

1 Hyperfiltration of saline water through clay-rich aquitards: chemical and
2 isotopic evidence from a vertical profiles in the North China Plain

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8

9 ABSTRACT

10 Clay aquitards are semipermeable membranes that allow groundwater
11 flow while retarding solute migration have been researched extensively
12 but also subjected to much debate. In this study, we collected clay
13 samples from drilling cores (30–90m) in the Hengshui area located in the
14 Hebei Plain, then extracted pore water using a high-pressure squeezing
15 device. Vertical hydrochemical and isotopic profile variation trends for
16 the pore water were revealed using hydrochemical (Cl^- , Na^+ , Ca^{2+} , K^+ ,
17 Mg^{2+} , and SO_4^{2-}) and stable isotopic measurements of H, O, and Cl. The
18 results showed that the hydrochemical clay interlayer pore water of the
19 saline aquifer is $\text{Cl}\cdot\text{SO}_4\text{-Na}\cdot\text{Mg}$ type and the average total dissolved
20 solids (TDS) is 10.17g/L. The hydrochemical clay aquitard pore water
21 is of the $\text{Cl}\cdot\text{SO}_4\text{-Na}\cdot\text{Ca}$ type with an average TDS of 1.9g/L. The
22 hydrochemical clay interlayer pore water of aquifer II is of $\text{Cl-Na}\cdot\text{Ca}$ type
23 with an average TDS of 1.1g/L. Our results showed that the water quality
24 of the aquifer II is not affected by the upper part of saline aquifer, thus the
25 clay aquitard acts as a significant barrier to salt movement. A polarization
26 layer concentrated in ions was formed between the upper part of saline
27 aquifer and the clay aquitard. The concentration polarization layer
28 increases the salt-inhibition effect. Isotopic H, O, and Cl results showed
29 significant fractionation. The pore water of aquifer II lacked heavy
30 isotopes (D , ^{18}O , ^{37}Cl), but had significant heavy isotope enrichment in the
31 concentrated polarized layer (the δD value was -76‰ , the $\delta^{18}\text{O}$ value was
32 -8.4‰ , and the $\delta^{37}\text{Cl}$ value was 1.59‰). Hyperfiltration thus played a
33 significant role in isotope fractionation.

34 **KEYWORDS:** Geologic membranes; Reverse osmosis; Hyperfiltration;
35 pore water; Aquifer

36

37 INTRODUCTION

38 Aquitards are an important part of ground water system. They are often
39 considered to be impermeable and completely blocked to water

40movement. Very few studies focused on the measuring movement of
41water and solute in the aquitard because more attention has been given to
42the hydrodynamic transmission processes in aquifers. In early research,
43clay layers were often considered to be an aquifuge rather than an
44aquitard. In the case of leakage caused by water head differences between
45the upper and lower aquifers, only the water flow and water quantity
46exchange in the aquitard was considered, and the effect of a clay aquitard
47on solute transport was completely ignored.

48

49Biochemical reactions, electrochemical actions, and ion exchange that
50occur in aquitards play an important role in the protection of ground
51water quality (McMahon , 2001). However, there is no effective method
52for evaluating the physicochemical controls on solute transport in
53aquitards. In an aquifer, solutes are transported primarily by convection,
54but in aquitards molecular diffusion typically has a much greater effect on
55the solute transport behavior. The mechanisms of solute transport and
56influencing factors are particularly important because of osmosis and
57reverse osmosis effects (Gillham and Cherry, 1982). Because of the
58difficulty in sampling pore water in aquitards, most studies on pore water
59are limited to muddy sediments on river and lake bottoms with shallow
60burial depths (Liu and Ball, 2002; Akamatsu et al., 2012). There are few
61studies on the pore water of deep clay layer with low water content, the
62hydraulic characteristics of aquitards, and geochemical processes (Shaw
63and Hendry, 1998; Hendry and Wassenaar, 2000). Recently, with
64increased research on industrial wastes and nuclear waste disposal sites,

65the reverse osmosis effect (often called hyperfiltration, occurs when a
66solute is partially rejected from a solution passing through a membrane).
67Within an aquitard, reverse osmosis can occur when the hydraulic head
68pressure exceeds the osmotic pressure across the membrane. (Graf, 1982;
69Whitworth and DeRosa, 1997; Cey et al., 2001; Oduor, 2004;Hart,
702013) . There are numerous studies on semipermeable membranes in the
71area of hydrogeological research (Elrick et al., 1976; Neuzil , 2000;
72Kocherginsky and Stucki, 2001; Bader and Kooi , 2005; Rebeix and La
73Salle, 2014; Cheng and Hendry , 2014).

