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2 **Recent seawater intrusion into deep aquifer determined by the radioactive**  
3 **noble-gas isotopes  $^{81}\text{Kr}$  and  $^{39}\text{Ar}$**

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## 26 KEY WORDS

27 Groundwater dating,  $^{81}\text{Kr}$ ,  $^{39}\text{Ar}$ , noble gases, radioactive isotopes, seawater intrusion

28

## 29 Abstract

30

31 Radioactive noble-gas isotopes tracers  $^{81}\text{Kr}$  and  $^{39}\text{Ar}$  are used for the first time to measure  
32 the residence times of deep (~1000 m) saline coastal groundwater, and to determine its  
33 connection mode with the sea. The average rate of seawater intrusion into the deep aquifer in  
34 Israel, located near the Mediterranean Sea, is estimated.  $^{81}\text{Kr}$ -ages of the saline water samples,  
35 found to be younger than 40 ka, contradict previously estimated ages of up to several million  
36 years based on hydrogeological considerations. The new results imply a stronger and more recent  
37 connection between the aquifer and the sea, and indicate that the intrusion occurred during the  
38 sea-level rise that began about 20 ka ago. These coastal aquifers need to be managed with  
39 caution because lowering of the adjacent fresh water level due to over pumping could accelerate  
40 seawater intrusion in a relatively short time. This study demonstrates the suitability of these two  
41 noble-gas tracers for the examination of hydrogeological systems in general and for the study of  
42 seawater intrusion in particular.

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47 **1. Introduction**

## 48 1.1. General

49 Coastal aquifers are potentially prone to salinization from multiple sources, including  
50 dissolution of subsurface evaporates, ancient trapped seawater, and ongoing seawater intrusion.  
51 The issue of coastal aquifer degradation has become increasingly acute in the past few decades due  
52 to over pumping that induces saline water into adjacent freshwater aquifers. In most cases,  
53 seawater intrusion rates are inferred from increase in salinity (Acworth and Dasey, 2003;  
54 Linderfelt and Turner, 2001), change of chemical composition (Russak et al, 2016; Mercado,  
55 1985), or movement of the fresh-saline water interface (Melloul and Zeitoun, 1999). Direct  
56 determination of the seawater intrusion rate has been done previously, based only on radiocarbon  
57 and tritium tracers (Sivan et al, 2005; Yechieli et al, 2001; Yechieli et al, 2009). However, the  
58 interpretation of radiocarbon results is complicated by water-rock interactions (Mook, 1980), and  
59 dating by tritium becomes ambiguous due to the low values in recent precipitation and its short  
60 half-life. Moreover, saline well water usually mixes with fresh water, further complicating the  
61 chronological interpretation. Noble-gas radionuclides, with chemical inertness, simple source  
62 function, and limited subsurface production, are thus emerging as ideal tracers of groundwater  
63 movement. Indeed, dating of fresh groundwater with noble gases has been performed recently in  
64 many parts of the world, using  $^{85}\text{Kr}$  (half life of 10.7 a) and  $^3\text{He}$  (decay product of  $^3\text{H}$ , whose half  
65 life is 12.4 a) for short-term hydrological processes (Althaus et al, 2009; Visser et al, 2013),  $^{39}\text{Ar}$   
66 (269 a) for intermediate, and  $^{81}\text{Kr}$  (229 ka) for long-term processes (Gerber et al, 2017; Aggarwal  
67 et al, 2015). Dating of saline water (even more saline than seawater) was conducted by Sturchio et  
68 al. (2014) but not for the issue of seawater intrusion.

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71           1.2.   Site description

72           The Yarkon-Taninim Basin (YTB) of Israel is the western portion of the regional Upper  
73 Cretaceous Mountain aquifer. The basin stretches over 10,500 km<sup>2</sup>, from the water divide in the  
74 Judea and Samaria mountains in the east to the Mediterranean coast in the west (Figure 1). The  
75 northern border of the basin extends to the Yizrael Valley, Mount Carmel, and to the Taninim  
76 spring. The southern border extends into the Sinai Peninsula in Egypt and to the northern Negev  
77 desert (Goldshstoff et al, 1980; Shachnai, 1980; Weinberger et al, 1994; Dafny et al, 2010).  
78 Precipitation in most of the YTB drainage basin is about 550 mm/year, all occurring in winter  
79 Mediterranean rain events, and the recharge coefficient is 30-33% (Dafny et al, 2010; Guttman and  
80 Zukerman 1995).

