



PORE WATER CHARACTERIZATION OF CLAYEY SEDIMENTS FROM THE MEKONG DELTA (VIETNAM)

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1. Introduction

The Vietnamese Mekong Delta provides a particularly relevant natural setting for the investigation of the role of S cycling on As mobilization.

Arsenic contamination of soils is of particular concern for rice cultivation, since rice efficiently takes up As from soils and is a dietary staple for approximately half of the global population. The bioavailability of Arsenic for uptake by rice depends on the chemical species present in the soil. Therefore, the characterization of the pore water chemistry of the sediments is crucial to characterize the mechanisms of As transport and transformation in rice paddy systems.

In this report, the chemical composition of the pore waters was obtained by the squeezing technique from four clayey sediments obtained by drilling in the Mekong Delta area.

2. Objectives

To obtain and characterize the pore waters from drillcores obtained at the Vietnamese Mekong Delta.

3. Methodology

3.1 Drillcore samples

Six drillcore samples were received at CIEMAT belonging to four clayey sediment layers (Tab. 1). The drillcores were received preserved inside two Al-foil bags at vacuum (Fig. 1).

Tab. 1: Drillcore samples for squeezing tests

Reference	Type	W.C. (%)	Dry density (g/cm ³)	Characteristics
QT-C5 m. 1-2 Bottom	I	25.9	1.60	Clay, dark brown, compacted
QT-C5 m. 12-13 Bottom	III	47.8	1.18	Clay, dark grey, plastic
QT-C5 m. 13-14 Bottom	III	52.7	1.12	Clay, dark grey, plastic
QT-C5 m. 14-16 Top Peat Layer	IV			Clay, disaggregated, black
QT-C5 m. 22-24 Botom	V	41.6	1.28	Clay, dark brown, plastic
QT-C5 m. 32-34 Middle	V	17.2	1.80	Clay, dark brown, compacted



Fig. 1: Drillcore samples preserved at vacuum in Al-foil bags.

3.2 Pore water chemistry

The pore water of the bentonite samples was obtained by the squeezing technique at high pressures (Fernández et al., 2003; Fernández, 2004; Fernández et al., 2014).

Squeezing is analogous to the natural process of consolidation, caused by the deposition of material during geological time, but at a greatly accelerated rate. The squeezing process involves the expulsion of interstitial fluid from the saturated argillaceous material being compressed (Entwisle and Reeder, 1993). In squeezing experiments, the volume of water extracted depends on the water content of the rock sample, the rock properties (e.g. dry density, the relative contents of easily-squeezed clays and of stiffer materials like quartz and calcite), and the experimental conditions, such as, the pressure applied, the duration time of squeezing and size of the squeezing cell (Fernández et al., 2003).

At CIEMAT the squeezing rig is similar to that developed by Peters et al. (1992) and Entwisle and Reeder (1993). The squeezer has been designed to allow a one-dimensional compression of the sample by means of an automatic hydraulic ram operating downwards, the squeezed water being expelled from the top and bottom of the cell into vacuum vials, specially prepared for maintaining anoxic conditions (Fig. 2 and Fig. 3). The compaction chamber is made of type AISI 329 stainless steel (due to its high tensile strength and resistance to corrosion) with an internal diameter of 70 mm. The compaction chamber is 250 mm high with 20 mm wall thickness and allows pressures up to 100 MPa.

The filtration system allows the extraction of interstitial water by drainage at the top and at the bottom of the sample. This system comprises a 0.5 μm stainless steel AISI 316L porous disk (Cr 17.36%, Ni 11.4%, Mo 2.15%, Si 0.94%, Mn 0.17%, C 0.027%, S 0.011%, P 0.022%, Fe 66.92%) in contact with the sample. The liquid is collected through stainless steel tubes (1/16 inch) inside a vacuum vial sealed by a septum.

Prior to the squeezing tests, the clayey samples for squeezing were prepared inside an anoxic glove bag flushed with Argon (Fig. 4). The external outer part of the core was

removed by using a knife in order to discard possible material contaminated. The sample was weighed and placed into the body of the cell, which was closed.

After assembling the cell in the hydraulic press, a small stress of 0.5 MPa was initially applied to remove most of the atmospheric gas from the cell and allow the sample to bed in. The whole system remains under ambient conditions (room temperature of about 25°C). However, the squeezing test can be considered to be done under anoxic conditions, because the squeezer was closed inside the anoxic glove bag during the preparation of the test, and the squeezing cell with the core sample inside was flushed with Ar prior to the loading of the sample to remove all the possible remaining air from the cell and the sample, avoiding any possible oxidation of the sample during the test. Besides, the sampling tubings and the sealed vials, where water is collected, were also flushed with Ar prior to start the squeezing test to prevent the oxidation of the water sample.

The applied stress progressively increased up to the selected pressure, rather than in a single step. This avoids overconsolidation or collapse of the clay-pore system. When the maximum of squeezed water was obtained, the septum vial was removed, keeping the sample inside an anoxic glove box (< 1 ppm), where the collected water was filtered and distributed in different vials for chemical analysis by using a < 2 µm syringe filter.