74

75Recently, research on the effect of clay aquitards on salt migration in the
76North China Plains has gained increasing research interest and debate.
77The Quaternary aquifer system of the North China Plain consists of salty
78shallow groundwater overlying fresh deep groundwater. Long-term over-
79mining of the deep aquifer has reversed the flow causing it to intake
80upper saltwater from the original outflowing system. (Zhang Zonghu et
81al., 2000). Hypothetically, the long-term exploitation of the deep

82freshwater should result in an increase in saltwater leakage through the
83clay aquitard. However, current ground water monitoring data reflect no
84large-scale salinization trend for the deep groundwater. The
85hyperfiltration should be responsible for this phenomena since a head
86difference across the clay aquitard was developed by deep aquifer
87exploitation. Thus, some hydrogeologists (Wang Jiabing , 2002) have
88pointed out that interactions between calcified microscopic clay particles
89and the aqueous solution at the bottom of salty aquifers reformed a “salt
90filtering bed”. This filtering has important consequences for the
91development and utilization of ground water resources. Existing
92laboratory tests (Barbour and Fredlund, 1989; Keijzer, 2000; Oduor,
932004; Hart, 2005; WangYing et al., 2014) conducted to drive the solute
94by pressure from a high concentration to a low concentration to simulate
95the solute selectively passing through the “semipermeable membrane” of
96an aquitard. Although this phenomenon was confirmed, there remains a
97lack of research at large scales; and the basic theory of traditional
98hydrogeology cannot adequately explain the “semipermeable membrane”
99mechanism.

100

101In this paper, the vertical hydrochemical and isotopic profiling of pore
102water from an aquitard in the field are recreated by studying the
103semipermeable membrane performance of a clay aquitard. A high-
104pressure squeezing method was used to extract the pore water from a 30-
10585m deep section of clay from the Hengshui test site. Hydrochemical (Cl
106⁻、Na⁺、Ca²⁺、K⁺、Mg²⁺、SO₄²⁻), and oxygen, hydrogen, and chlorine
107isotope analysis was used to analyze the chemical evolution of pore water
108in the aquitard to reveal the “hyperfiltration” mechanism of low clay and
109its effect on saltwater. This allowed an assessment of the development
110and evolution of the membrane effect and its possible impact on the
111downward movement of saltwater at the field-scale.

112

113Study area and sample site

114The Hebei Plain is located north of the Yellow River close to the Bohai
115Sea in the east and to the Taihang Mountain in the west with the northern
116boundary at the Yanshan Mountain. The area is a typical plain landscape
117under 100 m elevation relative to sea level. The surrounding topography
118inclines from the north, west and southwest towards the Bohai Bay with a
119gradient of 0.2–1 % in the frontier mountain and 0.1–0.2 % in the coastal
120plain.

121The Plain can be divided into piedmont, central and coastal areas based on
122its geomorphic features. The Hengshui study area is located in a low
123alluvial plain formed by the ancient Yellow and Haihe Rivers in the

124central and eastern Hebei Plain. The study area consists of low terrain
125with small slopes. It has a temperate–warm climate with occasional
126humid and arid conditions and continental monsoons. Winters can be cold
127with snow, summers are hot, humid with frequent rain, springs can have
128common windy days, and autumns cool. The region has an annual
129average temperature of 12–13°C. The average precipitation is 500-600mm
130with the record high of 702.4mm (1983), and low of 307mm (1986). The
131bulk (more than 80%) of the precipitation occurs in summer months from
132June to September mostly as heavy rain. Annual evaporation ranges from
1331100 to 1800mm. (Wang et al. 2008).

134Controlled by palaeoclimate, palaeogeography, sedimentary environment
135and neotectonism in different geological history, the thickness of
136Quaternary in Hebei Plain is 200–300 m in the foothills of the leading
137edge; the majority of the low plain area is 350–500 m; and the thickest
138reaches up to 550–600 m. The distribution patterns and developing
139degree of aquifers vary spatially. According to the features of the
140stratigraphy, it can be divided into four aquifers: (1) aquifer groups of
141Holocene (Q4) and the upper Pleistocene (Q3) (2) mid and lower
142Pleistocene (3) mid Pleistocene and (4) the lower Pleistocene (Jingli et al.
1432013).

