

Behaviour of humic-bentonite aggregates in diluted suspensions

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Abstract

Processes of aggregate formation and disaggregation are common in both waters and soils and are widely used in different industries. Aggregates composed of clays and humic substances (HSs) are, either directly or indirectly, associated with almost all biological, chemical, and physical phenomena in waters and soils. Formation and disaggregation of micron-size aggregates in a diluted suspension made up of HSs and bentonite (B) were studied by tracing distribution of aggregate sizes and their counts in freshly prepared and aged suspensions, and at high (10 000) and low (1.0) [HS]/[B] ratios. Diluted HSB suspensions are unstable over time with respect to number of aggregates, and distribution of aggregate sizes at particular [HS]/[B] ratios. The observed disaggregation to aggregation and aggregation to disaggregation events are probably a consequence of exposure of fresh clay surface upon disaggregation of HSB aggregates, partitioning of adsorbed humic substances between old and freshly exposed clay surfaces, adsorption of dissolved HSs on fresh bentonite surface, and decomposition of large units of HSs into smaller ones, a process probably catalysed by clays. Successive aggregation to disaggregation or disaggregation to aggregation events yield both qualitative and quantitative transformations in HSB aggregates, which thus may affect availability, transport and fate of adsorbed chemicals in both aquatic and terrestrial systems.

Keywords: aggregates, clays, humic substances

Nomenclature

bentonite (B)
fulvic acids (FAs)
humic acids (HAs)
humic substances (HSs)

Introduction

Processes of aggregate formation and disaggregation are common in both waters and soils and are widely used in different industries. Natural aggregates usually contain inorganic, gaseous, microbial, and organic fractions that determine behaviour of a particular aggregate in waters or soils.

Clays are a common inorganic fraction in natural aggregates. A huge amount of bentonite clay (B), primarily made of montmorillonite, is used each year in various industries (Lagaly and Ziesmer, 2003); part of it finds its way to waters and soils. Catalytic and adsorption properties of clays make them important in soil/water-chemistry but also in retention/transport of organic and inorganic chemicals through the environment (Kersting et al., 1999; Plaschke et al., 2001; Schwartz and Matijevic, 1974). Montmorillonite clay, $[(1/2\text{Ca}, \text{Na})_{0.7}(\text{Al}, \text{Mg}, \text{Fe})_4(\text{Si}, \text{Al})_8\text{O}_{20}(\text{OH})_4 \cdot 7\text{nH}_2\text{O}]$, is an inorganic fraction of aggregates found in both poorly drained soils and those of arid regions (Donahue et al., 1983). Montmorillonite has a substantial internal surface area, elevated ion-exchange capacity, and expands up to 10 times its dry volume upon contact with water by crystalline and osmotic swelling (Luckham and Rossi, 1999; Norrish, 1954).

Humic substances (HSs) exist in dissolved and particulate forms in sediments, soils and waters (Tipping, 2002). They are reported to facilitate transport of contaminants to lower soil horizons and within aquifers, participate in removal and release of organic and inorganic compounds to/from bulk media, and influence availability of inorganic phosphate (Alvarez et al., 2004; Fitch and Du, 1996; Tipping, 2002).

HSs are formed by decomposition of biological material but organics in secondary effluents are quite similar to HSs in soil (Rebhun and Manka, 1971). HSs contain alcohol, amino, carboxyl, and other functional groups (Stevenson, 1994; Tipping, 2002) and their molecular weights are in the range of 600 to more than 200 000 (Stevenson, 1994; Tipping, 2002) with highest values, probably, a consequence of aggregation of smaller units into larger ones (Stevenson, 1994). HSs are polyelectrolytes containing both hydrophilic and hydrophobic moieties (Schulten and Schnitzer, 1995; Schulten and Gleixner, 1999) so they behave like surfactants (Rebhun et al., 1996). Different research schools are currently arguing whether HSs are macromolecules randomly coiled in a solution, associations of relatively small molecules held together by weak interactions, or micellar or pseudomicellar structures (Clapp and Hayes, 1999; Sutton and Sposito, 2005). Knowledge of sizes and shapes of HSs in a solution could improve understanding of their behaviour in both soils and waters.