81           The major hydrogeological unit of the YTB is the Judea Group built of 600-900 m thick  
82 Upper Cretaceous karstic limestones and dolomites with some marls and chalks. The aquifer is  
83 divided into upper and lower sub-aquifers by a leaky marly aquitard. The units in the aquifer are  
84 continuous throughout the entire basin and generally dip to the west. In the eastern areas (Judea  
85 and Samaria mountains), the aquifer is exposed and directly replenished by rainfall (Figure 2).  
86 Westwards, the aquifer becomes confined under relatively thick impermeable chalks and marls of  
87 the Senonian Mount Scopus Group and the Eocene Avedat Group. The phreatic parts of the  
88 aquifer, as well as the eastern confined part, contain mostly high-quality young groundwater. A  
89 lateral lithological transition from the karstic permeable Judea Group rocks to the mainly  
90 argillaceous and impermeable Talme Yafe facies (Figure 2) occurs at the western margins of the  
91 basin, mostly along the Mediterranean shoreline (Bein, 1974). This impermeable unit was assumed

92 to act as a bidirectional hydrological barrier between the Mediterranean Sea and the Judea Group  
93 aquifer, preventing flow toward the sea. This results in northward flow of the fresh water within  
94 the confined part of the aquifer towards the two natural outlets: the Yarkon springs in the central  
95 part of the basin and the Taninim springs at its northern tip (Figure 1). This main and long S-N  
96 flow trajectory is fed all along by recharge water that joins the main trajectory from the east  
97 (Figure 1).

98 The northwestern confined portion of the YTB, north of the city of Netanya, contains saline  
99 groundwater (Rosenthal et al, 1999) (Figure1). In this area, an unusually sharp (~10m from 20% to  
100 80% seawater) and almost horizontal interface between saline and fresh water is recognized in  
101 deep monitoring boreholes (Figure 2). The salinity and chemical composition of this saline water  
102 resembles that of the Mediterranean Sea (Cl~22,000 mg/l), while always containing also a small  
103 fraction of fresh water of Cl~100 mg/l (at least 10%). Because of the impermeable nature of the  
104 Talme Yafe facies, a current hydraulic disconnection to the Mediterranean Sea was assumed, and  
105 Neogene trapped seawater (age of several millions years) origin of the salinity in the northwestern  
106 part of the aquifer has long been postulated (Rosenthal et al, 1999; Bein and Burg, 2001). In the  
107 Neogene, the impermeable clayey Yafo Formation was deposited, which could explain the  
108 confinement of this saline water body. However, it should be noted that few hydrological studies  
109 suggest current seawater intrusion either directly or along a main fault zone at the northern tip of  
110 the basin (Kafri and Arad, 1979; Paster et al, 2006).

111 In this work,  $^{81}\text{Kr}$  and  $^{39}\text{Ar}$  tracers are employed for the first time to determine the time  
112 scale of the seawater penetration into an adjacent aquifer. These tracers can serve as a diagnostic  
113 tool for distinguishing between trapped saline water of Neogene age and active, current seawater  
114 intrusion from the Mediterranean Sea. In particular, the results are essential for estimating the

115 degree of connection between the sea and any nearby active and exploited aquifers, and for  
116 minimizing salinization of such coastal aquifers.

117

## 118 **2. Materials and Methods**

### 119 2.1. Field sampling and analytical methods.

120 Five deep boreholes in the saline part of the western mountain aquifer of YTB (Figure 1)  
121 were sampled for chemical analysis of major ions, stable isotopes of oxygen and hydrogen,  $^{81}\text{Kr}$ ,  
122 and other noble gases: two in June 2014 and three in November 2015. Technical details, such as  
123 depths of boreholes and intervals of screens, are given in Table 1. Additional samples for  $^{39}\text{Ar}$   
124 and  $^{14}\text{C}$  analyses were collected in the 2015 campaign. Onsite measurements of pH, dissolved  
125  $\text{O}_2$ , water temperature and electrical conductivity were carried out. Two to five cubic meters of  
126 groundwater were degassed in the field for radioactive noble gases  $^{39}\text{Ar}$ ,  $^{81}\text{Kr}$  and  $^{85}\text{Kr}$ . The field  
127 degassing device is based on the hydrophobic membrane contactor. The details about the device  
128 and the procedure can be found in Purtschert et al (2013) and Yokochi (2016).

