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The use of fluorescent dyes as tracers in highly saline groundwater

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Received 29 November 2007; received in revised form 22 May 2008; accepted 28 May 2008

KEYWORDS

Artificial tracers;
Saline groundwater;
Sorption;
Dead Sea brine;
Fluorescent dye

Summary The capability of five fluorescent dyes to serve as conservative tracers in highly saline groundwater was evaluated by a series of batch experiments on pure minerals and natural sediments. Dye sorption was tested in four different salinities (from fresh rainwater to Dead Sea water) on five pure minerals and four natural sediments taken from boreholes drilled along the Dead Sea shore. It was found that the dyes Sulfo-Rhodamine B and Eosin are strongly adsorbed on pure minerals and sediments and therefore cannot be used as conservative tracers in saline groundwater. Uranine and Pyranine sorption is increased at higher salinities, therefore they can be used as tracers in moderately saline groundwater only. Na Naphthionate was found to be the best tracer for fresh and saline water, with minimal sorption in all cases. Sorption of the dyes on four natural sediments was measured and values were found to be in accord with those of previous sorption on pure minerals. Sorption on natural sediments was also estimated based on the mineral composition of the sediment and the known sorption on the pure minerals. The estimated sorption values were usually 25% lower than those of the sorption directly measured. Nevertheless, sorption on pure minerals can be used as a first approximation for sorption on natural sediments.

The impact of sediment to solution ratio was tested for Uranine as a model dye. The distribution coefficient (K_d) of Uranine in highly saline Dead Sea water was found to be dependent on the sediment to solution ratio (mass/volume), where low ratios resulted in higher values of K_d . Also, higher K_d values were calculated for fine grain size due to higher sorption capacity on larger surface areas. The difference in K_d , however, is not directly related to the specific surface size of the grains and should be examined separately.

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Introduction

Exploring hydrological processes in highly saline groundwater is important and scientifically challenging. Saline groundwater can be found in many arid and semi-arid areas throughout the world (e.g., Eugster and Hardie, 1978; Rogers and Dreiss, 1995; Yechieli and Wood, 2002). For example, highly saline groundwater is located along the Dead Sea shore with salinities varying between brines of 220 g Cl/l and relatively fresh groundwater (1.9 g Cl/l, Gavieli et al., 2001). The rapid dropdown of the Dead Sea level is causing dynamic changes in the fresh-saline water interface and as a result, the groundwater salinities along the Dead Sea shore are changing over short time periods (Yechieli, 2006). Thus, using artificial tracers becomes of special interest in quantifying the hydraulic processes in groundwater with a wide range of groundwater salinities.

Various chemicals are being used as artificial tracers in groundwater. These include salts, radioactive and stable isotopes (such as ^{82}Br and deuterium), gases (such as SF_6) (Bauer et al., 2001; Becker and Copen, 2001; Dillon et al., 1999; Kass, 1998) and fluorescent dyes (Chua et al., 2007; Flury and Wai, 2003; Kass, 1998). The properties required of groundwater tracers are: long-term stability in the aquifer, low toxicity and easy and precise measurement at low cost (Kass, 1998). The background concentration of the tracers in groundwater should be low due to practical considerations of the amount of tracer needed for an appropriate tracing experiment. Therefore, natural high background concentration of salts such as Cl and Br prevent them from being used as tracers in saline environments. Furthermore, minimum sorption of the tracers on the aquifer minerals is important for quantitative analysis of groundwater flow.

Fluorescent dyes are most commonly used for groundwater tracing (Flury and Wai, 2003; Kass, 1998; Smart and Laidlaw, 1977). However, a major disadvantage of fluorescent dyes is their sensitivity in some cases to solution properties (pH, salinity and chemical composition) both in terms of spectrographic character and amount of dye sorption on the sediment. The impact of solution chemistry on the fluorescent dye properties has been examined in previous studies. For solutions of low salinity, the salinity affects the dye fluorescence intensity (FI) to a much smaller degree than does pH (Flury and Wai, 2003). Smart and Laidlaw (1977) reported a minor decrease of up to 8% in the FI of eight dyes (including Uranine, Pyranine and Sulfo-Rhodamine B) in diluted solutions with NaCl concentration of a few grams per liter (Flury and Wai, 2003). The pH solution has a negligible effect on the fluorescence of most dyes (Smart and Laidlaw, 1977). Exceptions are Pyranine and Uranine, where the FI decreases as the pH decreases (Smart and Laidlaw, 1977). Pyranine FI is dependent on pH due to proton exchange reactions with the solution forming two molecules with different excitation wave lengths (Behrens, 1986; Lounay et al., 1980).

Sorption of fluorescent dye on minerals in low salinity solutions have been widely investigated (Aldous and Smart, 1988; Kasnavia et al., 1999; Sabatini, 2000; Shiau et al., 1993; Smart and Laidlaw, 1977; Trudgill, 1987). Kasnavia et al. (1999) found that except for extreme pH conditions,

fluorescent dye sorption is dominated by electrostatic interactions (ion exchange) rather than hydrophobic interactions (partitioning into organic content). Moreover, the ability of dyes to resist sorption was explained by the structure of the dye molecule, mainly the type and number of functional groups (Kasnavia et al., 1999; Shiau et al., 1993; Smart and Laidlaw, 1977; Sutton et al., 2001). Therefore, dye sorption in groundwater is influenced by the combined effect of the dye type, mineral composition of the aquifer sediments and groundwater chemistry.