Particles, made of clays and HSs, are frequently carriers of atrazine (Lesan and Bhandari, 2000), mercury (Amirbehman et al., 2002; Bilanovic et al., 2001), lead and copper (Hizal and Apak, 2006), plutonium (Kersting et al., 1999) and other pollutants (Rebhun et al., 1992).

Clays and HSs are, either directly or indirectly, associated with almost all biological, chemical and physical phenomena in waters and soils. Quantitative and qualitative advances in understanding of mobilisation and deposition of colloidal aggregates

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made of humic substances and clays are needed for better understanding of:

- Soil erosion
- Transport and fate of pollutants in soils and waters
- Irrigation
- *In situ* remediation and other processes (Kretzschmar et al., 1999).

The same is true for micron-size aggregates made of humic substances, clays and other colloidal and non-colloidal matter.

HSs are generally considered to be ‘cementing’ compounds in aggregates (Donahue et al., 1983) but within a certain concentration range, HSs disperse the aggregates (Tarchitzky and Chen, 2002; Visser and Callier, 1998). Aggregate formation may lead to the removal of chemicals from a given environment while disaggregation probably releases chemicals to the environment (Bilanovic and Spigarelli, 2002). Processes of aggregate formation and disaggregation are triggered by change of: pH, ionic strength, redox potential, concentration and form of aggregate fractions, fractions chemistry/reactivity, and other bio-geo-chemical factors. A change in concentration of clay(s) and/or HSs can be irregular, like during flooding, and regular, like seasonal change.

Humic substances are composed of fulvic acids (FAs) soluble in both acid and base, and humic acids (HAs) insoluble in acid but soluble in base, and humin insoluble in acids and bases (Tipping, 2002). FAs and HAs are of different solubility and of different adsorption properties implying that HAB and FAB suspensions should differ with respect to the number of aggregates, and the distribution of aggregate sizes. These differences may have profound effects on availability, transport and fate of chemicals in the environment. Two model systems made out of: FAs and B, and HAs and B are being studied. Formation and disaggregation of micron-size aggregates were analysed by tracing distribution of aggregate sizes and their count at different concentrations of HAs and B (i.e. different HAs/B ratio), and at different time intervals. The focus of this paper is on the HAB aggregates with a brief comparison of the FAB aggregates.

Materials and methods

FAs and HAs were isolated from a reed-sedge peat, pH = 4.5, H6 at Von Post Humification Scale (Von Post and Granlund, 1926) according to the procedure adapted from Spigarelli (1994). Isolates were dialysed against deionised water (17.52 MΩ-cm) for 72 h with one change of water every 12 h. Concentrations of dialysed HAs and FAs in their stock solutions were adjusted to $[FA]_0 = 2.0 \text{ mg/l}$ and $[HA]_0 = 2.0 \text{ mg/l}$. HCl and NaOH were used to adjust pH to 6.35 ± 0.05 . Deionised water was used to make up the following dilutions: 2.0, 0.2, 0.02, 0.002, 0.0002 and 0.00002 mg HA/l or FA/l.

Thirty-six x 25 ml aliquots of HAs solutions were then placed in 36 x 100 ml Pyrex bottles with screw caps. Thirty-six

x 25 ml aliquots of FAs solutions were also placed in 36 x 100 ml Pyrex bottles with screw caps. To avoid microbial growth all samples were exposed to microwave radiation for 2 min/d for 3 consecutive days.

An amount of 0.5 g of Na-bentonite (Fisher Scientific) was added to 500 ml of deionised water, mixed on a magnetic stirrer for 24 h then diluted to 5 000 ml and mixed for an additional 48 h. HCl and NaOH were used to adjust the pH to 6.35 ± 0.05 . The concentration of B in its stock suspension $[B]_0$ was adjusted to 2 mg/l with deionised water. The following suspensions were made by diluting $[B]_0$ with deionised water: 2.0, 0.2, 0.02, 0.002, 0.0002 and 0.00002 mg B/l. Seventy-two x 25 ml aliquots of B suspensions were then placed in 72 x 100 ml Pyrex bottles with screw caps. To avoid microbial growth all suspensions were exposed to microwave radiation for 2 min/d for 3 consecutive days (Bilanovic et al., 2004).