129 Composition of major ions and stable isotopes were determined according to standard  
130 methods in the laboratories at the Geological Survey of Israel, with a maximum error of 3% for  
131 chemical parameters (Burg et al., 2006; Russak et al, 2016). The isotopic results of  $\delta^{18}\text{O}$  are  
132 reported on the SMOW scale and the precision of the measurement is  $\pm 0.1\%$ . Radiocarbon  
133 samples were collected in 200-ml dark sealed glass and measured in the AMS Laboratory, New  
134 Zealand. The activities are expressed as a percentage of modern carbon (pMC). The  $\delta^{13}\text{C}$   
135 contents were measured in both AMS and GSI Laboratories, and are expressed in permil  
136 variations from the Vienna Peedee Belemnite Standard (% VPDB). Analyses of  $^3\text{H}$ , He isotopes  
137 and Ne were conducted at the noble gas laboratory of the Institute of Environmental Physics,

138 University of Bremen. For the He and Ne analyses, bulk water samples collected in 40-ml copper  
 139 tubes sealed with pinch-off clamps, were degassed and cryogenically separated by a quadrupole  
 140 mass spectrometer (Balzers QMG112A) and a high-resolution sector-field mass spectrometer  
 141 (MAP 215-50). For groundwater samples, the precision of the He and Ne concentrations is better  
 142 than 1% and for the  $^3\text{He}/^4\text{He}$  ratio better than 0.5%.  $^3\text{H}$  was analyzed with the  $^3\text{He}$ -ingrowth  
 143 method (Clarke et al, 1976; Sültenfuß et al, 2009) with a precision of  $\sim 0.03\text{TU}$ : 500 g of water  
 144 were degassed and stored for the accumulation of the  $^3\text{H}$  decay product ( $^3\text{He}$ ) in dedicated He-  
 145 free glass bulbs. After a storage period of 2-3 months,  $^3\text{He}$  was analyzed with a mass  
 146 spectrometric system.

147 Separation and purification of krypton and argon from the bulk gas were done in the  
 148 laboratories of both the University of Chicago and University of Bern using cryogenic absorption  
 149 and gas chromatography (Purtschert et al, 2013; Yokochi, 2016; Riedmann and Purtschert 2016).  
 150 The  $^{39}\text{Ar}$  activities were measured by low-level gas proportional counting in the Deep  
 151 Laboratory of the Physics Institute, University of Bern (Loosli, 1983; Loosli et al, 1986; Forster et  
 152 al, 1992; Riedmann and Purtschert 2016).  $^{81}\text{Kr}/\text{Kr}$  and  $^{85}\text{Kr}/\text{Kr}$  were measured using the Atom  
 153 Trap Trace Analysis (ATTA) method (Lu et al, 2013; Jiang et al, 2012; Chen et al, 1999) in the  
 154 Laboratory for Radiokrypton Dating, Argonne National Laboratory, USA. At least 10  $\mu\text{L}$  STP of  
 155 Kr gas sample is required for measurement. The  $^{81}\text{Kr}$  partial modern values ( $R_{81} = (^{81}\text{Kr}/\text{Kr})_{\text{sample}} / (^{81}\text{Kr}/\text{Kr})_{\text{modern}}$ ) are reported with 1-sigma uncertainty. Partial modern values which exceed  
 156 the modern atmospheric value defined as due to statistical fluctuations of the  $^{81}\text{Kr}$  atom count  
 157 would represent unphysical groundwater ages of less than zero. The  $^{81}\text{Kr}$  apparent age can be  
 158 calculated with the formula  $Age_{81\text{Kr}} = -t_{1/2}^{81\text{Kr}} \ln(R_{81}) / \ln 2$ , where  $t_{1/2}^{81\text{Kr}}$  is the half-life of  $^{81}\text{Kr}$ .  
 159  
 160 When the sample is young, the measured  $^{81}\text{Kr}$  partial modern values could be larger than 1 due to

161 statistical fluctuations which will result in a negative  $^{81}\text{Kr}$  age (younger than modern). In these  
162 cases, we adopt the unified method, which is commonly used and well accepted in the high-  
163 energy physics community (Feldman and Cousins, 1998). In this approach, we redistribute the  
164 groundwater age probabilities into the physical range and obtain  $^{81}\text{Kr}$ -age limits with a  
165 confidence level of 90%. With this technique, the yielded limit from the measurements will  
166 always be physical even when the measurements is not (when  $R_{81} > 1$ ). When the measured data is  
167 far from the unphysical region, the errors are simply statistical.

168

169 2.2. Relevant processes for data interpretation.

