	0.101	0.101	0.120	0.100	0.84	1.02
Diluted	10	0.053	0.051	0.066	0.050	0.81	1.02
Diluted	20	0.030	0.025	0.041	0.025	0.73	1.02
Diluted	50	0.016	0.010	0.027	0.010	0.60	1.02
Diluted	100	0.009	0.005	0.028	0.005	0.28	1.02
Diluted	200	0.005	0.003	0.018	0.002	0.29	1.02
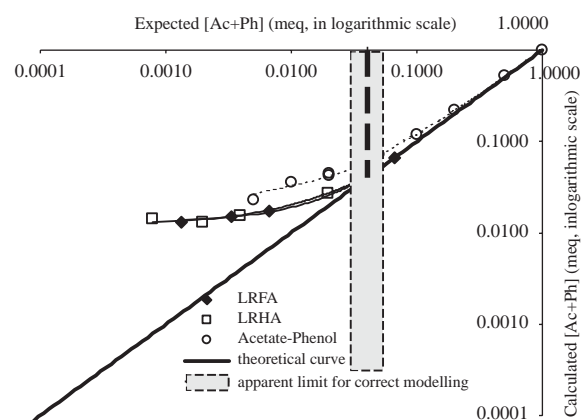
Fig. 4. Calculated total sites concentrations as a function of expected ones for model and extracted NOM solutions.

samples collected on the Seine river. The detailed analysis of spatio-temporal variability of the obtained acidic parameters is presented elsewhere (Garnier, 2004), compares to other biogeochemical factors as DOC content, fluorescence characteristics, chlorophyll A and phaeo-pigments concentrations…

The obtained carboxylic/phenolic ratios for these 17 natural samples reach an average value of 0.83, which is close to the values obtained for isolated NOM, analysed at higher DOC content (Kinniburgh et al., 1999; Christensen and Christensen, 2000; Lu and Allen, 2002, Milne et al., 2001). These calculated values range, between 0.23 and 1.50, shows the great behaviour heterogeneity of the studied NOM. All the calculated total sites amount range between 0.077 and 0.255 meq (mean value of 0.149 meq). When compared to the limit for a correct modelling, previously defined in this study as 0.04 meq, these sites amounts are above and so attest the feasibility of studying these non-extracted natural samples. It is to point out that PROSECE-modelling of NOM acid–base properties are done taking account of

major cations concentrations, which means hydroxides formation. On the other hand, the presence of possible inorganic colloids could not be considered, due to the obvious difficulty for their isolation and acid–base characterisation. So, this should induce a bias on the calculated amounts of NOM acid sites.

4. Conclusion

The determination of NOM acid–base properties, in particular the contents of carboxylic- and phenolic-like sites, has been conducted using potentiometric titrations, and modelled by means of a discrete sites distribution. The obtained results for LRFA and LRHA are comparable to those calculated in previous studies with similar extracted organic matter. The use of a new software, PROSECE, has allowed the acid–base properties optimisation of 6 different sites: 3 carboxylic-like and 3 phenolic-like, according to the calculated acidic constants. It can be noticed that LRFA and LRHA phenolic sites densities are similar, while the FA is 2.5 times richer in carboxylic sites than the LRHA ones.

This work has particularly pointed out that, for diluted solutions, there is a threshold value for a confident determination of the acidic sites concentrations. Indeed, LRFA and LRHA diluted solutions analysis draw attention to an over-estimation of the acidic sites concentrations when NOM concentration decreases. This phenomenon, especially noticeable for phenolic-like sites, leads to important variations of carboxylic/phenolic ratio values during dilution. Moreover, the analysis of natrium acetate and phenol model solutions, at different dilution factors, has confirmed these results, i.e. an increase of sites densities, especially for phenolic-like, when dilution is too important. This phenomenon could be the result of an electrode troubleshooting which happens at basic pH values, this effect being amplified when analysed sites concentration is low. Indeed, it is known that selective electrodes are

not linear under an infinite range. At very low proton concentrations (pH higher than 11), this type of micro-electrode should be disrupted, and so induce an incorrect signal interpreted by the optimisation software used as an phenolic one. Similarly, non-linearity at acidic pH (lower than 3), should lead to an incorrect carboxylic signal. However, LRFA acid–base properties obtained by titration PROSECE-modelling of LRFA concentrated and diluted solutions for different pH ranges (2.5–11.5, 3–11, 3.5–10.5 and 4–10), have unexpectedly shown the necessity to model the largest pH range to minimize this phenomenon. The use of RHOSS micro-electrode could maybe decrease it. Ionic strength and conformational changes do not seem, again, to be responsible for this increase of sites densities. Therefore, in this study, the limit for a correct modelling has been defined as 0.04 meq of total acid–base sites amount.

However, the analysis of natural samples collected in the Seine river without pretreatment, has shown that the modelling of non-concentrated NOM is possible, even at low DOC contents (average value of $3.6 \, \text{mg} \, \text{l}^{-1}$), because of the apparently high acidic sites densities of these samples. Indeed, the obtained carboxylic/phenolic ratios values are close to those determined by Ritchie and Perdue (2003), and so, not disrupted by a high error on phenolic sites density as pointed out when studying LRFA and LRHA at similar DOC contents. In fact, the total acid–base sites concentrations calculated for these natural samples are greatly above the defined modelling limit which can explain the correct modelling.

The presented results highlight the challenge to correctly analyse acid–base properties of solutions with low organic carbon contents. However, the analysis of natural samples collected in the Seine river, in different sampling sites and at different time periods, so, gathering together NOM of various origins and concentrations, has proved that it is possible to model the behaviour towards proton of non-treated samples, because of their high acidic sites content.

Acknowledgements

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