144(1) Aquifer I: the lower boundary depth of this group is 48m. It contains
145shallow saltwater, and is mainly located in the Holocene strata. Clay and
146silt clay layers are often present between the aquifers. The transmissivity
147is generally 10–50m²/d, and the specific capacity is generally 2.5–
1485m³/h·m. Because of the shallow depth of this aquifer group, it is easily
149recharged by rainfall infiltration.

150

151(2) Aquifer II: This group is located in the upper Pleistocene and has a
152lower boundary at 120m. The aquifer is mainly composed of fine silt and
153sand with a thickness of about 20–40m. The specific capacity is generally
154greater than 10m³/h·m. Because of the thick silt layers, the hydraulic
155connection between this aquifer group and the overlying aquifer group is
156poor thus limiting lateral flow. The western part of aquifer group II at
157Cangzhou City only contains freshwater.

158

159(3) Aquifer III: The bottom boundary of this group is at 250m. It contains
160freshwater, and is located in the middle Pleistocene. The aquifer is mainly
161composed of medium to medium-fine sand. The sand layer thickness is
162typically 30–60m and less than 30m locally with the specific capacity of
1635–20m³/h·m. In the study area, ground water is mainly exploited from
164this aquifer.

165

166(4) Aquifer IV: The bottom boundary of this group is 380m below the
167surface and is located in the lower Pleistocene. Freshwater is found in this

168aquifer group in most of the study area. The aquifer is mainly composed
169of medium-fine and silty-fine sand, which has a relatively low
170permeability and recharge with a specific capacity of 5–10m³/h·m. The
171thickness of the aquifer is generally greater than 30m. Lateral recharge is
172limited because of clay layers and distance from the recharge area.

173Local stratigraphy

174

175The borehole (Fig. 1) was taken from Zhangzhuang Village in Southern
176Hujiachi located in northern Hengshui City with geographical coordinates
177of the borehole sites at N37° 54'23.0" and E115° 40'44.3" respectively.
178According to lithology and on-site drilling conditions, two aquifers were
179discovered. The first aquifer can be found at a depth of 48–29 m, where
180sediments mainly consist of sand and clay particle interlayers.
181Groundwater in this aquifer has a TDS of 9.65 g/L. The other aquifer can
182be found 90–59 m deep which mainly is composed of sand, gravel and
183clay interlayer. According to [Wu \(2008\)](#), the bottom boundary of the
184Holocene is approximately 35 m deep with the bottom boundary of Late
185Pleistocene exceeding 170 m. Therefore, the period of stratum in this
186borehole is Q4 and Q3. Figure 1 shows the lithologic profile of the
187borehole. The profile shows mainly clay and silt with only clay at the
188depths of 90–59 and 48–29 m.

189 Saline aquifers (aquifer I) formed in the late Quaternary (Q3) are
190widely distributed in the study area that gradually increase in thickness
191from west to east (Fig. 2). Their bottom boundaries are mostly equivalent
192to the bottom boundary of aquifer I, although in some areas the bottom
193boundary is located in the middle of aquifer group II. An aquitard
194commonly occurs between the bottom boundary of the salt water and the
195deep (freshwater) aquifer with a thickness of 10–20m. The base of the
196shallow saline aquifer can be found at a depth of 40–60m. Clay and silt
197are widely distributed above and between aquifers with limited
198precipitation infiltration and lateral flow. A single well can yield water at
199a rate of 2.5–5m³/h with limited saltwater with a TDS concentration of 1–
2005g/L. Freshwater in the deep confined aquifer is the primary layer of
201interest in the studied area. This layer's base is located 450–600m below
202surface and is mainly composed of medium to medium-fine sand, with
203calcareous silt commonly found between the aquifers and limited
204recharge. The water yield of a single well is typically 5–15 m³/h. The
205deep aquifer is artesian with the water head above the ground surface
206under natural conditions. Discharge by this deep aquifer is by upward
207leakage and anthropogenic use. Because of intensive groundwater
208exploitation since the late 1960s, there has been a general decline in water
209levels which led to a groundwater depression cone beneath Hengshui

210City.