Thirty-six HAB suspensions, each with a different HAs/B ratio, were prepared by adding a 25 ml aliquot of a particular HAs solution to a 100 ml Pyrex bottle containing 25 ml of a particular B suspension.

Thirty-six FAB suspensions, each with a different FAs/B ratio, were prepared by adding a 25 ml aliquot of a particular FAs solution to 100 ml Pyrex bottle containing 25 ml of a particular B suspension.

To avoid potential microbial contamination bottles containing FAB and HAB suspensions were kept closed throughout the remainder of the experiments.

Following addition of HAs or FAs to B each bottle was shaken for 5 min at 250 oscillations/min, then left to rest for an additional 5 min prior to determination of particle counts and sizes. The count and sizing were conducted in triplicate at 0 h, 24 h, 3 600 h and 14 688 h; in-between the bottles were stored in the dark at room temperature of $23 \pm 3.0^\circ\text{C}$.

A laser particle counter (Spectrex = PC 2000) and accompanying software (Spectrex -Spercount) were used to count the number of aggregates and determine the distribution of their sizes in each FAB and HAB suspension. Readings were conducted in triplicate with the threshold set at ten and count time $t = 20 \text{ s}$. Standards provided by the manufacturer were used to calibrate the instrument. Throughout the experiments the average count for Standard-1 was $463 \pm 25 \text{ particles/cm}^3$ and $1\ 038 \pm 65 \text{ particles/cm}^3$ for Standard-2; according to the manufacturer the standards are stable in excess of 10 years. The minimum detection limit of the counter used is $0.5 \mu\text{m}$; for this reason aggregates of diameter $\leq 1.0 \mu\text{m}$ were reported in the $1.0 \mu\text{m}$ class throughout the experiments. Measurements were conducted at $23 \pm 0.5^\circ\text{C}$.

Results and discussion

The total count and the percent distribution of aggregate sizes in Suspension B at zero dilution, $[B]_0 = 2.0 \text{ mg/l}$, are given in Fig. 1a. This suspension contained $1\ 277 \pm 74 \text{ aggregates per cm}^3$;

TABLE 1
Average number of aggregates and distribution of their sizes in bentonite (B), fulvic acid-bentonite (FAB), and humic acid-bentonite (HAB) suspensions; $[B]_0 = 2.0 \text{ mg/l}$, $[FAB]_0$ made of $[B]_0 = 2.0 \text{ mg/l}$ and $[FA]_0 = 2.0 \text{ mg/l}$, $[HAB]_0$ made of $[B]_0 = 2.0 \text{ mg/l}$ and $[HA]_0 = 2.0 \text{ mg/l}$.

	Aggregate diameter (μm)										Total (#/cm ³)
	1	2	3	4	5	6	7	8	9	10	
B_0 Count (#/cm ³)						274	226	318	459		1 277
FAB_0 Count (#/cm ³)				162	231	180	482	18	14	1	1 088
HAB_0 Count (#/cm ³)				73	259	213	567				1 112

the diameters of the aggregates were in the range 6.0 to 10.0 μm (Fig. 1a and Tables 1 and 2). Ten minutes after mixing $[\text{B}]_0$ and $[\text{FAs}]_0 = 2 \text{ mg}/\ell$, a total of $1\,088 \pm 70$ aggregates per cm^3 was counted in FAB_0 suspension; aggregate diameters were in the range of 4.0 to 10.0 μm , no aggregates of diameter smaller than 4.0 μm were found in the suspension (Fig. 1b. and Tables 1 and 2).