The available literature on tracer experiments in saline environments is very limited. Richardson et al. (2004) reported retardation of Rhodamine WT that was injected into fresh waste water plumes that penetrated into a salt marsh, yet its retardation could not be simply related to groundwater salinity.

Here, in order to systematically evaluate the possible use of fluorescent dyes as tracers in highly saline groundwater, a series of sorption experiments was conducted. The major objective of this study was to assess the sorption of various fluorescent dyes on pure minerals and natural sediments in different water salinities. In addition, the impact of the sediment–solution ratio and the sediment grain size on sorption at high salinities was explored.

Materials and methods

Tracers

Five fluorescent dyes were tested in this study: Uranine, Pyranine, Eosin, Sulfo-Rhodamine B (SRB) and Sodium Naphthionate (Naph, Table 1). These dyes were chosen for the experiments because of their frequent use in groundwater studies and the fact that they can be easily purchased from most chemical suppliers. All dyes were purchased as dry powders and were dissolved in solution in order to produce concentrations of 10 and 100 ppb (20 and 200 ppb for Eosin).

Solution

Each of the five fluorescent dyes was mixed with four solutions. The solutions were: (1) Dead Sea water (DSW); (2) DSW diluted 50% by distilled water (0.5 DSW); (3) DSW diluted for 1% of DSW (0.01 DSW); and as a reference solution, (4) artificial rain water (ARW), prepared according to the average composition of rains in southern Israel (Herut, 1992). The chemical compositions of the solutions are presented in Table 2.

Sediments

Two types of sediments were used for the sorption experiments (Table 3): first, a group of pure minerals: clays (bentonite, kaolinite), quartz, calcite and dolomite. Two different grain sizes of quartz, calcite and dolomite were used (Table 3); second, a group representing natural sediments characterizing a local assemblage of minerals and salts deposited at different depths along the Dead Sea shore. Samples of sediments were collected from three boreholes drilled along the Dead Sea shore (Yechieli and

Table 1 Properties of fluorescent dyes

Dye	Commercial name	Manufacturer	Excitation/Emission (nm)
Uranine	Fluorescein sodium	Riedel-de-Haen	491/512
Pyranine	8-Hydroxy-1,3,6-pyrenetri-sulfonic acid, tri sodium salt (~75%)	Aldrich Chemical Company Inc.	455/512
Eosin	Eosin Y	Aldrich Chemical Company Inc.	516/538
Sulfo-Rhodamine B	Sulforhodamine B monosodium salt	Fluka Biochemika	564/584
Na Naphthionate	1-Naththylamine-4-sulfonic acid sodium salt hydrate	Fluka Chemika	320/420

Table 2 Chemical analysis of the experiment solutions

Sample	Date	pH	Na	K	Ca	Mg	Sr	Cl	SO ₄	HCO ₃ ^a	Br
			g/l								
Dead Sea water (DSW)	20/5/2003	5.4	32.5	7.4	17.5	45.1	0.3	215	0.4	0.24	5.6
0.5 DSW		6.8	16.2	3.7	80.7	22.5	0.16	107	0.2	0.12	2.8
0.01 DSW		7.6	0.326	0.074	0.175	0.45	0.003	2.15	0.004	0.002	0.056
ARW ^b			0.013		0.012	0.004		0.022	0.014	0.035	

^a Measured as alkalinity. In Dead Sea water there are other alkalinity sources other than HCO₃⁻, such as B⁻.

^b Artificial rain water.

Table 3 Description of sediment type

A	Source			Mineral composition	Grain size				
A1	Wyoming Bentonite			75% Smectite, 8% Quartz, 16% Feldspar ^a	5.6 μm ^c				
A2	Georgia Kaolinite			96% kaolinite ^a	1.2 μm ^c				
A3	Hatira Formation			Quartz	Coarse: 1–2 mm Fine: 0.22–0.42 mm				
A4	Shivta formation			Calcite	Coarse: 1–2 mm Fine: 50 nm ^c				
A5	Veradim formation			Dolomite	Coarse: 1–2 mm Fine: 36 nm ^c				
B	Zeelim formation	Well ^b	Depth (m)		Gravel 2 mm<	Coarse sand 2–0.25 mm	Fine sand 0.25 mm – 62 μm	Silt 62–2 μm	Clay <2 μm
B1	AR2	11.5–13	65% dolomite, 20–25% Quartz, 5% clays	68	25	2	4	1	
B2	AR2	0–2	55% calcite, 20% dolomite, 20% quartz	48	44	4	3	1	
B3	AR2	26–26.5	35% quartz, 25–30% dolomite, 10% clays ^d , 5–10% calcite, 5% plagioc.	0	4	23	55	18	
B4	AR3	8–10	55% calcite, 25% dolomite, 15% quartz	48	22	12	14	4	

A, pure minerals; B, natural sediments collected from boreholes along the Dead Sea coastline.

^a From Chipera and Bish (2001).

^b Samples from boreholes in the coastal area of the Dead Sea (Yecheili and Lewenberg, 2003).