211Samples were collected from a core taken at 30–90m, using double helix
212drilling to minimize disturbances to the sample. To assess rock
213characteristics like age, hydrogeological conditions, and natural clay, the
214cores were kept in a constant temperature and humidity environment to
215preserve the detail in the samples. The overall average drilling core
216recovery rate was 80% with 50% from sand layers and 90% from clay
217layers.

218

219METHODS AND MATERIALS

220Extraction of pore water

221Original clay samples were squeezed by a high pressure squeezing device
222specifically designed for extracting moisture from clay. The device is
223shown in Fig. 3 (Chinese patent, No. ZL201420093113.6, A Clay
224Moisture Evaporation prevention High-Pressure Squeezing Device From
225the Institute of Hydrogeology and Environmental Geology, Chinese
226Academy of Geological Sciences, 2014). This device squeezed the pore
227solution extracting water from the clay samples while maintaining the
228original composition. The resulting solution obtained was the pore water
229from the clay layer. The complete apparatus is schematically illustrated in
230Fig. 4. A W1-30 universal material testing machine and WPM3000 large
231solidification stress apparatus were used with a maximum loading of 3,
232000 KN.

233

234A total of 26 samples were used including:

235

236(1) 23 pore water samples squeezed from clay samples at different layers,
237Samples #1–4 from the saline aquifer, #5–12 from the aquitard, and #13–
23823 from the deep freshwater aquifer. The core samples were cut into 12
239cm long cylinders with a diameter of 50mm. Physical indicator tests such
240as the length, wet and dry densities, water content, and conductivity were
241measured on each sample before and after testing. The test device was an
242improved WPM3000KN press machine (Fig. 3), with a maximum
243pressure of 200 KN. Column samples squeezed at gradually increasing
244force. According to preliminary tests, the water pressure required for deep
245clay extraction was larger than shallow clay. So the load test for shallow
246clay samples was started at 1 KN and gradually increased to 50 KN at
247intervals of 2 KN and 5 KN. Deep clay sample load test started at 1 KN
248and was gradually increased to 180 KN at intervals of 5 KN, 10KN, and
24920KN. In these tests, a 2 mm scales were used to measure the
250deformation and a custom-made non-evaporative graduated test tube was
251used to collect and measure the released water. When the extracted water
252reached 5 mL it was transferred into a beaker for conductivity

253 measurements and the remaining into another dry tube for further water
254 collection.

255

256(2) Three samples were collected from monitoring wells at varying depths
257 near the borehole: 30 m deep (H1, top of the saline water), 48 m deep
258 (H2, top of the aquitard), 65 m deep (H3, top of the aquifer).

259

260 **Experimental procedures**

261 Hydrochemical tests were completed at the Ground and Mineral Water
262 Environmental Monitoring Center at the Ministry of Land and Resources.
263 These testing process are as follows: cations of interest were acidified with
264 pure nitric acid to $\text{pH} < 2$. The dissolved solution was injected into an
265 inductively coupled plasma atomic emission spectrometer (ICP-AES
266 model: IRIS Intrepid II XSP with an instrument precision of 0.01). Anions
267 were quantified by ion chromatography (IC model DIONEX-120 with
268 instrument precision of 0.1). Alkalinity was tested by Instrument. For
269 aqueous solutions, the electrical conductivity (EC) was measured with an
270 electrometric cell at 25°C .

271

272 The ratios of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ were measured with a stable isotope mass
273 spectrometer (model Finnigan MAT 253). The isotope compositions were
274 reported in standard δ -notation representing per mil deviations from the
275 Vienna Standard Mean Ocean Water (V-SMOW) standard. Instrument
276 precisions for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ determination are $\pm 0.1\text{‰}$ and $\pm 0.05\text{‰}$,
277 respectively.

