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Supporting documents

Interactions of mercury with different molecular weight fractions of humic substances in aquatic systems

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Cleaning Procedures for Containers.

All containers used were made of Teflon. After cleaning with ultrapure water, all the containers were filled to the top with 10% (v/v) nitric acid and allowed to stand at the room temperature for 1 week. They were then rinsed five times with ultrapure water, filled with ultrapure water, and allowed to stand until they were used. The filling water was renewed periodically to ensure continued contact with clean water.

Ultrafiltration technique

The separation of the humic acid with different molecular weight fraction was carried out by using an Amicon Ultrafiltration Stirred Cell 8400 (Beverley, MA, USA). The ultrafiltration membranes (regenerated cellulose, diameter of 76mm, Millipore corporation, Billerica,MA) with a nominal cut off of 300 kDa, 100 kDa, 50 kDa, 30 kDa, 10 kDa, 5 kDa and 1 kDa were used. To determine the possible retention of Hg by chemical reaction with membranes, blank filter tests were performed. The schematic diagram of the set up is shown below



Determination of Hg by Direct Mercury Analyzer:

Mercury was anaylyzed by Direct Mercury Analyzer (Tri cell DMA-80) from Milestone, Italy. The DMA-80 combines the techniques of thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry. Controlled heating stages are implemented to first dry and then thermally decompose a sample introduced into a quartz tube. A continuous flow of oxygen carries the decomposition products through a catalyst bed where interferences are trapped. All mercury species are reduced to elemental Hg and are then carried along to a gold amalgamator where the mercury is selectively trapped. The system is purged and the amalgamator is subsequently heated which releases all mercury vapours to the single beam, fixed wavelength atomic absorption spectrophotometer. Here, absorbance measured at 253.7 nm is proportional to mercury content in the sample.

Determination of dissolved humic-like compound (a major part of DOC) by UV/Visible spectroscopy

UV absorbance of humic acid solutions was carried out at 254 nm using 100707 UV-VIS Spectrophotometer (Pharo 300 Spectroquant® from Merck Millipore) and a 1 cm quartz cell and the respective values were converted to total organic carbon using a calibration curve. For that purpose, serial dilutions of the concentrated HA stock solution in the range 0.01–10.0 mg dm⁻³ were prepared. The calibration curve is presented in Fig. 1



Figure 1

Figure 1SD An external calibration curve used for the quantification of HA in the test solutions.

		300-		50-		10-		
[Hg] _T	>300kDa	100kDa	100-50kDa	30kDa	30-10kDa	5kDa	5-1kDa	<1kDa
8.3 nM	3.2 ± 0.2	1.2 ± 0.2	1.0 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.8 ± 0.3	0.7 ± 0.1	0.6 ± 0.1
16.5 nM	4.2 ± 0.4	4.9 ± 0.4	2.6 ± 0.5	1.8 ± 0.2	0.9 ± 0.3	0.6 ± 0.1	0.2 ± 0.1	1.3 ± 0.3
58nM	21.2 ± 2.1	11.8 ± 1.0	6.7 ± 0.6	7.4 ± 0.3	3.7 ± 0.5	2.0 ± 0.1	1.0 ± 0.1	4.1 ± 0.2
156 nM	91.1 ± 3.2	19.6 ± 2.1	18.1 ± 0.7	17.9 ± 0.4	7.9 ± 0.2	0.3 ± 0.1	0.2 ± 0.1	2.2 ± 0.2
225nM	137.7 ± 4.3	32.6 ± 1.2	38.0 ± 0.8	1.1 ± 0.2	7.2 ± 0.3	6.3 ± 0.2	0.0 ± 0.0	2.0 ± 0.2
434 nM	$287.5{\pm}2.4$	12.6± 1.3	88.3±2.1	12.6 ± 0.4	12.2 ± 0.4	18.7±1.4	0.0 ± 0.0	3.0 ± 0.3

Table 1SD: Distributions of Hg associated with different molecular weight fractions of HA at different Hg loading. The association of Hg are presented as the total concentrations of Hg (in nM).