^c Mean diameter from the Mastersizer[®] analysis.

^d 55% Illite–smectite (montmorillonite), 15% kaolinite, 15% illite, 5–10% palygorskite.

Lewenberg, 2003, Table 3). Grain-size distribution was determined by sieving for the coarse fraction and the fine fraction was separated by decantation (Lahav et al., 1999, see pp. 26–27). Distribution of grains smaller than 550 μm was measured by laser scattering with a Malvern™ Mastersizer® Micro-Puls, (Malvern Instruments Ltd., Worcestershire, UK). Semi quantitative bulk mineralogical composition was carried out on a Philips XRD diffractometer PW1830/3710/3020, Holland.

Pre-treatment of the dolomite and calcite included crushing and sieving to grains of 1–2 mm and to a fine fraction smaller than 0.062 mm. Both size groups were washed by distilled water in order to remove dust. The oxide coatings of the quartz grains were removed by heated HCl (36.46% diluted to 1:4). Sample B3 (Table 3) was dried in the oven at 70 °C and was crushed by hammer to small pieces (diameter, 0.5–1.5 cm) because of its clayey nature.

Batch experiment

A sediment sample and dyed solution were placed in a 50 ml tube. The tubes were continuously rotated 360° at 8 rpm by Labquake® tube rotator (Thermolyne, USA) in the dark at room temperature (17–25 °C) for 12–14 h, in order to achieve equilibrium concentration. The solution was removed from the sediments by centrifuging for 20 min at a rate of 3000 rpm and was analyzed by fluorescence spectrophotometry (Cary Eclipse Fluorescence Spectrophotometer, Varian®, Palo Alto, CA). The concentration of the dyes in the samples was determined separately for each experiment by using calibration curves prepared with solutions of similar salinity and composition to those of the experiment solutions. In the first set of experiments, 5 g of sediment was placed together with 5 ml of solution, except for the clays (bentonite and kaolinite) for which, due to difficulty of separating liquids from the sediment, a higher volume of solution was needed (20 ml for bentonite and 10 ml for kaolinite). The concentration of dye in the solution was 100 ppb except for Eosin, for which a 200 ppb solution was used (because of the low absorption of the dye). Sorption was tested separately for coarse and fine fractions of quartz, dolomite and calcite (Table 3). Only the results from the coarse fraction sorption experiments are presented here. With 2–3 duplications of each experiment, about 500 batch experiments were carried out.

In a second set of experiments, the influence of sediment to solution ratio and grain size on sorption of Uranine in DSW solution was tested. Uranine was chosen as an example since it is a dye that is often used in groundwater tracing and it has moderate sorption in DSW. Solutions of 10, 20, 40, 60 and 100 ppb of Uranine were used, with sediment to solution ratios of 5 and 0.5 g/5 ml on coarse and fine grains of quartz, dolomite and calcite.

Blanks were prepared by repeating experimental procedures with solutions without dyes. The fluorescence intensities (FI) of the blanks were analyzed and calculated to determine the “apparent dye concentration” from the FI measurements. It was found that except for Naph, FI of the blank solutions was close to zero. The FI’s in the emission–excitation wavelength similar to that of Naph in the blank solutions were found to be comparable in values to

20–30 ppb. The high background of Naph was attributed to the occurrence of a natural source of fluorescence in natural waters rather than to fluorescence emissions of Naph (Leibundgut and Wernli, 1988).

Calculations

The amount of dye sorption on sediments equals the amount of dye loss after mixing with sediment during the batch experiment. Other dye losses such as dye precipitation are thought to be negligible since in the experiment the dye concentrations were a few orders of magnitude lower than its solubility (a few grams per liter). Dye sorption was calculated as percentage of initial concentration:

$$\text{Sorption (\%)} = \frac{(C_0 - C)}{C_0} \times 100, \quad (1)$$

where C is the dye concentration in solution at equilibrium and C_0 is the initial dye concentration (ppb). Adsorbed concentration (C_{ads}) was calculated as follows:

$$C_{\text{ads}} = (C_0 - C) \frac{V}{W}, \quad (2)$$

where V is the solution volume in the batch experiment (ml) and W is the sediment weight (g). The distribution coefficient (K_d) was achieved from linear isotherms in different dye concentrations, according to the following equation:

$$C_{\text{ads}} = K_d C. \quad (3)$$

Results and discussion

Effect of solution salinity on dye fluorescence intensity

The impact of the solution salinity on the FI of dyes is presented in Fig. 1. Of the five dyes tested, the FI of three decreased when salinity increased (Uranine SRB and, Eosin, Fig. 1). For the two other dyes, Naph and Pyranine, the trend was inconsistent (Fig. 1).