278

279 Sample measurements for Cl isotopes were performed at the Salt Lake
280 analytical and test department at the Qinghai Institute of Salt Lakes,
281 Chinese Academy of Sciences. The method used for Cl isotope analysis
282 was first proposed by Xiao and Zhang (1992) and modified by Xiao et al.
283 (1995). The water sample was run successively through ion exchange Ba-
284 form and H-form resins to remove sulfate and cations then through Cs-
285 form resin to yield a solution of Cs_2Cl^+ . The Cl isotope ratio was
286 measured with Cs_2Cl^+ ions on a thermal ionization mass spectrometer
287 (model Triton with test accuracy within 0.2%). For reference, NaCl
288 ISL354 was analyzed with each sample set with a mean value of
289 $0.319078 \pm 0.000054\text{‰}$ ($n=9$, 2σ). The ion current intensity ratio R303/301
290 was used to determine the $^{37}\text{Cl}/^{35}\text{Cl}$ ratio. The sample $\delta^{37}\text{Cl}$ was calculated
291 as follows: $\delta^{37}\text{Cl} (\text{‰}) = \{[(^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}} - (^{37}\text{Cl}/^{35}\text{Cl})_{\text{standard}}] / (^{37}\text{Cl}/^{35}\text{Cl})_{\text{standard}}\} \times 1000$, where the average value calculated was based on the
292 ISL354 NaCl chlorine isotope reference standard ($(^{37}\text{Cl}/^{35}\text{Cl})_{\text{standard}} = 0.318925 \pm 0.000053(20)$) with sample size of 18.

295

296 **RESULTS**

297 **Chemical composition of pore waters**

298 Water samples were taken from pore water squeezed from clay samples
299 from different layers with the main components projected onto a Piper
300 diagram (Fig. 4) to compare hydrochemical characteristics. The diagram
301 show that the pore water from underground clay can be divided into three
302 groups: saline aquifer, clay aquitard, and aquifer II.

303 The following patterns were observed:

304 (1)

305 Layer 1 is the saline aquifer with hydrochemical type $\text{Cl}/\text{SO}_4\text{-Na/Mg}$:

306 the average TDS concentration is 10.17 g/L, the cation concentration

307 ranks high to low: $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$, and the anion ranking from : $\text{Cl}^- >$
308 $\text{SO}_4^{2-} > \text{HCO}_3^-$.

309 Layer 2 is the clay aquitard in the lower part of the saline aquifer with
310 hydrochemical type $\text{Cl}/\text{SO}_4\text{-Na/Ca}$: the average TDS concentration is 1.9
311 g/L, the cation order from large to small is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$, and the
312 anion order from large to small is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$.

313 Layer 3 is aquifer II, the hydrochemical type is Cl-Na/Ca , the average
314 TDS is 1.1g/L, the cation order from large to small is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$,
315 and the anion order from large to small is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$.

316

317 (2) The hydrochemical type of sample H1 is $\text{Cl}/\text{SO}_4\text{-Mg/Na}$ with TDS
318 concentration of 9.65 g/L; the hydrochemical type of sample H2 is $\text{Cl}/$
319 $\text{SO}_4\text{-Mg/Na}$ and the TDS is 10.53g/L; and the hydrochemical type of H3
320 is Cl-Na/Ca and the TDS is 0.78g/L.

321

322 **Distribution of hydrogen, oxygen, and chlorine isotopes**

323 All 23 samples obtained from the clay pore water in the study area were
324 analyzed for isotopic composition. Table 1 shows isotope sampling
325 depths and analytical results. For clay interlayer pore water of the saline
326 aquifer the δD values were -76‰ to -80‰ , the $\delta^{18}\text{O}$ values were -8.4‰
327 to -9.5‰ , and the $\delta^{37}\text{Cl}$ values were -0.07‰ to 1.59‰ ; for the clay
328 aquitard pore water the δD values were -76‰ to -88‰ , the $\delta^{18}\text{O}$ values
329 were -8.0‰ to -10.4‰ , and the $\delta^{37}\text{Cl}$ values were -0.01‰ to 0.63‰ ; for
330 the clay interlayer pore water of aquifer II the δD values were -74‰ to
331 -88‰ , $\delta^{18}\text{O}$ values were -8.7‰ to -10.6‰ , and $\delta^{37}\text{Cl}$ values were
332 -0.22‰ to 1.13‰ .

333 **Discussion**

334 1. Hydrochemical evidence

335 The hydrochemical pore water directly reflects the main ions (Na, K, Ca,
336 Mg) found and indirectly reveals the evolution of the water flow system
337 and the hydrogeochemical evolution. Table 1 shows the ion concentration
338 gradually declines with increasing depth, and that all ion components and

339 TDS have abrupt inflection points at the saltwater/clay layer interface.

340

341 Hydrogeochemical changes were determined for the saline aquifer
342/aquitard and the aquitard/aquifer II interface. The ion content at the
343 upper saline/clay interface is relatively stable. The same result was
344 observed between the saltwater/aquitard interface (51m). The ground
345 water changes from saltwater to freshwater as supported by the TDS
346 concentration decrease from 10.86g/L to 1.9g/L and by the change in
347 hydrochemical type from LS-NM to LS-NC. The concentration of main
348 ions in the aquitard decrease except for Ca^{2+} where it anomalously
349 increases.

