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Cent. Eur. J. Chem. • 9(4) • 2011 • 598-604
DOI: 10.2478/s11532-011-0035-5

Central European Journal of **Chemistry**

Assessment of different sorbents efficiency for solid phase extraction of aquatic humic acids

Research Article

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Received 11 August 2010; Accepted 22 February 2011

Abstract: In the present study, a simple procedure for the isolation by solid-phase extraction (SPE) and quantification by UV-Vis spectrometry (400 nm) of the humic acids (HAs) in the natural waters was developed. Seven different sorbents: Porapak P (polystyrene-divinylbenzene copolymer), Florisil (chemical composition: 84.0% SiO_2, 15.5% MgO and 0.5% Na_2SO_4), Silica gel C18 (octadecyl silane), Strata X (surface modified polystyrene-divinylbenzene), Strata NH_2 (silica-based trifunctional amino ligand), Strata SAX (silica-based trifunctional quaternary amine) and Strata C18-E (silica-based trifunctional C18 with hydrophobic end-capping of silanols) were tested. The HAs, adsorbed on SPE cartridges, were eluted using: NaOH (0.1 M), sodium dodecyl sulphate (SDS) (20 g L^{-1}), and a 1:1 v/v mixture of SDS (20 g L^{-1}) and NaOH (0.1 M). The extraction efficiency was evaluated by comparing the HAs recovery levels. The repeatability of results was estimated by the relative standard deviation (RSD). The data confirmed that Porapak P, Silica gel C18, Florisil, Strata NH_2 and Strata X could be good alternatives for the traditional isolation of the aquatic HAs with XAD resin. The proposed method was applied for the determination of HAs in some waters sampled from the Western Romanian Plain. The content of HAs was correlated with the arsenic concentration and total organic carbon (TOC) level.

Keywords: *Aquatic humic substances • Solid phase extraction • Sorbent efficiency • UV-Vis spectrometry*

1. Introduction

The humic substances (HSs) are ubiquitous natural materials occurring in high amounts in soils, sediments and waters and represent a significant source of non-living organic material. Approximately 80% of the total carbon in the terrestrial media and 60% of the dissolved carbon in the aquatic media are made up of HSs [1]. The HSs are formed during the humification process, which is the second largest biogeochemical process on the Earth after photosynthesis.

According to their solubility, HSs can be divided into three categories: humic acids (HAs), fulvic acids (FAs) and humin. HAs represent the fraction which is insoluble in water under acidic conditions (pH < 2), but is soluble at higher pH values. The FAs are soluble in water under all pH conditions, while the humin are insoluble in water at any pH value. The most explored are the HAs and their salts (humates), which represent the main fraction (~70%) of the HSs [2].

Compared to other chemical compounds, the HSs are difficult to define considering their complex chemical structure. They can be described as acidic, hydrophobic, aromatic polymers, containing functional groups like carboxylic, phenolic or/and aliphatic hydroxyl, amine, *etc.* [3]. The HSs have molecular weights in the range of several hundreds to tens of thousands Daltons. The HAs molecular weight ranges from 7×10^2 to 2×10^6 Daltons, while that of FAs is less than 1×10^4 Daltons [3].

Because of their relatively high reactivity, the HSs have a significant role in the environment: they can enhance biotic and abiotic degradation of phenols, polycyclic aromatic hydrocarbons (PAH), and toxic compounds like pesticides [2,4]; they can interact with clay minerals, or combine with the chlorine used during the water treatment and generate toxic trihalomethanes [5]. They can serve

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as carriers of toxic metals, by forming stable complexes, and they can also significantly affect the bioavailability and mobility of metals in soils, sediments and aquatic systems [6-8].

Different techniques such as UV-Vis spectrometry [3,9,10], high performance liquid chromatography (HPLC) [11-13], or gel permeation chromatography (GPC) [14], can be used to analyse the HSs. In order to increase the sensitivity of these methods, the water samples are generally concentrated by SPE, before the analysis. Compared to other techniques such as solvent extraction [19], ultrafiltration [20] or gel permeation chromatography (GPC) [14], SPE seems to be one of the most suitable methods used for HSs isolation, pre-concentration and purification. The most used sorbents are the XAD resins, especially XAD-2 (polystyrene-divinylbenzene) [15-18] and XAD-7 (polymethacrylate) [15,16].