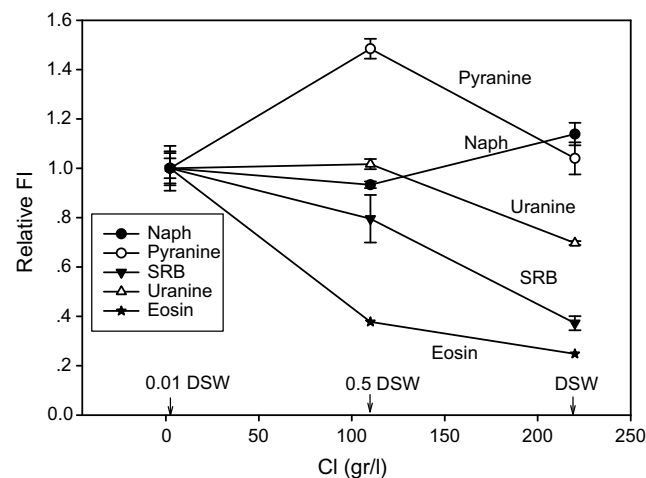


Figure 1 Changes of relative fluorescence intensity (FI) of the dyes at high salinity.

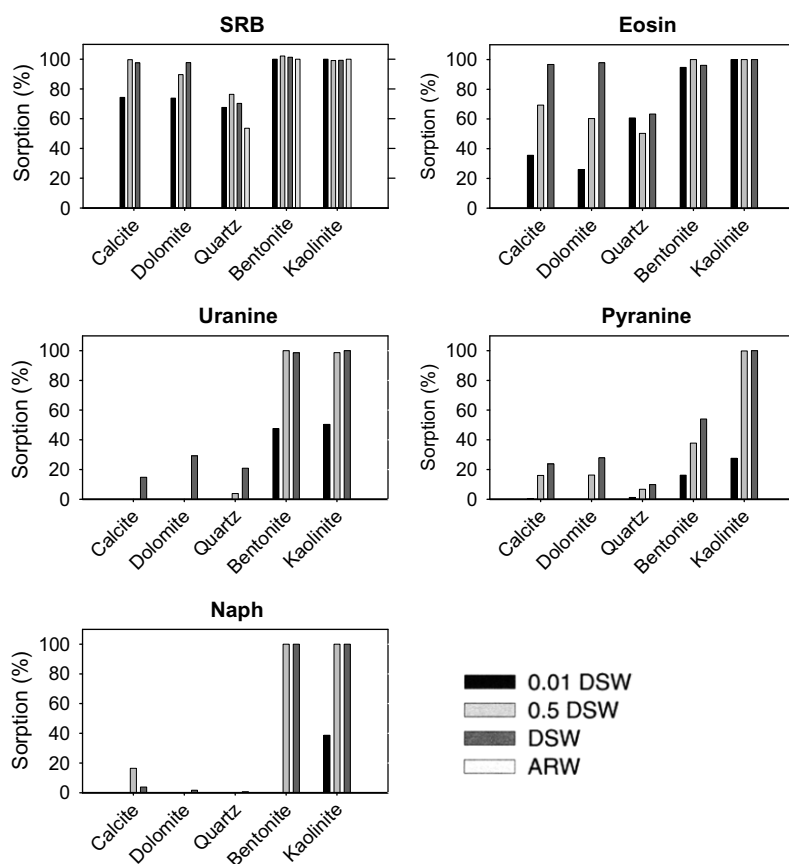


Figure 2 Sorption of dyes (in percentage): (a) SRB; (b) Eosin; (c) Uranine; (d) Pyranine; and (e) Naph, on pure minerals.

The FI of Uranine was similar in 0.01 DSW and 0.5 DSW and decreased by 30% in DSW (in respect to FI of 0.01 DSW, Fig. 1). FI's of SRB and Eosin decreased by 20–63% and by 23–88% in respect to the initial intensity in 0.01 DSW (0.5 DSW and DSW, respectively). Under the same conditions, Naph's FI slightly decreased (7%) in 0.5 DSW and increased by 14% in DSW. Pyranine's FI increased by 48% in 0.5 DSW and decreased by 7% in DSW. In general, changes of FI might also result from changes of the solution pH (Smart and Laidlaw, 1977). It is known that dilution of DSW increases pH (Amit and Bentor, 1971, Table 2), but the actual meaning of pH in these extreme saline brines is not clear. It should be noted that the solutions of the experiments were compared to standard solutions of similar composition; the changes in the FI were normalized and did not affect the experiment results.

Sorption on pure minerals

The percentage of dye sorption on pure minerals in three solution salinities (0.01 DSW, 0.5 DSW and DSW) and also in ARW (SRB only) is presented in Fig. 2 and in Table 4. The measurement error estimated according to four duplications is ± 4 –7%. In general, the results indicate that more dye sorbs at higher salinities of the solution (Fig. 2). At higher salinities the solubility of the dye as an organic compound decreases, therefore its affinity to sorb increases (Turner and Rawling, 2001). The following discussion is presented according to the level of dye sorption.

SRB is the dye that adsorbed most on all types of the tested minerals. The lowest SRB sorption was on quartz, 54%, 68%, 76% and 70% for ARW, 0.01 DSW, 0.5 DSW and DSW, respectively. Sorption on calcite and dolomite was higher (74%, 90–100% and 97–98% on 0.01 DSW, 0.5 DSW and DSW). The results are consistent with previous results of higher sorption of SRB on positively charged minerals (calcite) and lower sorption on negatively charged minerals (quartz) due to the permanent positive charge of the SRB molecule (Sabatini, 2000). The sorption on clay minerals was expected to be high due to the large surface area of clays, and the results of the current research show that sorption of SRB on both clays tested was close to 100% at all salinities.