350

351 (1) K^+ , Na^+ , Ca^{2+} , and Mg^{2+}

352 The vertical cation concentration gradient is primarily due to cation
353 exchange. Ca^{2+} and Mg^{2+} concentrations increase initially but start to
354 decrease with increasing depth. The decrease in K^+ and Na^+
355 concentrations and increase in Ca^{2+} and Mg^{2+} concentrations in the saline
356 aquifer are mainly due to cation exchange. As the K^+ and Na^+
357 concentrations decrease within the aquitard, K^+ and Na^+ from the
358 groundwater will exchange with Ca^{2+} and Mg^{2+} in the clay layer. The Na^+
359 and Mg^{2+} concentrations in aquifer II are essentially stable.

360

361 There exist a large amount of exchangeable cations on the surface of the
362 clay aquitard. When saltwater enters the shallow aquitard, cation exchange
363 reactions occur which includes Na-Ca and Na-Mg. As a result, the cation
364 compositions of the intruded saltwater changes as it reaches equilibrium.
365 To balance charge, two Na^+ ions are required for each Ca^{2+} or Mg^{2+} , but
366 the total mass of cations decreases leading to a drop in the TDS
367 concentration of intruded saltwater. This is the believed mechanism of
368 cation exchange in the aquitard leading to TDS concentration drop of
369 intruded saltwater.

370

371 (2) Cl^-

372 Chloride content in ground water is a robust indicator of the initial state
373 of ground water. Chlorides are generally not derived from the dissolution
374 of aquifer matrices (Liu Cunfu, 1997) and are not involved in large-scale
375 ion exchange reactions. Chloride ion concentration changes which leads to
376 hydrogeochemical evolution.

377

378 All ion concentrations decreased significantly in the clay transition zone
379 of the lower saltwater layer (Fig. 5). The Cl^- content initially increased
380 with increasing depth until the interface between saltwater and the
381 aquitard. Then the TDS concentrations gradually reduced, and stabilized

382in the lower part of the aquitard.

383

384The TDS concentration of the saltwater is very different from that of the
385clay aquitard and aquifer group II (Fig. 5). From the clay aquitard to
386aquifer group II, the hydrochemical designation shifts from LS-NC to L-
387NC while the TDS and ion concentrations remains essentially the same.
388Thus, the main ion concentrations in the pore water from the lower parts
389of the clay aquitard and the upper part of aquifer II are similar. This
390suggest that these two zones may belong to the same body of
391groundwater. The results also suggest the thickness of the clay greater
392than 10 m more effectively blocks the movement of saline water.

393

394It is possible that hyperfiltration results from salinity concentration
395differences and the subsequent movement of saltwater through the clay
396aquitard. Pressure on one side of the saltwater overcomes the osmotic
397pressure and flow from high to low concentration. However, solutes
398cannot fully pass through the clay aquitard.

399

400At the depth between 34 m to 48 m, all ion concentrations show an
401increasing trend (Fig. 5). This enrichment is thought to be caused by
402solutes retaining to the surface of the clay particles causing the
403concentration of ions on the clay aquitard surface to exceed the aqueous
404solution. Because of the concentration gradient, solutes diffuse from the
405membrane surface to the bulk solution, resulting in boundary effects.

406

407When the rate of water and solutes flow to the membrane surface is
408sufficient, solutes will diffuse to the bulk solution until equilibrium is
409reachedforming a stable concentrated boundary layer on the membrane
410surface. This boundary layer is the concentration polarization layer (CPL)
411(Fig. 5). Although the background TDS concentration may be much lower
412than saturation, the solution concentration of the concentrated
413polarization layer can be severalto hundreds of times higher than the
414background ([Whitworth and Fritz,1994](#); [Hart and Whitworth, 2005](#)).

415

416Anion exchange adsorption is different from cation exchange. Due to
417these differing processes, ions cannot be concentrated and separated from
418the infiltration solution. This process difference provides further evidence
419that the “Membrane Effect” of clay enables solutes of saltwater to be
420separated. So, it can be concluded that that the solute TDS concentration
421below the clay aquitard is lower than the solution in the upper saline
422aquifer.