In the present article, a comparative study regarding the efficiency of different sorbents used for the isolation of HAs from aquatic matrices is described. After the isolation, the HAs were quantified by UV-Vis spectrometry. The proposed method was applied for the determination of HAs in some natural waters, originating from aquifers located in the Western Plane of Romania, a rich arsenic area [21]. The samples were collected from four medium-depth (<200 m) aquifers (Ciumeghiu, Avram Iancu, Zerind and Cermei) and two deep (>1,300 m) geothermal aquifers (Săcuieni and Oradea). The HAs concentrations were correlated with the arsenic level in order to estimate the influence of HAs on arsenic mobilization and their deleterious effects on human health [22]. Considering that HAs represent an important source of organic and inorganic carbon in the environment, the correlation between the HAs and the TOC level was also evaluated.

2. Experimental Procedure

2.1. Instrumentation

A 540 GLP pH-meter (WTW GmBH, Weilheim, Germany) was used to measure the pH during the sampling and the further adjustments in the laboratory. All weightings were performed by XA60/220 analytical balance (Radwag, Šumperk, Czech Republic). A Sonorex Longlife RK 103H ultrasonic bath (Bandelin, Berlin, Germany) was used for the sample preparation.

The solid phase extractions were performed using a SPE Supelco Visiprep ™ DL (Bellefonte, USA) device. Seven types of sorbents were tested: Porapak P, Silica gel C18 and Florisil, manufactured in the laboratory by using 6 mL syringes filled with 500 mg of sorbents, and Strata X, Strata NH_2, Strata SAX and Strata C18-E purchased by Phenomenex (Torrance, Canada). Some of the main properties of the evaluated sorbents are summarised in Table 1.

The HAs content was determined at 400 nm wavelength, using a Lambda 25 UV/Vis Spectrometer (Perkin Elmer, Beaconsfield, UK) with 1 cm glass cells. The arsenic concentration was measured by an SCIEX Elan DRC II inductively coupled plasma mass spectrometer (Perkin-Elmer, Toronto, Canada) fitted with a quadrupole for ion m/z discrimination and a dynamic reaction cell (DRC) for the interference removal. The dynamic reaction cell was pressurized with oxygen for As determination in high chlorine matrix, by shifting determined mass form ^{75}As to ^{91}AsO, removing ^{75}ArCl interference. TOC determination was carried out using a Multi N/C 2100S Analyzer whit NDIR detector (Analytic Jena, Jena, Germany)

2.2. Reagents and stock solutions

All the used chemicals were of high purity grade and they were provided by Merck (Darmstadt, Germany), Fluka (Buchs, Switzerland), Aldrich (St Louis, US), and Lachema (Czech Republic). All the solutions were prepared by using ultrapure water (Direct-Q3, Millipore, Molsheim, France) and kept at 4°C. All the used glassware was soaked in 5 M HNO_3 for a minimum of 12 h and was washed with ultrapure water. The cartridges washing and conditioning was carried out using methanol and acetone.

The SDS solution (30 g L^{-1}) was prepared by dissolving solid SDS in 0.1 M NaOH. The humic acid stock solution (0.2 g L^{-1}) was made by dissolving humic acid powder in 0.1 M NaOH and passing it through 0.45 μm cellulose acetate filters.

2.3. Sampling

The waters were sampled directly from the artesian wells, in polyethylene bottles that had been previously washed three times with ultra pure water (Millipore Milli-Q). Prior to the sampling, the bottles had been rinsed two times in situ, with the sampled water. After sampling, the waters were filtered through 0.45 μm cellulose acetate filters and acidified to a pH=1.5 with HCl (2 M). The sampling flasks were transported to the laboratory, stored at 4°C, away from sunlight, and analyzed within one-week from sampling.

2.4. Solid Phase Extraction (SPE) of HAs

The HAs were extracted by SPE method using Porapak P sorbents. Before the extraction, the sorbents were conditioned by passing through the cartridges a volume of 10 mL sodium hydroxide (0.1M); followed by 10 mL methanol; 10 mL acetone; another 10 mL methanol, 100 mL ultrapure water; 10 mL sodium hydroxide (0.1M) and 10 mL hydrochloric acid (2M) [18]. The sorbents were left in the acidic state before the extraction. Next, the filtered and acidified (pH = 1.5) samples were loaded into the cartridges, at a flow-rate of 2 mL min^{-1}, under vacuum (10 kPa) condition. Finally, the analytes of interest (HAs) were eluted with 10 mL of SDS (30 g L^{-1}).