High sorption was measured also for Eosin, with values varying between 26–61% in 0.01 DSW and 63–100% in DSW. The sorption of Eosin on quartz was over 50% at all salinities and increased on calcite and dolomite from 26–36% in 0.01 DSW to 60–69% and 97–98% in 0.5 DSW and DSW, respectively. The sorption on both clay minerals was close to 100% at all salinities. Due to its high sorption affinity Eosin can be used in low salinities only and for sediments of low clay content.

The sorption of Uranine on calcite, dolomite and quartz was close to zero in 0.01 DSW and 0.5 DSW. In the experiments with DSW, sorption was 15%, 29% and 21%, on calcite, dolomite and quartz, respectively. Uranine sorption on the negative-charged surface of quartz was expected to be low due to the absence of a positive charge of its molecule,

Table 4 Percentage of sorption of the dyes SRB, Eosin, Pyranine, Uranine and Naph on pure minerals and sediments at four salinity solution (0.01 DSW, 0.5 DSW, DSW and ARW)

Mineral	Water type				Sed. Sample	Water type		
	0.01 DSW	0.5 DSW	DSW	ARW		0.01 DSW	0.5 DSW	DSW
<i>SRB</i>								
Quartz	74	100	97		B1	98	99	92
Calcite	74	90	98		B2	97	100	94
Dolomite	68	76	70	54	B3	96	100	90
Bentonite	100	102	101	100	B4	97	99	96
Kaolinite	100	99	99	100				
<i>Eosin</i>								
Quartz	36	69	97		B1	85	98	100
Calcite	26	60	98		B2	57	93	100
Dolomite	61	50	63		B3	74	85	100
Bentonite	95	95	100		B4	66	90	100
Kaolinite	100	100	100					
<i>Uranine</i>								
Quartz	0	16	24		B1	0	58	84
Calcite	0	16	28		B2	0	35	77
Dolomite	1	7	10		B3	50	90	100
Bentonite	16	38	54		B4	0	73	93
Kaolinite	28	100	100					
<i>Pyranine</i>								
Quartz	0	0	15		B1	28	48	64
Calcite	0	0	29		B2	53	59	88
Dolomite	0	4	21		B3	41	83	98
Bentonite	48	48	99		B4	33	38	76
Kaolinite	50	50	100					
<i>Naph</i>								
Quartz	0	16	4		B1	9	24	0
Calcite	0	0	2		B2	14	3	0
Dolomite	0	0	1		B3	46	63	74
Bentonite	0	100	100		B4	14	19	7
Kaolinite	39	100	100					

whereas a higher sorption is expected on positive-charged surface minerals such as calcite (Kasnavia et al., 1999). The differences in the amount of sorption of Uranine on quartz and calcite were in the range of the measurement error (4–7%) and are therefore insignificant. The sorption of Uranine on clay minerals was 48% and 50% in 0.01 DSW (bentonite and kaolinite, respectively) and 100% in 0.5 and DSW. The high sorption of Uranine on clay minerals suggests that Uranine sorption in field experiments will depend strongly on the presence of clay in the natural sediment.

The Pyranine sorption on quartz, calcite and dolomite was 0 in 0.01 DSW, 7–16% in 0.5 DSW and 10–28% in DSW. While sorption of Pyranine on bentonite was 16%, 38% and 54% (in 0.01 DSW, 0.5 DSW and DSW, respectively), considerably higher sorption was found on kaolinite (28%, 100% and 100% on 0.01 DSW, 0.5 DSW and DSW, respectively). The relatively low dye sorption on the bentonite compared to that on kaolinite is unclear and further research is needed to explore these differences. Still, it should be noted that because of the bentonite tendency to adsorb water efficiently, twice the volume of solution was used

for bentonite relative to kaolinite, and lower sorption is expected (Aldous and Smart, 1988). Also the bentonite used (Wyoming) in our experiments contains 25% non-clay minerals (feldspar and quartz), which might have lowered the sorption affinity.

The sorption of Naph is the lowest of all dyes. Sorption on calcite, dolomite and quartz was lower than 16% at all salinities. In a diluted solution of 0.01 DSW even sorption on clay minerals was low (0 and 39% on bentonite and kaolinite, respectively); again sorption on bentonite was lower than on kaolinite. Sorption on bentonite and kaolinite in 0.5 DSW and DSW was 100%. Therefore, Naph is expected to be ideal for low salinity groundwater but sensitive to clay content at high salinities.

In summary, the SRB and Eosin dyes were found to be strongly adsorbed on pure minerals. Uranine and Pyranine sorption is increased at higher salinities, therefore they can be used as tracers in moderately saline environments. Naph was found to be the best tracer for both fresh and saline groundwater, with minimal sorption on most minerals except for clays.

Sorption on sediment

Sorption of dyes on sediments as a function of salinity is presented in Fig. 3 and Table 4 for four samples (Table 3). The samples represent different assemblages of minerals composing typical sediments along the Dead Sea coastal area. Measurement error was estimated, according to four duplications of the same batch experiment, to be 3–5%.