423

4242. Isotopic evidence

425 Stable isotopes measurements in water play an important role in the study
426 of dynamic processes such as recharge, migration and mixing. These
427 measurements can serve as a “fingerprint” of the aquifer [Georg, 2014;
428 Asimov, 2012; Giuliani, 2005]. ^2H and ^{18}O are considered to be stable in
429 low temperature water–rock interactions and strong evaporation
430 conditions; which can be ideal for tracing hydrodynamic processes
431 [Penna, 2010; Gaj, 2016]. Studying isotope fractionation mechanisms can
432 help enhance the understanding of different physical and chemical
433 processes which will deepen the knowledge of geological processes of
434 water evolution, deposit genesis, and evolution.

435

436 **Fractionation of stable H and O isotopes**

437

438 Research has shown that stable hydrogen and oxygen isotope
439 fractionation occurs when water molecules pass through a
440 montmorillonite membranes (Coplen & Hanshaw, 1973 ; Benzel & Graf,
441 1984; Haydon & Graf, 1986; Fritz et al., 1986; Kang, 2011; Whitworth &
442 Fritz, 1994; Malusis, 2012; Mazzieri, 2010; Kang, 2010) However
443 hydrogen and oxygen isotope fractionation effects are rarely reported in
444 large regions.

445

446 Results for stable hydrogen and oxygen isotope compositions from each
447 monitoring well and core samples are shown in Table 2. A total of 23
448 isotope water samples were tested.

449

450

451 Isotope results for hydrogen and oxygen show that average $\delta^2\text{H}$ value was
452 -78‰ and the average $\delta^{18}\text{O}$ value was -8.9‰ in the saline aquifer; the
453 average $\delta^2\text{H}$ value was -83‰ and the average $\delta^{18}\text{O}$ value was -9.6‰ in
454 the clay aquitard; and the average $\delta^2\text{H}$ value was -85‰ and average $\delta^{18}\text{O}$
455 value is -10.2‰ in aquifer II. Thus, the average $\delta^2\text{H}$ value decreased by
456 7‰ , and the average $\delta^{18}\text{O}$ value decreased by 1.3‰ in the vertical
457 direction (from the upper saltwater to the lower freshwater). ^2H and ^{18}O
458 are enriched in the superficial layer of clay membrane to form the
459 concentration polarization layer ($\delta^2\text{H}$ is -76‰ and $\delta^{18}\text{O}$ is -8.4‰).

460

461 The mechanism for the hyperfiltration of ^2H and ^{18}O involves the
462 preferential influx of heavy isotope ions into the hydration layer and
463 exclusion by the clay membrane. There is no ^2H and ^{18}O in the pore water
464 of the clay, because heavier isotopes concentrate on the side with highest
465 pressure. The concentration polarization layer ($\delta^2\text{H}$ at -76‰ and $\delta^{18}\text{O}$ at
466 -8.4‰) is formed by heavy isotopes on the upper side with higher
467 pressure of the aquitard.

468

469In the saltwater solution, isotope fractionation can occur between bound
470water in the hydration layer and free water (Truesdell, 1974). The effect
471of dissolved salts component on ^2H activity ratio can be explained by the
472interaction between ions and water molecules which relates to the charge
473and atomic radius of the ions. The clay minerals selectively absorb ^2H and
474 ^{18}O which reduces ^2H and ^{18}O in the water of aquifers below the aquitard
475leading to accelerated heavy isotope fractionation.

476

477**Membrane-induced fractionation of chlorine isotopes**

478

479The Table 2 results show that the average $\delta^{37}\text{Cl}$ value was 0.4‰ in the
480saline aquifer, 0.35‰ in the clay aquitard, and 0.3‰ in aquifer II. The
481aquitard had an absolute ^{37}Cl reduction of 0.1‰ which is due to the
482formation of a concentration polarization layer. The total Cl^-
483concentration and average $\delta^{37}\text{Cl}$ value in the vertical direction are strongly
484correlated with the burial depth of the pore water. The Cl^- concentration
485initially increases with depth but then decreases. The average $\delta^{37}\text{Cl}$ value
486becomes increasingly negative with increasing burial depth.