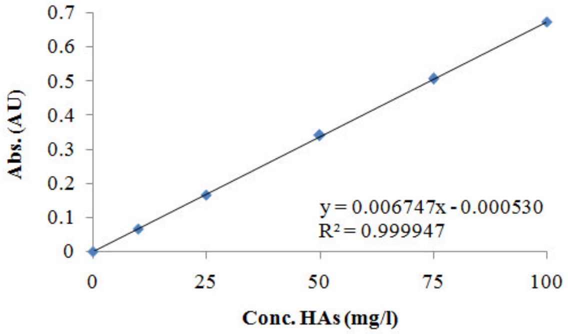

Figure 1. Calibration curve.

2.5. Calibrations

The HAs concentrations were calculated using a calibration curve made of five standard solutions: 10, 25, 50, 75 and 100 mg L^{-1} (Fig. 1). The correlation coefficient (R^2) of the calibration curve was 0.999.

3. Results and Discussions

3.1. The optimisation of the SPE extraction

3.1.1. The HAs adsorption performances of the tested sorbents

In order to optimise HAs adsorption, seven types of sorbents were tested (Table 1). A volume of 200 mL artificial water sample was spiked with 1 mg HAs and passed through the cartridges. The HAs adsorption performances of the sorbents were evaluated by directly comparing the absorbances of the original samples and the column effluents. The HAs adsorption performances of each type of sorbent are presented in Table 2. All the tested sorbents proved to have high HAs adsorption capacity, ranging between 88.7% (Strata C18-E) and 101.3% (Silica gel C18).

Table 1. The properties of the used sorbents.

Sorbent	Retention mechanism	Surface area (m^2 g^{-1})	Particle size (mesh)	Pore size (Å)
Porapak P **(polystyrene-divinylbenzene (PS-DVB))**	-non-polar -hydrophobic -reversed phase	200	80-100	80
Silica gel C18 **(octadecyl silane (ODS))**	-non-polar -hydrophobic -reversed phase	500	270	70
Florisil **(MgO (15.5%); SiO_2 (84.0%); Na_2SO_4 (0.5%))**	-polar -hydrophilic -normal phase	300	80	80
Strata SAX **(silica-based trifunctional quaternary amine)**	-strong anion exchange -hydrophilic	470	270	74
Strata NH_2 **(silica-based trifunctional amino ligand)**	-polar -weak anion exchange -normal phase	478	270	72
Strata X **(surface modified polystyrene-divinylbenzene (PS-DVB))**	-non-polar/polar -hydrophobic/hydrophilic -reversed phase	800	450	85
Strata C18-E **(silica-based trifunctional C18 end-capping)**	-non-polar -hydrophobic -reversed phase	461	270	76

3.1.2. The HAs elution power of different eluents

A volume of 200 mL artificial water sample spiked with 1 mg HAs was passed through the sorbents and eluted with different eluents. In order to optimise the SPE extraction of HAs, for each type of sorbent the following eluents were tested: NaOH (0.1M), SDS (20 g L^{-1}) and a 1:1 v/v mixture of SDS (20 g L^{-1}) and NaOH (0.1 M). The efficiency of the tested eluents was estimated by comparing the recovery levels of the eluted HAs. Each experiment was made in triplicate and the relative standard deviation (RSD) was calculated. The data regarding the performances of the tested eluents are summarised in the Table 3.

The results showed that, the use of NaOH (0.1 M), lead to a poor recovery for the sorbents: Strata C18-E (33.5±7.2%), Silica gel C18 (52.2±2.3%) Florisil (61.3±4.3%) and Strata X (69.3±1.3%). For the other sorbents the HAs recovery ranged between 70 and 80% (Table 3).

By using SDS (20 g L^{-1}), an alkaline solution containing anionic surfactant, the HAs desorption was notably improved, because the surfactants enhance the water-solubility of slightly soluble organic compounds. In the case of non-polar sorbents, the use of SDS improved the recovery of HAs up to 91.5±1.3% (Porapak P), 89.0±1.5% (Silica gel C18) and 82.3±2.5% (Strata X). The lowest HAs recovery was obtained in the case of Strata C18-E sorbent, where only 59.3±3.2% of the added HAs were recovered.