The effect of salinity on dye sorption on natural sediments is generally similar to that on pure minerals. Higher sorption was found at higher salinities in most cases. More than 90% of the SRB was adsorbed on all sediments tested at all salinities. Therefore, SRB cannot be used as a tracer in saline groundwater. Eosin sorption was 57–85%, 85–98% and 100% in 0.01 DSW, 0.5 DSW and DSW, respectively (Fig. 3). Thus, Eosin cannot be defined as a conservative tracer in general. Uranine sorption in 0.01 DSW was low, excluding sample B3 (50%), probably because of the high clay content in B3 (10%, Table 3). Uranine sorption in 0.5 DSW and DSW was 35–73% and 77–93%, respectively, again excluding sample B3 (90% and 100% in 0.5 DSW and DSW, respectively, Table 4). Pyranine sorption was 29–53% (0.01 DSW), 38–59% (0.5 DSW) and 64–88% (DSW), except for sample B3 (41%, 83% and 98%, 0.01 DSW, 0.5 DSW and DSW, respectively). The sorption of Naph was extremely low on all sediments, excluding B3: 9–14% (0.01 DSW), 3–24% (0.5 DSW) and 0–7% in DSW. The sorption on B3 was 46%, 63% and 74% in 0.01 DSW, 0.5 DSW and DSW, respec-

tively. Therefore Naph is the least adsorbing tracer among the tracers explored and is suitable as a conservative tracer even in extremely saline groundwater. As demonstrated by results from pure mineral and sediment sorption experiments (Figs. 2 and 3, Table 4), the sorption of Naph correlates with sediment clay content. However, it is still more suitable than all the other dye tracers studied.

Natural sediment is an assemblage of pure minerals in different ratios. Therefore, assessment of dye sorption can be modeled by applying a simplified method of multiplying the weight fraction of each mineral in the sediment by the percentage of dye sorption on pure fine minerals (for clays, results of sorption on kaolinite were used). Table 5 presents results of measured and modeled sorption values as well as their differences. The experimental sorption was usually higher than the estimated sorption by an average of 25%. A few general conclusions can be drawn from the data presented in Table 5: (1) in cases where high sorption was detected (SRB at high salinities), the agreement between the sorption directly measured on the sediment and that calculated according to the mineral composition was relatively good; (2) for Naph, where the real sorption was close to zero in many cases, the calculated sorption was higher than the actual sorption in several cases; and (3) for sample B3, the measured sorption of all dyes was higher by 40% on average than that calculated. The uniqueness of sample B3 is in its high clay content (10%, see Table 3 for details) and its larger specific surface area. This appar-

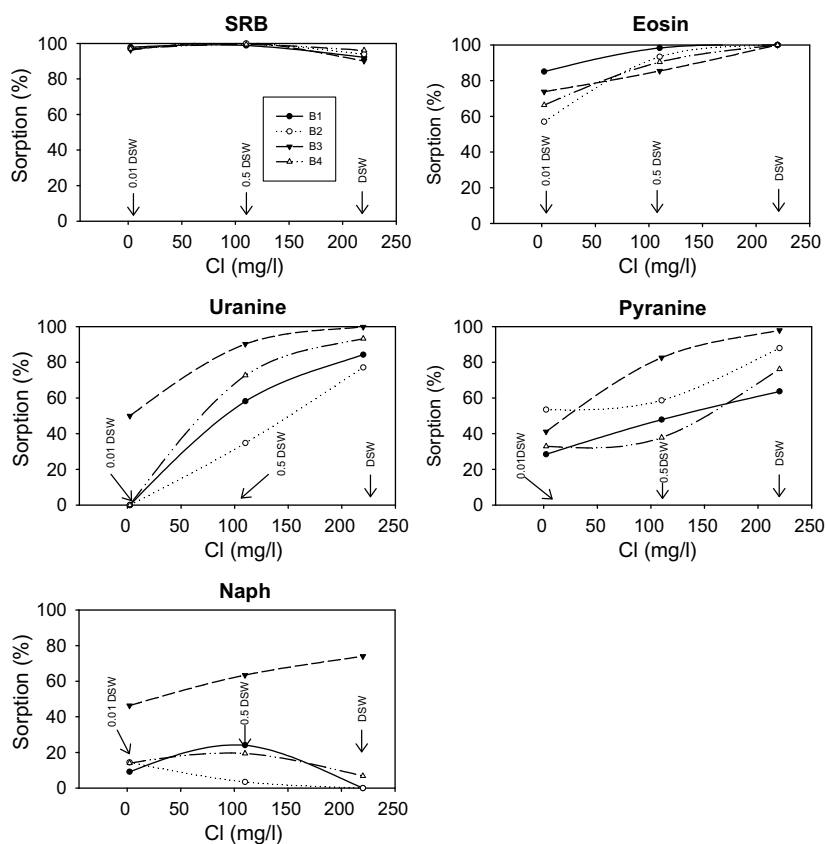


Figure 3 The sorption of: SRB (a); Eosin (b); Uranine (c); Pyranine (d); and Naph (e) on natural sediment samples from the Dead Sea area (details in Table 3).