In Suspension B at zero dilution, ($[\text{B}]_0 = 2.0 \text{ mg}/\ell$), there were 777 aggregates per cm^3 of diameter equal to or larger than 8.0 μm (Fig. 1a and Table 1). FAB_0 suspension, made up of aliquots of $[\text{B}]_0$ and $[\text{FA}]_0$, contained 33 aggregates per cm^3 of diameter equal to or larger than 8.0 μm . Adsorption of FAs on B and subsequent reactions in the freshly formed aggregates resulted in almost complete disappearance of aggregates of diameter equal to or larger than 8.0 μm , and formation of aggregates of diameter equal to or smaller than 5.0 μm (Fig. 1b and Table 1).

Ten minutes after aliquots of Suspensions HA_0 and B_0 had been mixed each cm^3 of Suspension HAB_0 contained $1\,112 \pm 63$ aggregates (Fig. 1b. and Tables 1 and 2). In Suspension HAB_0 , made up of aliquots of $[\text{B}]_0$ and $[\text{HA}]_0$, aggregate diameters were in the range of 4.0 to 7.0 μm (Fig. 1b and Table 1). No aggregates of diameter equal to or larger than 8.0 μm were found in Suspension HAB_0 (Fig. 1 and Table 1). Adsorption of HAs on B and subsequent reactions among them resulted in a complete disappearance of aggregates of diameter equal to or larger than 8.0 μm , and formation of aggregates of diameter equal to or smaller than 5.0 μm (Fig. 1b. and Table 1).

B platelets have an aspect ratio of approximately 10 (Hunter, 1989) and are of irregular shape. For simplicity we assumed that the volume of fully hydrated B aggregates equals $4r^3\pi/3$ in diluted suspensions. Aggregates in FAB and HAB suspensions are also fully hydrated so their volumes were also assumed to be equal to those of a sphere in their diluted suspensions. Under this assumption, the volume of an average aggregate in Suspension B was roughly 4.0 times larger than the volume of an average aggregate in either Suspension FAB or HAB. Volume estimation also showed that total volume of FAB aggregates was roughly 16.0 % smaller than the total volume of aggregates in Suspension B (Tables 1 and 2). HAB aggregates had a total volume 12.0% smaller than the total volume of aggregates in Suspension B (Tables 1 and 2). Volume changes observed after adsorption of HAs on B and adsorption of FAs on B can be explained by:

- i) Compaction of aggregates with concurrent release of water from its hydration shell,
- ii) Decomposition of micron size aggregates into even smaller aggregates having diameter smaller than $< 0.5 \mu\text{m}$; particles of this size and smaller could not be detected with the particle counter we used, or
- iii) Simultaneous occurrence of (i) and (ii).

Total aggregate counts in each of the 36 HAB suspensions, each aged for 14 688 h and each of different HA/B ratio, are presented in Fig. 2. Aggregate counts fluctuated rather dramatically in some suspensions. For example the suspension prepared from

$[\text{HA}]_0 = 2.0 \text{ mg}/\ell$ and $[\text{B}]_0 = 2.0 \text{ mg}/\ell$, contained 1 112 aggregates/ cm^3 at time zero (Fig. 1c. and 'T = 0 h' in Fig. 2). The number of aggregates in the suspension decreased by almost 80% after 24 h of aging ('T = 24 h' in Fig. 2). The number of aggregates