By using the 1:1 (v/v) mixture of SDS (20 g L^{-1}) and NaOH (0.1 M) as eluent, the HAs recovery was improved in the case of the polar sorbent Florisil (85.4±2.9%), anion exchange sorbents Strata NH_2 (78.9±2.1%), and Strata SAX (74.9±1.7%). For Porapak P, Silica gel C18 and Strata X, the recovery levels slightly decreased compared to the elution with SDS (20 g L^{-1}). This could be a consequence of the hydrophobic interaction that occurs between HAs and the sorbent surface.

As shown in Table 3, the Porapak P, Silica gel C18, Florisil, Strata NH_2 and Strata X sorbents assure a good recovery of HAs, therefore they can be a good alternative for the traditional isolation with XAD resin. Other studies reported total recoveries for HAs in the range of 10-75% (XAD-2) or 67-87% (XAD-8) by using NaOH (0.2 M) as eluent [9]. Due to the fact that the sorbents based on silica gel (Silica gel C18, Silica gel C18 E, Strata NH_2 and Strata SAX) have a poor chemical stability under high acidic condition (pH≤1.5), the use of sorbents with high stability at all pH levels, like Porapak P and Strata X are recommended.

In order to increase the HAs recovery, different concentrations of eluents: NaOH (0.05-0.2 M) and SDS (5-50 g L^{-1}) were tested. These tests were done on Porapak P cartridges, characterized by high sorption/desorption capacities and good stability on a wide pH range. There was no significant improvement of the HAs recovery due to the increase of the NaOH concentration. Moreover, the recovery of HAs increased remarkably due to the increase of SDS concentration. Between 5 and 30 g L^{-1} of SDS, the HAs total recovery increased from 40.5% to 101.6% (Fig. 2).

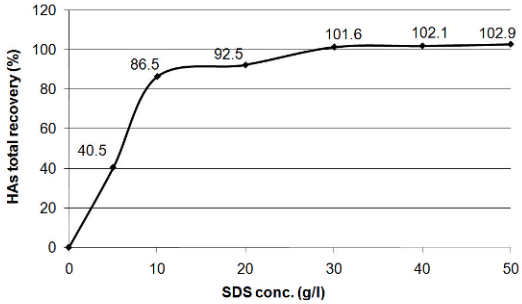

Figure 2. The effect of the eluent (SDS) concentration on the HAs desorption from Porapak P sorbent.

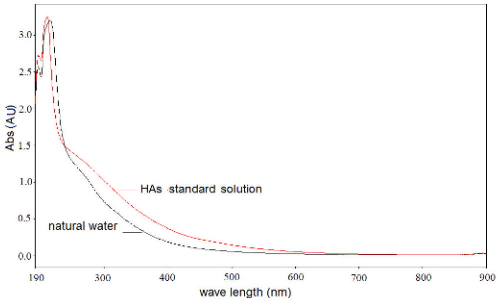

Figure 3. The UV-Vis spectra of a standard HAs solution (50 mg L^{-1} HAs) and a natural water sample (25 mg L^{-1} HAs).

Table 2. The adsorption performances of the tested sorbents (200 mL ultrapure water spiked with 1 mg HAs).

		Porapak P	Silica gel C18	Florisil	Strata C18-E	Strata SAX	Strata NH_2	Strata X
HAs adsorbed on cartridges (%)	Test 1	99.1	101.7	94.8	87.9	96.9	99.4	100.5
	Test 2	99.6	101.1	97.3	89.9	97.6	99.1	98.4
	Test 3	98.8	100.9	94.2	88.4	96.3	99.4	100.3
	average±RSD	99.1±0.4	101.3±0.4	95.4±1.7	88.7±1.2	96.9±0.7	99.3±0.2	99.8±1.2

**RSD - Relative Standard Deviation*

3.2. The HAs quantification by UV-Vis spectrometry

Fig. 3 presents the UV-Vis spectra of a standard HAs solution (50 mg L^{-1}) and a natural water sample, over the range of 190 to 900 nm. Both spectra have a maximum of absorbance at 210-220 nm and then show a gradual decrease with the increase of the wavelength. Similar UV-Vis spectra for HAs solutions are reported in other studies [10,23-25].