Table 5 Amount of dye sorption (%) on natural sediment

Dye	Solution salinity	Sample											
		B1			B2			B3			B4		
		Exp.	Est.	Δ	Exp.	Est.	Δ	Exp.	Est.	Δ	Exp.	Est.	Δ
SRB	0.01DSW	98	76	21	97	86	11	96	76	21	97	77	20
	0.5DSW	99	90	9	100	98	2	100	87	14	99	90	9
	DSW	92	91	2	94	98	-4	90	85	5	96	92	4
Eosin	0.01DSW	85	49	36	57	64	-7	74	57	17	66	48	18
	0.5DSW	98	66	33	93	82	11	85	64	21	90	67	24
	DSW	100	89	11	100	98	2	100	82	18	100	91	9
Uranine	0.01DSW	0	8	-8	0	23	-23	50	9	41	0	9	-9
	0.5DSW	58	9	49	35	23	12	90	11	79	73	10	63
	DSW	84	35	49	77	54	23	100	36	64	93	37	56
Pyranine	0.01DSW	28	5	24	53	13	41	41	5	36	33	5	28
	0.5DSW	48	27	21	59	54	5	83	27	56	38	29	9
	DSW	64	34	30	88	58	30	98	32	66	76	36	40
Naph	0.01DSW	9	6	3	14	17	-3	46	7	39	14	7	7
	0.5DSW	24	19	5	3	53	-49	63	20	43	19	20	-1
	DSW	0	17	-17	0	47	-47	74	19	55	7	19	-12

The deviations (Δ , %) represent the difference between experimental and calculated values.

ently increases the overall sorption more than could be estimated from its relative weight fraction in the sediment. It can be concluded that the results from the dye sorption on pure minerals can give only general qualitative insights for tracer selection, whenever groundwater salinities and sediment compositions are known. Actual sorption might be higher than calculated, especially when the sediment has a high clay content. The observed discrepancy could be the result of: (1) smaller sediment grain sizes than those of the mineral grains that were used for determining sorption; therefore higher sorption is expected due to the larger surface area of the grains; (2) the sediments possibly containing minerals in small quantity, below the detection limit of the X-ray, which play a role in the overall sorption capacity of the sediments. For example, sorption of the four dyes on ferric hydroxide was found to be higher in comparison to sorption on kaolinite (Aldous and Smart, 1988), therefore even a small amount of ferric hydroxide could result in a major dye loss to sorption.

Impact of sediment to solution ratio and grain size on Uranine sorption at high salinity

The effect of sediment to solution ratio (SSR), which due to practical reasons can vary in a range of 1:1–1:50 in batch experiments (Kasnavia et al., 1999), and the effect of grain size of the minerals on Uranine sorption was analyzed. Uranine was used due to its moderate sorption at high salinity. The isotherms of Uranine sorption on dolomite, calcite and quartz in DSW solution were determined for SSRs of 1:1 and 1:10 (Fig. 4, Table 3). The distribution coefficient (K_d) was calculated assuming a linear sorption isotherm that passes through the origin of the coordinate and using the linear regression technique (Table 6), a valid assumption for low

dye concentrations. Distribution coefficients with an SSR of 1:10 were 3–7 times higher than the K_d with an SSR of 1:1 (Table 6). Higher K_d values are expected in lower SSR experiments since in low SSR experiments there is more dye for the same amount of sediment. Where a higher amount of dye is present, more dye adsorbs on the minerals, resulting in higher K_d values. The fact that the K_d is influenced by the sediment to solution ratio makes comparison between studies with different SSRs very difficult. Similar results were obtained in fresh water for sorption of Uranium (VI) (Phillippi et al., 2007). The authors stated that the SSR is critical when extrapolating results of batch experiments, generally conducted at low SSR, to column experiments and then to the field.

The impact of grain size on the K_d value of the pure minerals was evaluated for two grain sizes (Table 6, Table 3). For the SSR of 1:1, the K_d of the fine sediments was higher than that of the coarse grains by 2.3, 2.6 and 8.6 times than that of dolomite, calcite and quartz, respectively. This result can be explained by the larger surface area on fine grains and therefore higher sorption capacity. The specific surface area (SSA) of the grains was computed assuming a sphere shape of the grains, and the ratio of fine to coarse grains was 42, 30 and 5 for dolomite, calcite and quartz, respectively. It is clear that while the K_d ratio of fine to coarse grains of dolomite and calcite is onefold smaller than the SSA ratio, the K_d of quartz is similar. Sabatini (2000) found that in fresh water the sorption of SRB decreased with increasing particle size, as one would expect. Nevertheless, although normalizing the sorption values by the SSA of the sorbing matrix reduces the variability between values, this does not generate a general value. Sabatini (2000) noted that further research is needed to evaluate the role of SSA in K_d values.