The data presented as mean values \pm standard deviations

pН	>300kDa	300- 100kDa	100- 50kDa	50- 30kDa	30- 10kDa	10- 5kDa	5-1kDa	<1kDa
2.5	3.4±0.3	1.5 ± 0.1	1.2 ± 0.1	1.0 ± 0.1	0.6± 0.1	0.2 ± 0.1	0.0 ± 0.0	4.3 ± 0.2
3.4	5.2 ± 0.2	1.6± 0.1	0.5 ± 0.1	0.4 ± 0.1	0.7 ± 0.1	0.1 ± 0.1	0.1 ± 0.0	3.7 ± 0.4
4.5	5.4 ± 0.6	0.0 ± 0.0	2.2 ± 0.3	2.7 ± 0.3	$0.9 {\pm} 0.1$	0.3±0.1	0.0 ± 0.0	0.8 ± 0.1
6.4	8.1 ± 0.9	0.4 ± 0.1	2.5 ± 0.1	$0.4 {\pm} 0.1$	0.3±0.1	0.5 ± 0.1	0.0 ± 0.0	0.1 ± 0.1
7.5	5.2 ± 0.6	0.9 ± 0.2	0.9 ± 0.1	1.7 ± 0.1	1.4 ± 0.2	1.8 ± 0.1	0.3 ± 0.1	0.0 ± 0.0

Table 2SD: Distributions of Hg associated with different molecular weight fractions of HA at different pH. The association of Hg are presented as the total concentrations of Hg (in nM). Initial concentrations of Hg was 12.3nM

The data presented as mean values \pm standard deviations

Table 3SD: Distributions of Hg associated with different molecular weight fractions of HA at different ionic strengths. The association of Hg are presented as the total concentrations of Hg (in nM). Initial concentrations of Hg was 12.4nM

Ionic strength	>300kDa	300- 100kDa	100-50 kDa	50-30 kDa	30-10 kDa	10-5 kDa	5-1 kDa	<1 kDa
0.0001M	1.2 ± 0.1	1.7 ± 0.2	2.9 ± 0.2	1.5 ± 0.2	0.1 ± 0.1	0.1 ± 0.1	1.3 ± 0.2	3.5 ± 0.6
0.001M	3.3 ± 0.3	1.9 ± 0.1	0.8 ± 0.1	0.9 ± 0.1	0.0 ± 0.0	0.9 ± 0.3	1.5 ± 0.2	3.1 ± 0.1
0.005M	6.7 ± 0.4	0.3 ± 0.1	0.8 ± 0.1	0.3 ± 0.1	1.0 ± 0.2	0.2 ± 0.1	1.5 ± 0.2	1.6±0.1
0.01M	9.6 ± 0.5	$1.1{\pm}0.1$	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.0 ± 0.0	0.9 ± 0.1

The data presented as mean values \pm standard deviations

Time (min)	pH2.5	рН3.4	рН3.6	pH3.8	pH4.0	pH4.5	рН6.4
0 min	100	100	100	100	100	100	100
342 min	100	98.8	99.7	98.2	90.9	91.9	88.3
1362 min	99.9	97.2	94.5	88.5	86.3	81.1	76.5
1742 min	99.6	96	91.8	86.4	73.1	79.6	75.9
2780 min	98.2	94.2	89	74.8	52.4	53.5	56.5
3050 min	97.1	92.8	88.7	64	46.3	48.3	55.6
4220 min	96.9	91.3	88.4	33	18.8	29.3	44.3

Table 4SD: Concentrations of Hg associated with HA at varying pH with the progress of time. The concentrations of Hg are presented as nM. (HA 5mg. dm⁻³, Hg (initial concentration =100nM).

 Table 5 SD: Concentrations of major cations and major anions in the freshwater sample collected from

 Godavari River

AnionsMCationsM
$$F^{-}$$
 1.9×10^{-5} Na $^{+}$ 1.8×10^{-5} CI^{-} 4.1×10^{-4} NH₄ $^{+}$ 5.3×10^{-8} NO_2^{-} 1.1×10^{-4} K $^{+}$ 2.4×10^{-6} SO_4^{-2-} 3.5×10^{-5} Mg²⁺ 1.1×10^{-5} Br $^{-}$ 7.5×10^{-7} Ca²⁺ 1.1×10^{-5} NO_3^{--} 2.8×10^{-5} VO_3^{--} PO_4^{-3-} 1.4×10^{-7} VO_3^{--}