One vial was used for chemical analysis at CIEMAT and other two ones were prepared for As(III/V) speciation and sulphide determination at EPFL. The vial for As(III)/As(V) speciation was buffered with a (EDTA (50 g/L) + 8.7 M acetic acid) solution in a relationship 4.9 mL pore water: 50 µg/L acetic acid: 50 µg/L EDTA.

3.3 Water chemical analyses

The total alkalinity of the water samples was determined with a specific Dynamic Equivalence point Titration (DET) method for analysing samples of 1-2 mL. The instrumentation consists on a Metrohm 796 Titroprocessor equipped with a 5 mL burette and a 6.0224.100 Metrohm combined pH micro-electrode.

The major, trace cations and silica were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) in Varian 735 ES spectrometer. Sodium and potassium were determined by flame atomic emission spectrometry, FAES, in a Agilent AA 240 FS spectrometer.

Anions were analyzed by ion chromatography (Dionex ICS-2000).

An ORION 901 microprocessor ion-analyzer, equipped with ion selective electrodes, has been employed for F- and I- determination

Fe(II)/Fe(III) ratio was determined by UV-Vis spectrophotometry with the ferrozine method after acidification of the samples to pH<1 with HCl.

The NPOC (non-purgable organic carbon) which refers to organic carbon present in a non-volatile form was analyzed with a TOC-VCSH analyzer (SHIMADZU, Shimadzu Scientific Instruments, Kyoto, Japan). Samples were acidified with HCl 2M acid and sparged with synthetic compressed air (99.999% purity) to remove inorganic carbon. The samples were then injected into a heated reaction chamber packed with platinum

catalyst. The CO₂ formed was transported to the detector in a carrier gas stream and measured directly by a non-dispersive infra-red (NDIR) gas analysis system. The amount of CO₂ is directly proportional to the TOC content in the sample.

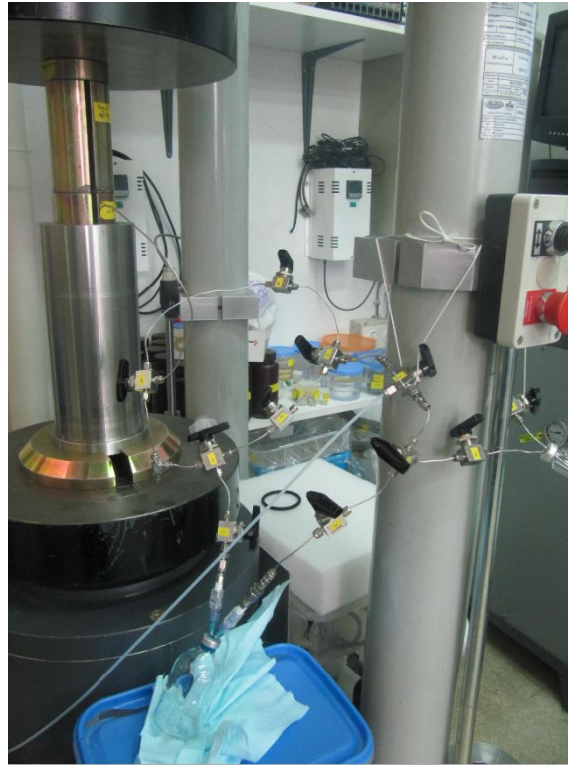


Fig. 2: Squeezed water extraction apparatus used at CIEMAT.



Fig. 3: Vacuum vials for collecting pore water preserving the anoxic conditions.



Fig. 4: Anoxic glove bag flushed with Ar for preparing the sample and the cell prior to the squeezing tests.

4. Results

The characteristics of the core samples prior and after the squeezing tests are shown in Tab. 2. In general, the samples were quite plastic, although some of them presented a more compact aspect (Fig. 5). The sample from the Peat Layer (m. 14-16) was quite moist and disaggregated. The sample from m. 32-34 showed some dark spots (Fig. 6). The samples were fully saturated, except the sample at the higher depth (m. 32-34), whose degree of saturation was of 92%.

Because of the low initial dry density of the samples, the pore water could be extracted in one-two days at squeezing pressures ranging between 1.5 and 3.1 MPa of pressure (Tab. 2). From the sample QT-C5 m. 32-35 a second aliquot of pore water was obtained at 5.1 MPa.

Due to the very fine fraction of the samples, the extracted pore waters showed some color/turbidity (Fig. 7). For this reason, all the samples were filtered by $< 0.2 \mu\text{m}$ syringe filter inside an anoxic glove box ($< 1 \text{ ppm O}_2$). Different aliquots were prepared from the different analyses. Some of them were used for chemical analysis at CIEMAT, and other ones at EPFFL. The samples for As speciation at EPFL were buffered with a EDTA/acetic acid solution.