170 All samples discussed here contain both fresh and saline water components, each with its  
171 distinct flow path and residence time. Henceforth, we define age for each component as the time  
172 since penetration or recharge of the water into the aquifer. When discussing the saline water, the  
173 age (or residence time) is considered to be from the time of penetration of the seawater into the  
174 bottom sediment (Yechieli et al, 2009). In such a case, there are three relevant processes: (1)  
175 long term seawater intrusion due to natural density-driven circulation near the sea shore; (2) the  
176 effect of sea level rise; (3) seawater encroachment landwards due to the short term effect of  
177 pumping. The rate of seawater intrusion, and therefore the age of the saline water, would be the  
178 result of the superposition of these three possible processes. The initial values of the penetrating  
179 seawater can be assumed to be similar to the current ones since the age of the bottom  
180 Mediterranean Sea water is probably not more than  $\sim 100$  years according to their radiocarbon  
181 values (Broecker and Gerard, 1969). The age of the fresh water component is determined as the  
182 time since recharge into the subsurface, where the water loses its contact with the atmosphere,  
183 down to the sampling point.

184 The interpretation of the ages concluded from two of the noble gases concentrations  
185 ( $^{81}\text{Kr}$ ,  $^{39}\text{Ar}$  - half-life of 229 ka and 269 years, respectively) is relatively simple since they do not  
186 chemically interact with the aquifer's rock and therefore do not require specific corrections for  
187 chemical processes (as is the case of  $^{14}\text{C}$ , see below). However, physical processes such as  
188 diffusive exchange with stagnant water bodies (all tracers, Sanford, 1997) or nucleonic production  
189 due to neutron activation of potassium for  $^{39}\text{Ar}$  may affect the tracers' concentrations (Lehmann et  
190 al, 1993; Purtschert et al, 2004). Practically, diffusion is more pronounced for tracers with longer  
191 half-life (e.g.  $^{14}\text{C}$ ) than for fast decaying tracers. The latter (e.g.  $^{39}\text{Ar}$ ) do not "see" the total  
192 inactive system volume since the time to diffusively reach the inactive volume is much longer  
193 than the mean lifetime of the tracer. Therefore,  $^{14}\text{C}$  (half-life of 5730 years) is more sensitive to  
194 the diffusion process than is  $^{39}\text{Ar}$  (half-life of 269 years) resulting in an apparent overestimation  
195 of  $^{14}\text{C}$  ages compared to  $^{39}\text{Ar}$  ages (Mayer et al, 2014).  $^{81}\text{Kr}$  ages are similarly affected by this  
196 process despite the slightly reduced diffusion coefficient due to the larger mass of the Kr atom.  
197 Uncorrected  $^{81}\text{Kr}$  ages therefore represent upper age limits if diffusive exchange is ignored.

198 Moreover, the translation of radiocarbon activities into ages could also be complicated  
199 and inconclusive due to chemical processes, such as water-rock interaction and isotopic  
200 exchange (Mook, 1980; Gonfiantini and Zuppi, 2013). Thus, dating by  $^{14}\text{C}$  is performed with the aid  
201 of mass balance equations, using computer codes such as the Netpath and PhreeqC, which take  
202 into account the known chemical reactions. These codes estimate one age for any mixed sample  
203 (the obtained saline water sample in our case) and do not provide the distinct age of each  
204 component in the mixed sample. Since seawater is the larger component in our mixtures, the  
205 obtained ages are regarded as a reasonable approximation. An estimated initial value of 60 pMC  
206 can be assumed for many cases, also according to the finding in the nearby coastal aquifer,

207 mainly due to oxidation of old organic matter in the seawater component (Sivan et al, 2005), and  
208 due to chemical processes in the unsaturated zone in the fresh water component (e.g. Carmi et al,  
209 2007).

210 The effect of diffusive exchange between young water in permeable units and old  
211 groundwater in less permeable units can increase the apparent radiocarbon age by ~50% in the  
212 case of granular aquiferic section separated by clayey impermeable layers and/or when the  
213 volume ratio between fractures and rock matrix is relatively low (Sanford, 1997). In the YTB  
214 there are indeed less permeable marly units in the karstic carbonate Judea Group aquifer but  
215 water and solute can exchange between the karstic channels characterized by very fast water  
216 flow and the surrounding porous massive rocks with almost stagnant pore water. The high degree  
217 of heterogeneity of the karstic system can lead to a highly dispersive flow and thus wide age  
218 distributions (Ghasemizadeh et al, 2012).