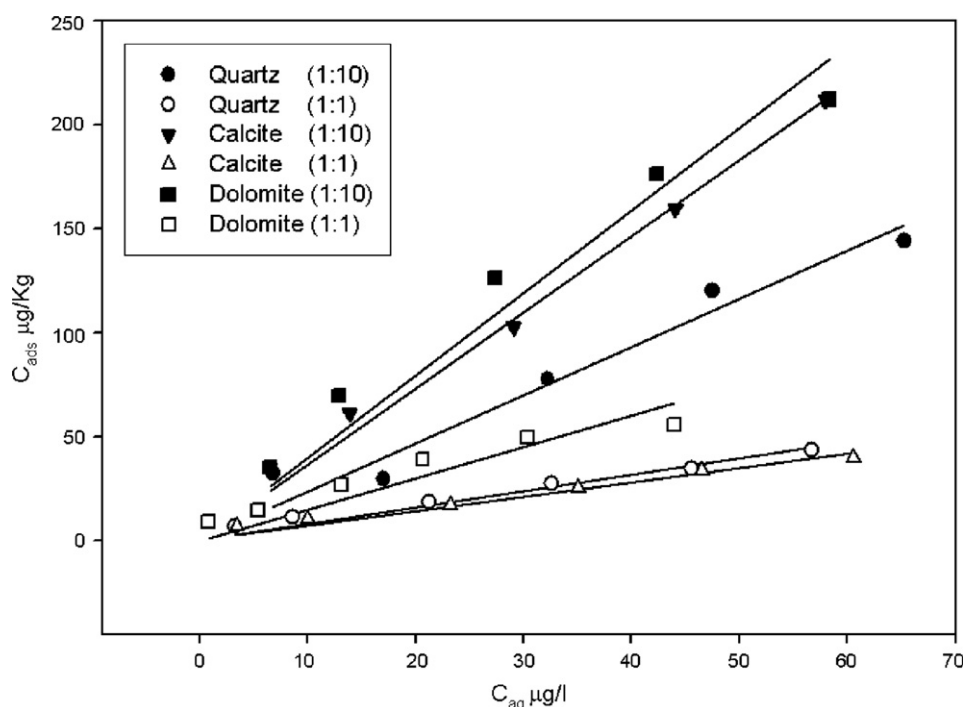


Figure 4 Isotherms of Uranine sorption in DSW solution on fine grains of quartz, calcite and dolomite for sediment to solution ratios of 1:1 (5 g in 5 ml) and 1:10 (0.5 g in 5 ml). Symbols represent experimental data, lines are linear regression.

Table 6 Distribution coefficient (K_{ads}) and determination coefficient (R^2) for Uranine isotherms in DSW, for sediment to solution ratios of 1:1 (5 g in 5 ml) and 1:10 (0.5 g in 5 ml)

Mineral	Sediment to solution ratio			
	1:1		1:10	
	K_d (l/kg)	R^2	K_d (l/kg)	R^2
Fine dolomite	1.50	0.81	3.97	0.95
Coarse dolomite	0.65	0.93	2.13	0.93
Fine calcite	0.69	0.96	3.66	0.99
Coarse calcite	0.26	0.96	2.18	0.89
Fine quartz	0.79	0.95	2.32	0.95
Coarse quartz	0.09	0.96	1.96	0.90

Comparison between measured experiment data (Exp.) and model calculated values according to relative mineral composition and experimental sorption on pure minerals (Fig. 2, Table 3).

Conclusions

The possible use of dyes as tracers in saline groundwater was studied. The impact of solution salinity and mineral composition on the sorption of five, frequently used, fluorescent dyes was investigated. It was found that the FIs of SRB and Eosin were significantly reduced in high salinity solutions. The FI of Pyranine was affected by salinity but did not show a clear trend. The FIs of Uranine and Naph were found to be almost unaffected by the solution salinity.

The sorption of dyes on natural sediment and pure minerals was evaluated by a series of batch experiments on solutions of different salinities. It was found that the SRB and Eosin have the highest sorption affinity on sediments and minerals, while the least sorption was found for Uranine, Pyranine and Naph. Therefore, SRB and Eosin cannot be recommended for use as tracers to characterize groundwater flow in saline environments. Uranine and Pyranine

have a moderate sorption affinity and can be used at salinities up to 0.5 DSW (110 g Cl/l); however, some dye sorption must be accounted for even at those salinities. Naph was found to be the dye tracer least sorbed for both fresh and saline solutions. Still, even Naph sorption was significant on clay minerals and sediments with high clay contents.

Sorption results can be used as a guideline for proper selection of tracers for field experiments based on mineral composition and groundwater salinity. Based on our experimental results, the sorption of dyes on natural sediments was calculated assuming a simple model of additive dye sorption on the weight fraction of each mineral in the sediment. The actual sorption on natural sediments was on average 25% higher than calculated sorption based on the sediment composition. It is recommended, therefore, to conduct sorption experiments using sediments from the field and to evaluate the amount of tracer loss to sorption.

Determination of the Uranine distribution coefficient (K_d) in highly saline solutions of DSW was found to be dependent on the sediment to solution ratio, where low ratios resulted in higher values of K_d . Also, higher K_d values were found for the fine grain size due to higher sorption capacity on larger surface areas. Yet, the difference of K_d is not directly related to the specific surface area of the grains and should be examined separately.

In summary, it was evident that salinity plays a significant role in the sorption of fluorescent dyes on sediments. The groundwater salinity, mineralogical composition of the sediment and probably the composition of the brine (that should be tested in future work) impact on the sorption of the dyes. Nevertheless, in general, some dyes (e.g., Naph.) are more suitable than others (e.g., SRB and Eosin) for conducting tracer field experiments in saline groundwater.

Acknowledgements

The authors are grateful to H. Hemo and N. Fruchter for their technical assistance, M. Sheinfeld for his the help and guidance in the usage of lab equipment. They thank Y. Nachmias and Y. Lakatosh for the granular analysis and A. Melamed for providing high purity calcite sediment.

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