487

488At shallow depths under 40 m, pore water is found in the saline aquifer
489and is affected atmospheric precipitation and pollution. The value of $\delta^{37}\text{Cl}$
490can be either positive, negative ($\delta^{37}\text{Cl}$ value of -0.07‰ at 34.35 m deep)
491or near 0.00‰ ($\delta^{37}\text{Cl}$ value of 0.08‰ at 30 m, and 0.05‰ at 40.2 m).
492Mixing is believed to change the ^{37}Cl in the saline aquifer. For phreatic
493water recharged by recent rainfall, the $\delta^{37}\text{Cl}$ value is generally
494positive trending upwards with increasing burial depth. Generally, the
495saline aquifer is ^{37}Cl rich and ^{35}Cl deficient.

496

497In the clay aquitard and aquifer II, the $\delta^{37}\text{Cl}$ value decreases with
498increasing depth. These layers are concentrated in ^{35}Cl and deficient in
499 ^{37}Cl , which is presumably the result of chlorine isotope fractionation
500caused by reverse osmosis. Fractionation of chlorine isotopes is caused
501by the different ion mobility of ^{35}Cl and ^{37}Cl (Campbell, 1985). It
502appears that ^{37}Cl cannot be enriched on the high pressure side because of
503the difference in ion mobility which results in higher ^{37}Cl (1.59‰)
504content in the concentration polarization layer. This hypothesis regarding
505chlorine isotope fractionation needs to be confirmed.

506

507**Mechanism of hyperfiltration**

508In summary, dense clay can act as a semipermeable membrane that cause
509hyperfiltration allowing water to pass through while preventing the
510passage of ions in solution (Fig. 6). This occurs because negative charges
511on the clay's surface repels anions. For clay, this effect (double electrode
512layer) enables the aquitard's surface to contribute towards preventing

513anions from entering the clay. The intensity of the rejection is inversely
514related to the water flow velocity. When the water flow exceeds a the
515critical velocity, it nearly loses all rejection effects. One possible
516explanation may be that the anion rejection effect of clay is limited to a
517certain range of influence. As flow velocity drops, anions diffusion has a
518greater relative effect. When diffusing into the influence zone, anions will
519move away from the surface of clay particles due to repulsive forces. This
520increases the anion's kinetic energy such that its relative velocity is more
521than that of the water flow. To reduce the effect of the clay's charge
522buildup, anions and cations enter into the clay together. In the clay layer,
523anions migrate faster by repulsion to form a larger concentration
524difference at the top of the clay which then induce counterions to enter
525the clay layer. It is difficult for anions to migrate into the clay layer
526without accompanied by counterions. To allow the lowest barrier
527pathway for migration of anions, all charges must be balanced and
528neutralized before entering the clay. Thus, charging anions allows them to
529be free from repulsion by the clay to drive the exchange of cations.

530CONCLUSIONS

531This study has shown that clay membrane induces the variations of
532hydrochemistry and fractionation of hydrogen , oxygen and chlorine
533isotopes by hyperfiltration. Establishing of a concentration polarization
534layer provides a means to concentrate solution at a clay's high-pressure
535interface at levels substantially above that of the input stock solution.
536This polarization effect appears to be capable of rendering
537supersaturating conditions at the high pressure interface between the clay
538and the hyperfiltrated solution. The conclusion is that hydrogen and
539oxygen isotopes are fractionated when distilled water has passed through
540a clay membrane because heavier isotopes "clusters of water molecules
541are preferentially retarded within the membrane structure.

542The leakage flow rate of clay aquitards is lower than that of permeable
543stratum under large head differences. In low flow states, the anion
544repulsion effect of clay may be more apparent and its resistance to
545salinity migration increase. It is possible that the effects of membrane
546behavior by clays in relation to subsurface waste emplacement. If highly
547concentrated liquid waste is emplaced in a subsurface environment
548containing shale capable of membrane response while the hydraulic head
549on the fluid phase increased, some ultrafiltration may occur. The imposed
550high hydraulic head could cause flow of ultrafiltrate through the shale
551thereby increasing the concentration of residual solution in the emplaced
552aquifer beyond the planned amount.

554Applying hyperfiltration mechanisms of membranes to aquitards have
555enriched the established principles of hydrogeology. This paper provides
556a theoretical foundation to assist in the development and protection of
557deep water resources in the North China Plain and elsewhere aquitards
558need to be incorporated in water management plans.

559

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