219

### 220 **3. Results and discussion**

221 The results of all dating tracers are summarized, along with other chemical parameters, in  
222 Table 1. The concentration of  $^{85}\text{Kr}$  in all gas samples are below the detection limit of  $\sim 0.5$   
223 dpm/ccKr (less than 1% of the current atmospheric concentration of 82 dpm/ccKr). This has two  
224 implications: first, contamination of the samples by ambient air during sampling is minimal.  
225 Therefore, no correction for air contamination is needed for the  $^{81}\text{Kr}$  and  $^{39}\text{Ar}$  concentrations.  
226 Second, waters are older than  $\sim 50$  years, thus the contribution of young water component is at  
227 most relatively small. The very low  $^3\text{H}$  concentrations in Raanana Deep (RD) and Taninim 7  
228 (T7) wells (0.01 and 0.05 TU respectively) compared to  $\sim 3.5$  TU in modern precipitation in  
229 Israel support the  $^{85}\text{Kr}$  data. For Bet Eliezer (BE) well, however, the measured value of  $^3\text{H}$  of

230 0.36 TU is significantly higher, indicating the presence of about 10% young water from the  
231 period of 1960-1985, when  $^3\text{H}/^{85}\text{Kr}$  ratios in the Earth's surface water were much higher.  $^3\text{H}$ -  
232  $^3\text{He}$  ages could not be calculated for these three samples since He isotopes and Ne results display  
233 large contributions of crustal and mantle helium. Ne concentrations are near equilibrium  
234 concentrations of saltwater. In general, crustal He is accumulated in the aquifer with time and  
235 therefore is often considered as qualitative age indicator (Sültenfuß 2011 and references therein).  
236 Helium concentrations measured in our wells are about two orders of magnitude higher than in  
237 air saturated water (ASW 10°C 4.8  $10^{-5}$  cc). Assuming in-situ production only, this corresponds  
238 to helium accumulation times in the order of 100kyr. However, the relatively high  $^3\text{He}/^4\text{He}$  ratio  
239 of  $\sim 10^{-6}$  indicates a significant contribution of mantle helium that must enter the aquifer from  
240 greater depth. Since external  $^4\text{He}$  fluxes can lead to helium accumulation rates 2-3 order of  
241 magnitude higher than in-situ production only (Suckow et al., 2013), the measured  $^4\text{He}$   
242 concentrations are in accordance with the  $^{39}\text{Ar}$  and  $^{81}\text{Kr}$  data, which indicate a mixture of water  
243 components in the age range of hundreds and 10 thousands of years respectively (see below).

244

245 The nearly modern  $^{81}\text{Kr}$  activities in all measured samples (Table 1) indicate short water  
246 residence time (in terms of  $^{81}\text{Kr}$  ages). The lowest value is measured in BE (0.94), indicating an  
247 apparent mean residence time of  $20 \pm 11$  ka. The relatively low  $^{39}\text{Ar}$  activities ( $< 27\%$  mod)  
248 implies an age that is older than several hundred years.

249 All three  $^{14}\text{C}$  samples (T7, RD, BE) have low radiocarbon contents (2.9, 3.6 and 5.3  
250 pMC, respectively). Other YTB saline groundwater samples previously analyzed (Burg et al,  
251 2006; Burg and Talhami, 2013) also present low  $^{14}\text{C}$  activities, with an inverse correlation between  
252  $^{14}\text{C}$  and salinity (Figure 3), suggesting that the fresh water component is much younger than the

253 saline water. The values of  $\delta^{18}\text{O}$  in the more saline samples are close to that of current seawater  
 254 and plot on a seawater-freshwater mixing line (Figure 4). Accordingly, all samples discussed  
 255 here are considered as containing different degrees of mixture of seawater and freshwater.

256

### 257 3.1. Residence times of mixed groundwater components.

258 The saline groundwater in the study area is a mixture of fresh groundwater from the east  
 259 with proportion ( $y$ ) and seawater with proportion ( $1-y$ ) that intruded from the west. The mixing  
 260 proportions are determined by assuming  $\text{Cl} \sim 22.5 \text{ g/L}$  and 0 for the seawater ( $\text{Cl}_s$ ) and fresh  
 261 water ( $\text{Cl}_f$ ) end members respectively according to the following Cl budget:

$$262 \quad \text{Cl}_m = y \cdot \text{Cl}_f + (1-y) \cdot \text{Cl}_s$$

263 where the subscript  $m$  refers to the measured chloride concentrations. The resulting fresh water  
 264 contribution ( $y$ ) in three samples listed above are in the range of 9-17%. Concentrations of Ar  
 265 and Kr in the fresh and seawater component are different, and are estimated based on the  
 266 recharge conditions of both water components: For seawater a recharge elevation of 0 m and  
 267 salinity of 39‰ and for the freshwater a recharge altitude of 400 meters and a salinity of 0‰ are  
 268 assumed. No excess air is considered for either water component. Additionally, the solubilities of  
 269 Ar and Kr are lower in sea water compared to freshwater by a factor of  $D=0.82$  (Weiss, 1971;  
 270 Weiss and Kyser, 1978), , which leads to an adjusted noble gas concentration budget where the  
 271 contribution of the saline water is reduced by the factor  $D$ . The proportion  $Y$  of Ar (and Kr) in  
 272 the freshwater components is then:

$$273 \quad Y = \frac{y}{y + (1-y) \cdot D}$$

274 and  $(1-Y)$  for the saline component

$$(1-Y) = \frac{(1-y) \cdot D}{y + (1-y) \cdot D}$$

276

277 For  $^{39}\text{Ar}$ , the possibility of underground production (Purtschert and Althaus, 2012) also  
 278 needs to be considered. The lowest measured value of 10% modern at Taninim 7 can be regarded  
 279 as an upper limit on the secular equilibrium concentration (P) due to underground production.  
 280 Therefore, an uncertainty range of 0-10% modern is assumed for all samples and for both the sea  
 281 and the fresh water components. This is justified by the fact that both components were sampled  
 282 from the same formation, which is built of shallow marine carbonate of relatively uniform  
 283 composition over a large area.

284 With the above-calculated mixing proportions of Ar and Kr and the measured  
 285 concentrations of  $^{39}\text{Ar}$  and  $^{81}\text{Kr}$ , the following activity budget can be formulated in Eq 1:

286

$$^{39}\text{Ar}_m = Y_{\text{Ar}} \cdot ((A_0 - P) \cdot \exp(-\lambda_{\text{Ar}} \cdot t_f) + P) + (1 - Y_{\text{Ar}}) \cdot ((A_0 - P) \cdot \exp(-\lambda_{\text{Ar}} \cdot t_s) + P) \quad (1a)$$

$$^{81}\text{Kr}_m = Y_{\text{Kr}} \cdot Kr_0 \cdot \exp(-\lambda_{\text{Kr}} \cdot t_f) + (1 - Y_{\text{Kr}}) \cdot Kr_0 \exp(-\lambda_{\text{Kr}} \cdot t_s) \quad (1b)$$

289

290 Underground production is thereby described as an ingrowth process as function of groundwater  
 291 residence time  $t$ , and the secular equilibrium concentration  $P$ . Here, the subscript  $m$  refers to the  
 292 measured tracer concentrations,  $\lambda$ 's are the decay constants, and  $t_f$  and  $t_s$  are the ages of the fresh  
 293 and saline water components, respectively.  $A_0$  and  $Kr_0$  are initial ratios which equals to present-  
 294 day atmospheric values. Equations (1a) and (1b) must be fulfilled for any valid pairs of  $t_f$  and  $t_s$   
 295 in consideration of the analytical uncertainties of  $^{81}\text{Kr}$  and  $^{39}\text{Ar}$  and the possible range of  
 296 underground production  $P$  of  $^{39}\text{Ar}$  between 0% modern and 10% modern.

297 The multi-tracer chronological constraints are depicted in Figure 5 a-c. Each tracer  
 298 defines an area in the  $t_f - t_s$  plane bound by the analytical uncertainties and the uncertainty range  
 299 of underground production.. The reddish area depicts all possible solutions for  $^{39}\text{Ar}$  (Eq 1a) and  
 300 the grey area for  $^{81}\text{Kr}$  (Eq. 2b). For Bet Eliezer, the  $^{81}\text{Kr}$  activity can be either mainly originated  
 301 from the saline water component (in this case the fresh water is over 50 ka old) or from the fresh  
 302 water component (in this case the saline water is between 13-40 ka). Any intermediate solution  
 303 between those two extremes is also possible (indicted by the gray band). By adding  $^{39}\text{Ar}$ , this  
 304 range is significantly reduced and only the two shaded areas are left (C1 and C2). Since only C1  
 305 is in accordance with the elevated  $^3\text{H}/^{85}\text{Kr}$  ratio of Bet Eliezer, indicating the presence of water  
 306 that recharged close to the peak of the atmospheric bomb tests period (1960-1985), we conclude  
 307 that the fresh water must be the younger component for this sample, as implied also from the  
 308 radiocarbon data that indicate an older age for the sea water component (Fig. 3). It can be  
 309 projected that this is also the case for the other wells,. We therefore add the constraint  $t_f < t_s$  for  
 310 all wells (green line). With these ranges, both the fresh (orange numbers in Fig. 5) and saline  
 311 (violet numbers) waters are constrained and listed in Table 2. Bet Eliezer is the sample with the  
 312 youngest fresh water (detectable  $^3\text{H}$ ) but with the oldest saline water. This is in accordance with  
 313 the location of the well, which is situated farthest from the coast and thus closest to the current  
 314 recharge zone in the mountain area