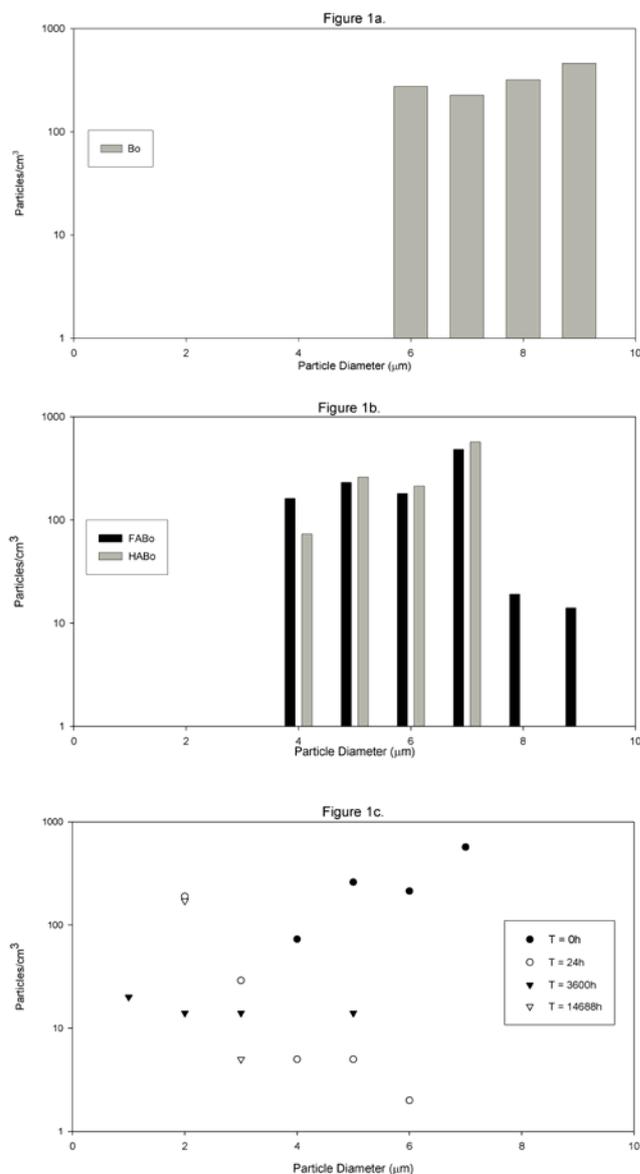


Figure 1

Number of aggregates and distribution of their sizes. (3a) Bentonite Stock Suspension (B), $[\text{B}]_0 = 2.0 \text{ mg}/\ell$; total count $1\,277 \pm 74$. (3b) Humic Acids – Bentonite (HAB) suspension made from $[\text{B}]_0 = 2.0 \text{ mg}/\ell$ and $[\text{HA}]_0 = 2.0 \text{ mg}/\ell$; Fulvic Acids-Bentonite (FAB) suspension made from $[\text{B}]_0 = 2.0 \text{ mg}/\ell$ and $[\text{HA}]_0 = 2.0 \text{ mg}/\ell$. (3c) HAB suspension at various time intervals; HAB suspension made from $[\text{B}]_0 = 2.0 \text{ mg}/\ell$ and $[\text{HA}]_0 = 2.0 \text{ mg}/\ell$.

	Average count ($\#/\text{cm}^3$)	Volume of average aggregate (cm^3/cm^3)	Volume ratios (B/FAB & B/HAB)
B_0	$1\,277 \pm 74$	2.59×10^{-7}	1
FAB_0	$1\,088 \pm 70$	6.23×10^{-8}	4.16
HAB_0	$1\,112 \pm 63$	6.53×10^{-8}	3.97