The determinations were performed at 400 nm, although this value does not correspond to the maximum of absorption. Langhals *et al*. [24] showed that in the range of 400 to 440 nm there is an excellent linear correlation between the absorbance and the concentration of humic substances, due to the lower noise of the spectrometer. The 400 nm wavelength was also a compromise between the sensitivity of the method and the avoidance of the possible interferences caused by the presence of other non-humic substances [19]. The results of the present study have shown that for low HAs concentrations (<0.02 g L^{-1}) the determinations can be performed at 230-250 nm, which correspond to the maximum absorbance (Fig. 4A). In the case of higher HAs concentrations (>0.02 g L^{-1}), the absorbances determined at 230-250 nm are very high, as a consequence determinations at 400 nm wavelength is recommended (Fig. 4B).

The quantification limit (LOQ) of the method was 0.5 mg L^{-1}. Our data proved that the presence of SDS or NaOH in different concentrations did not affect the spectrophotometric determination of HAs, even at very low absorbances (≈0.015 AU at 400 nm). As a consequence, there is no influence of matrix solution on HAs concentrations.

3.3. The application of the proposed method for the determination of HAs content in natural waters

The HAs content of the sampled waters is presented in Table 4. The thermal waters proved to have a relatively low content of HAs (4 mg L^{-1} in Săcuieni), compared to the waters originating from the medium-depth aquifers,

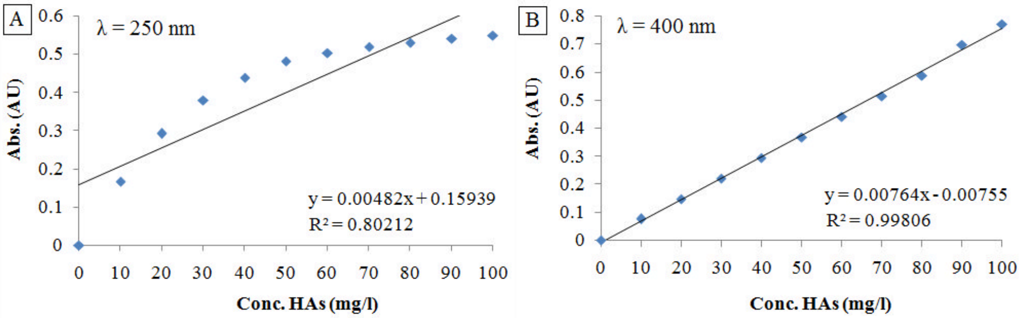

Figure 4. The influence of the wavelength value in the HAs quantification.

Table 3. The HAs recovery by using different eluents (200 mL ultrapure water spiked with 1 mg HAs).

Eluent		HAs recovery from different sorbents (%)						
		Porapak P	Silica gel C18	Florisil	Strata C18-E	Strata SAX	Strata NH$_2$	Strata X
NaOH (0.1M)	Test 1	77.7	53.1	63.5	36.3	71.8	76.9	70.3
	Test 2	76.2	52.6	58.4	32.4	68.7	75.0	68.4
	Test 3	76.0	50.9	62.0	31.9	70.0	75.3	69.1
	average±RSD	*76.7±1.2*	*52.2±2.3*	*61.3±4.3*	*33.5±7.2*	*70.2±2.2*	*75.7±1.3*	*69.3±1.3*
SDS (20 g L^{-1})	Test 1	90.2	89.4	72.1	58.5	70.2	75.8	81.9
	Test 2	92.5	90.2	76.7	61.5	70.8	77.6	80.5
	Test 3	91.9	87.5	73.7	58.0	72.4	77.3	84.5
	average±RSD	*91.5±1.3*	*89.0±1.5*	*74.2±3.1*	*59.3±3.2*	*71.1±1.5*	*76.9±1.2*	*82.3±2.5*
SDS:NaOH (1:1 v/v)	Test 1	91.1	85.2	85.2	54.8	73.4	79.3	73.3
	Test 2	88.6	82.0	83.1	52.4	75.7	80.2	74.7
	Test 3	88.74	84.7	88.0	55.3	75.5	77.0	75.8
	average±RSD	*89.5±1. 6*	*83.9±2.0*	*85.4±2.9*	*54.2±2.9*	*74.9±1. 7*	*78.9±2.1*	*74.6±1. 7*