315

### 316 3.2. Implications of radiocarbon signatures.

317 An activity budget similar to the above Eq (1b) can be formulated for  $^{14}\text{C}$  in Eq 2:

318 
$$^{14}C_m = Y_C \cdot C_0 \cdot \exp(-\lambda_C \cdot t_f) + (1 - Y_C) \cdot C_0 \exp(-\lambda_C \cdot t_s) \quad (2)$$

319 The following assumptions are taken into account: (1) an initial activity of 60 pMC; (2) the  
320 above introduced mixing proportion  $Y_c$ , using a depletion factor  $D_c$  of  $\sim 0.5$  (DIC of saline water  
321 is 50% less compared to freshwater; Burg and Talhami, 2013), and (3) the ages of the fresh and  
322 saline water component deduced above.

323 Accordingly, the calculated  $^{14}\text{C}$  activities are 18, 20 and 15 pMC for BE, RD and T7,  
324 respectively. These values are much higher than those measured in the range of 2.9 - 5.3 pMC  
325 (Table 1). Groundwater dating using  $^{14}\text{C}$  in the present case, therefore, requires the consideration  
326 of additional processes that reduce the  $^{14}\text{C}$  activities in DIC. Meanwhile, the  $\delta^{13}\text{C}$  values of the  
327 saline water component are lighter than those of the current seawater, indicating the effect of  
328 oxidation of organic matter of seafloor sediments, containing dead carbon during the seawater  
329 penetration (similar to the process in the shallow coastal aquifer; Sivan et al, 2005). Entering  
330 both the  $^{14}\text{C}$  activities and  $\delta^{13}\text{C}$  values into PhreeqC or Netpath geochemical codes leads to  
331 adjusted residence time of 21 - 27 ka for the saline water of the YTB (Table S2). The codes  
332 calculated the seawater fractions in the saline groundwater, and the mass transfers (moles) of the  
333 different chemical processes. The main processes are ion exchange (mainly Ca versus Na) and  
334 Ca and Mg dissolution due to dissolution of rock-forming minerals. Another process that might  
335 be of affect is the  $\text{CO}_2$  addition due to oxidation of organic matter upon the penetration of the  
336 seawater through the bottom sea sediment and into the aquifer. The apparent difference between  
337 the relatively old apparent radiocarbon ages, and the ages deduced from the  $^{39}\text{Ar}$  and  $^{81}\text{Kr}$  dating  
338 methods, can be explained by several chemical (water-rock interaction, e.g. Mook, 1980) and  
339 physical (matrix diffusion, Sanford, 1997) processes.

340 Our data can be used to constrain not only the time of seawater intrusion but also the  
341 residence time of the fresh groundwater (constituting 9-17% of the samples). Since  $\text{HCO}_3$  in

342 most fresh water samples is about double than in of seawater, the contribution of carbon from the  
343 fresh water could be up to 18-34% of the total. At such mixing ratios, the radiocarbon of the  
344 fresh groundwater component has to be 9-30 pMC in the three samples in order to fit the  
345 obtained values in these samples which are values of a mixture (Figure 3; Table S1) of fresh and  
346 saline water bodies.

347       Regarding the BE sample, with its relatively high  $^{39}\text{Ar}$  and  $^3\text{H}$ , there is an unexpected  
348 contradiction between the relatively old radiocarbon ages (several thousands of years, 16-30  
349 pMC; Table S1) and the young  $^{39}\text{Ar}$  ages (several hundreds of years,  $>0.27$ , Table 1) of the fresh  
350 component. Pronounced mixing of the water components with different ages, as expected in a  
351 karstic system, is a process that may explain this discrepancy because of the concave exponential  
352 decay curve and the shorter half-life of  $^{39}\text{Ar}$  compared to  $^{14}\text{C}$ . Yet, details of the mixing process  
353 cannot be resolved with the restricted available data. It is suggested that the discrepancy could be  
354 due to dispersive mixing of several fresh water bodies of different ages and flow rates. The  
355 youngest could be the component that percolates into the Samaria Mountains in the east while  
356 the oldest could be the water body that moves more slowly at the fresh-saline water interface  
357 zone or the component that flows from the farther southern part of the aquifer (Dafny et al, 2010).  
358 The mixing of these components is probably due to natural flow near the interface zone.