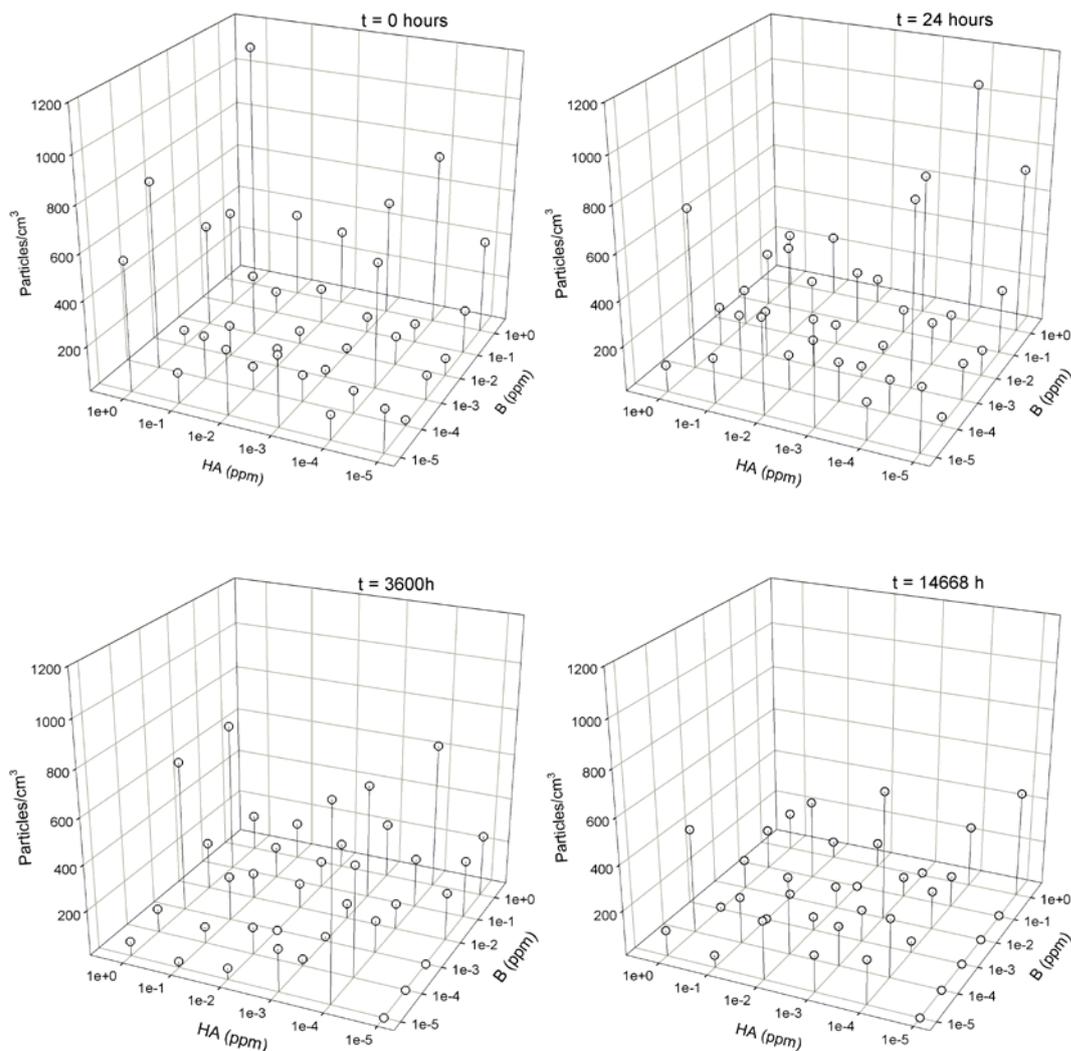


Figure 2
 Number of particles in fresh and aged HAB suspensions; fresh HAB ($T = 0$ h), HAB aged 1 d ($T = 24$ h), HAB aged 150 d ($T = 3\ 600$ h) and HAB aged 612 d ($T = 14\ 688$ h). Bentonite (B), humic acids (HA). Averages of three readings are reported, at each data point maximum and minimum where within $\pm 11.2\%$ of average.

in the suspension was rather constant throughout the rest of the experiment ($T = 3600$ h' and $T = 14688$ h' in Fig. 2).

The suspension, prepared from $[HA] = 0.2$ mg/l and $[B] = 0.2$ mg/l, contained 104 aggregates/ cm^3 at zero time ($T = 0$ h' in Fig. 2). The number of aggregates in the suspension increased to 153/ cm^3 after 24 h of aging ($T = 24$ h' in Fig. 2). After 3 600 h there were 143 aggregates/ cm^3 of suspension ($T = 3\ 600$ h' in Fig. 2). After 14 688 h the number of aggregates in the suspension increased to 356 aggregates/ cm^3 ($T = 14\ 688$ h' in Fig. 2).