The chemical composition of the pore water from the samples analyzed at CIEMAT is shown in Tab. 3.

Tab. 2: Characteristics of the squeezing tests.

Core Sample	Initial mass (g)	Initial dry density (g/cm ³)	Initial w.c. (%)	Time elapsed (hours)	Squeezing Pressure (MPa)	Pore fluid extracted / mass loss (g)	Final mass (g)	Final dry density (g/cm ³)	Final w.c (%)	Efficiency (%) ⁽¹⁾	Total Efficiency (%) ⁽²⁾
QT-C5 m. 1-2	343.8	1.60	25.9	48.61	3.1	16.0	327.9	1.74	22.8	73.0	22.6
QT-C5 m. 12-13	373.4	1.18	47.8	23.41	1.5	49.0	324.3	1.52	27.9	99.0	40.6
QT-C5 m. 13-14	392.2	1.12	52.7	8.64	1.5	56.7	335.5	1.71	39.2	70.5	41.9
QT-C5 m. 14-16	240.6			33.49	1.5	91.1	149.5			79.5	
QT-C5 m. 22-24	328.2	1.28	41.6	18.12	2.0	37.5	290.7	1.58	25.6	82.3	38.9
QT-C5 m. 32-34	305.3	1.80	17.2	123.68	3.1 & 5.1	14.1	291.2	2.00	14.1	59.2	31.5

⁽¹⁾ Efficiency (%) = (Collected water x 100)/Extracted water;

⁽²⁾ Total Efficiency (%) = (100 x extracted water)/(P_{initial} - P_{dry})



Fig. 5: An example of the squeezed drillcore samples.



Fig. 6: Appearance of the sample QT-C5 from m.32-33: a) initial sample, b) initial sample after drying at 110 °C for water content determination prior to the squeezing test, and c) sample after squeezing.



m. 1-2



m. 12-13



m. 13-14



m. 14-16



m. 22-24



m. 32-34

Fig. 7: Color/turbidity of the pore water samples extracted by squeezing.

Tab. 3: Chemical composition of the pore water collected from the BB-47-8 bentonite block at different pressures.

Sample			QT-C5 m. 1-2	QT-C5 m. 12-13	QT-C5 m. 13-14	QT-C5 m. 14-16	QT-C5 m. 22-24	QT-C5 m. 32-34
Pressure		MPa	3.1	1.5	1.5	1.5	1.5	3.1
Extracted water		g	16.0	49.0	56.7	91.1	37.5	14.1
Sensoric Parameter Lab								
Color / Turbidity			Clear	turbid	Clear	turbid	turbid	clear
Physical-Chemical Parameter								
pH value (20 °C)	pH		8.3	7.8	7.7	7.3	7.8	7.8
Alkalinity (pH 4.3)	Alk.4.3	meq/L	9.07	14.9	14.4	4.3	6.3	2.98
Main Ions								
Sodium	Na ⁺	mg/L	727	1425	1475	1025	1150	831
Potassium	K ⁺	mg/L	5.5	34	34	26	17	7.8
Calcium	Ca ²⁺	mg/L	160	110	100	50	120	185
Magnesium	Mg ²⁺	mg/L	69	170	160	80	82	110
Chloride	Cl ⁻	mg/L	787	2800	2700	2000	2500	1900
Sulfate	SO ₄ ²⁻	mg/L	607	7.9	1.6	8.7	1.0	6.8
Nitrate	NO ₃	mg/L	<1	< 1.0	< 1.0	1.8	< 1.0	2.5
Bromide	Br ⁻	mg/L	2.7	9.7	9.3	7.2	9.4	6.7
Phosphate	PO ₄ ³⁻	mg/L	<1	<1	<1	<1	<1	<1
Thiosulfate	S ₂ O ₃ ²⁻	mg/L	<1	<0.1	<0.1	<0.1	<0.1	<1
Fluor	F ⁻	mg/L	<0.5	<0.1	<0.1	<0.1	<0.1	<0.5
Trace Compounds								
Aluminium	Al	mg/L	<0.3	<0.03	<0.3	<0.03	<0.3	<0.3
Silicon	Si	mg/L	7.4	23	25	18	16	9.6
Iron	Fe	mg/L	<0.3	0.28	<0.3	0.22	<0.3	<0.3
Manganese	Mn	mg/L	1.1	0.12	0.27	0.09	0.15	0.3
Strontium	Sr	mg/L	0.9	1.32	1.3	0.64	1.1	2
Barium	Ba	mg/L	0.3	0.62	0.70	0.60	1.86	1.6
Arsenic	As	mg/L	<0.3	<0.03	<0.3	0.04	<0.3	<0.3
Organic Parameter								
Total organic carbon	TOC	mg/L	18.9	38.3	42.6	29.2	30.4	94.6
Acetate	CH ₃ -COO-	mg/L	<1	9.79	12.1	< 0.10	< 0.10	19
Formiate	HCOO-	mg/L	0.51	<1	0.95	<1	<1	1.8

5. References

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