**RSD - Relative Standard Deviation*

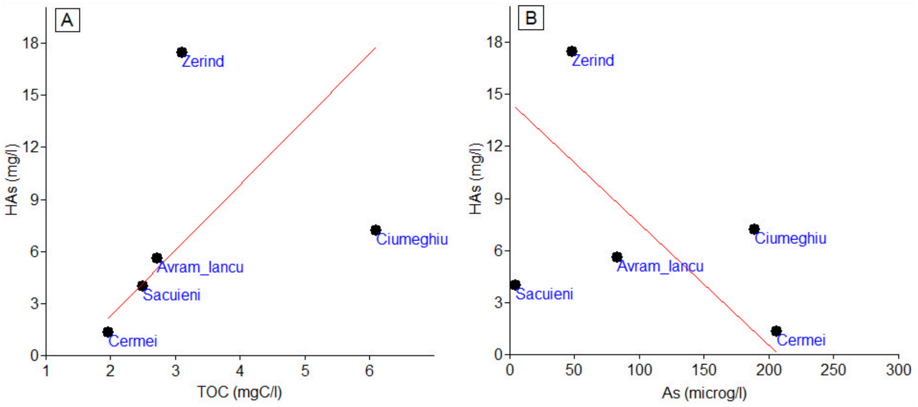

Figure 5. HAs concentration versus TOC level (A) and total arsenic content (B).

Table 4. Determination of HAs in natural waters.

Location	Coordinate	Aquifer depth (m)	Water temp. (°C)	HAs (mg L^{-1})	As (μg L^{-1})	TOC mgC L^{-1}
Săcuieni	47.367 N, 22.083 E	1,400-2,000	80	4±0.19	4.7	2.5
Oradea*	47.051 N, 21.940 E	2,200-3,400	90	nd*	7.7	nd*
Ciumeghiu	46.732 N, 21.576 E	100-200	18.9	7.2±0.8	189	6.1
Avram Iancu	46.667 N, 21.525 E	100-200	21.4	5.6±0.4	83	2.7
Zerind	46.623 N, 21.516 E	100-200	21.0	17.4±0.1	48	3.1
Cermei	46.548 N, 21.844 E	100-200	17	1.3±0.3	206	1.9

**nd-not detected*

where the HAs level ranged between 1.3 mg L^{-1} (Cermei) and 17.4 mg L^{-1} (Zerind). The presence of HAs in Săcuieni and medium-depth aquifers is a consequence of the lithological characteristics of the area, where several coal layers were identified, compared to Oradea aquifer, were these coal layers are missing [28].

HAs represent an important source for the organic and inorganic carbon from the environment. As shown in Fig. 5A for most of the water samples, the HAs level is directly correlated with the TOC concentration. The data showed that high levels of HAs corresponded to low arsenic concentrations (except for Săcuieni) (Fig. 5B). This trend could indicate the influence of HAs in arsenic mobilization by forming stable complexes. Similar correlations were reported by Buschmann *et al*. [29].

4. Conclusions

In this study, an alternative method for the isolation (SPE) and quantification (UV-Vis spectrometry) of the aquatic HAs was proposed.

The results of the present work showed that the Porapak P, Florisil, Strata NH_2 and Strata X sorbents can be a good alternatives for the HAs determination in the natural waters, having good sorption/desorption capacities and chemical stability on a wide pH range. For the non-polar sorbents (Porapak P, Silica gel C18, Strata X and Strata C18-E) the best HAs recovery levels were registered using SDS (20 g L^{-1}) as eluent, while for the polar sorbent (Florisil) and the anion exchange sorbents (Strata NH_2 and Strata SAX) the HAs recovery was improved considerably by eluting with a 1:1 v/v mixture of SDS (20 g L^{-1}) and NaOH (0.1 M).

The proposed method was applied for the determination of the HAs content in the natural waters. The results proved that the method could be used in the routine analyses of the HAs from the natural waters at levels as low as 1.3 mg L^{-1}. These preliminary data have indicated that the HAs level can be indirectly correlated to the arsenic concentration and directly correlated to TOC level.

These results can be further used to start a complex study regarding the correlations between the HAs content and TOC, or to investigate the HAs influence upon the arsenic mobilization for different aquifers.

Acknowledgements

This paper is a contribution of the AquaTRAIN Marie Curie Research Training Network (Contract No. MRTN-CT-2006-035420) funded under the European Commission Sixth Framework Programme (2002-2006) Marie Curie Actions, Human Resources & Mobility Activity Area – Research Training Networks.

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