The number of aggregates in suspension prepared from $[HA] = 0.002$ mg/l and $[B] = 0.00002$ mg/l, increased from 316 to 465/ cm^3 during first 24 h of aging ($T = 0$ h' and $T = 24$ h' in Fig. 2). After 3 600 h the number of aggregates in the suspension decreased to 189/ cm^3 and remained at approximately that level for the rest of the experiment ($T = 3\ 600$ h' and $T = 14\ 688$ h' in Fig. 2).

A few other suspensions, like those prepared from:

- $[HA] = 0.0002$ g/l and $[B] = 2.0$ g/l
- ii) $[HA] = 0.00002$ mg/l and $[B] = 2.0$ mg/l

- $[HA] = 0.0002$ mg/l and $[B] = 0.00002$ mg/l
- $[HA] = 2.0$ mg/l and $[B] = 0.00002$ mg/l, also exhibited notable fluctuations in aggregate count

Fluctuations in aggregate count were observed in the other HAB suspensions tested but were much less pronounced (Fig. 2).

In addition to fluctuations in aggregate count the changes in distribution of aggregate sizes in response to aging were also observed in each suspension tested as illustrated for Suspension HAB_0 (Fig. 1c).

FAB suspensions show similar response on aging to HAB suspensions. Maximum counts and distribution of aggregate sizes in FAB suspensions were found at different FA/B ratios when compared to maximums and size distributions in HAB suspensions; this will be reported in a forthcoming paper.

In concentrated clay suspensions, [Montmorillonite] = 25 g/l, addition of a small amount of humic acids, $[HA] = 0.1$ g/l, resulted in dispersion of clay aggregates as observed

by viscosity measurements (Tarchitzky and Chen, 2002). In a diluted HAB suspension at particular [HA]/ [B] ratio, the number of aggregates may:

- Decrease rather fast, then stay constant, as in the suspension made of [HA]₀ = 2.0 mg/l and [B]₀ = 2.0 mg/l (Fig. 2)
- Fluctuate while the suspension ages, as in the suspension made of [HA]₀ = 2.0 mg/l and [B] = 0.0002 mg/l (Fig. 2)
- Increase rather fast, decrease, and then stay constant, as in the suspension made of [HA] = 0.002 mg/l and [B] = 0.0002 mg/l (Fig. 2)
- Stay constant for a rather long time, then increase as in the suspension made of [HA] = 0.02 mg/l and [B] = 0.002 mg/l (Fig. 2).

Humic substances are heterogeneous, relatively large, polyelectrolytes characterised by numerous and different functional groups (Stevenson, 1994; Tipping, 2002). In freshly prepared HAB suspensions HAs cover a portion of B surfaces. The fraction of the surface covered changes with a change in [B] and [HA] or change in [HA]/ [B] ratio. At some [HA]/ [B] ratios disaggregation of the aggregates is probably due to steric stabilisation. Disaggregation yields smaller aggregates and exposes fresh, HA-unoccupied, clay surface. This triggers redistribution/ re-adsorption of previously sorbed HAs between the old and freshly available B surface. Likewise dissolved and previously un-adsorbed HAs will adsorb on a fresh B surface. Clays are known for their catalytic properties; large HAs units may be decomposed into smaller ones upon close contact with B.

Changes in the ionic composition of aggregate hydration shells are also probable. The consequence will be sequences of aggregations and disaggregations accompanied by fluctuations in qualitative and quantitative composition of HAB aggregates as observed in aged HAB suspensions. This result is supported by Narkis et al. (1970) who stated that HSs affect association-dissociation equilibrium of montmorillonite. Fluctuations in qualitative and quantitative composition of micron size HAB aggregates should affect adsorption/desorption of various chemicals present in both aquatic and terrestrial systems. Fluctuations in qualitative and quantitative composition of micron-size HAB aggregates indicate that both qualitative and quantitative composition of colloidal HAB aggregates changes in response to aging and/or environmental changes. Such changes could profoundly affect availability, transport, and fate of chemicals in both aquatic and terrestrial systems. Experiments in progress are focused on adsorption/desorption of nutrients and other chemicals in diluted HAB and FAB suspensions of different HA/B and FA/B ratios and different ages.

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