359       Loss of  $^{14}\text{C}$  from the groundwater into the surrounding aquifer matrix by diffusion is  
360 another process that could lead to much older apparent  $^{14}\text{C}$  ages (Sanford, 1997). This process  
361 would also affect  $^{39}\text{Ar}$  and  $^{81}\text{Kr}$  but to a different extent as a function of half-life, diffusion  
362 coefficients and geometry and spacing of permeable and stagnant zones. This process can  
363 explain at least part of the above contradiction in the ages of the BE sample. By assuming similar  
364 conditions for the intruding seawater, and similar diffusion with old connate water during the

365 inland intrusion, the age can be reduced by ~50%. In accordance, the age of the saline water  
366 would be younger than that discussed above by ~50% (~10 ka instead of ~20 ka).

367

### 368 3.3. Other age constraints.

369 More constraints on the age of the saline water can be derived from the isotopic  
370 signature. According to the mixing line (Figure 4), the isotopic signature of the old, sea water  
371 component is quite similar to that of the present seawater (e.g.  $\delta^{18}\text{O}$  of ~1.5‰ and 1.8‰ in old  
372 and recent seawater, respectively). Since the isotopic values during most of the period between  
373 15 and 120 ka are different from the present ones by ~1-2‰, it implies that the intrusion took  
374 place in sea conditions similar to those of the last 15 ka, or in previous high sea level periods in  
375 the Pleistocene (~120 ka ago). Only the former scenario is in accordance with the  $^{81}\text{Kr}$  data  
376 (Figure 5).

377 Taking into account all the above age results and analyses, it can be summarized that the  
378 intruding seawater is of Holocene age, except the BE sample farther away from the coast  
379 showing late Pleistocene age. The intrusion may have been mainly during the last sea level rise  
380 or continuous since then.

381

### 382 3.4. Hydrological implication.

383 The much younger than expected ages of the saline groundwater suggest an active  
384 hydraulic connection between the Judea Group aquifer and the Mediterranean Sea. There are two  
385 primary hypotheses for the location of this recent penetration (Paster et al, 2006; Dafny, 2009).  
386 First is from the northern part of the YTB going southward, either from Or Akiva fault or from  
387 the submarine exposure of this aquifer. The second option is through several hydraulic openings

388 in the impermeable marly Talme Yafe facies, either due to lithological changes or through faults  
389 or buried erosional channels filled with coarse-grained sediments with higher permeability. The  
390 first hypothesis would result in age gradient from north to south, which was not found in the five  
391  $^{81}\text{Kr}$  ages that were obtained in this study. The second hypothesis anticipates increasing seawater  
392 residence time with distance from the sea, the indication for this being the oldest age of the BE  
393 sample farthest from the coast.

394         The average rate of seawater intrusion may be estimated from the subsurface residence  
395 times. As discussed above, this rate would be superposition of three processes: the natural  
396 circulation of seawater in the aquifer, the increased rate due to the rapid rise of sea level in the  
397 beginning of the Holocene and effects of over pumping. The effect of sea level rise is expected to  
398 be especially significant due to the increase in hydraulic gradient when the sea level rose by 120  
399 m in a relatively short time (Morrissey et al, 2010). Thus, the intrusion of seawater could have  
400 occurred over a much shorter time at the transition to the Holocene and could be less active  
401 today. However, since the above three processes cannot be separated, the estimation of the rate  
402 of intrusion is an average value for the entire distance from the sea to the sampled wells and  
403 ignores heterogeneity in this rate. Accordingly, assuming that the flow is from the west to the  
404 east and the distance from the contact zone of the aquifer with the sea to the sampled wells is  
405 ~20-30 km (Figure 2), and the ages of saline water are about 10 ka, a rough estimation of the  
406 average rate of seawater intrusion into the aquifer yields a value of about 2-3 m/year. It is  
407 interesting to note that this value is quite similar to a previous estimate in the coastal aquifer of  
408 Israel based on geochemical tracers (Sivan et al, 2005), despite the difference in lithology and  
409 hydrological conditions. As stated above, this flow rate of saline water could be due partly to

410 circulation of the seawater below the interface and partly to movement of the whole saline water  
411 body inland.

412

413 The most important aspect of these results is that the saline water is not Neogenic  
414 seawater trapped in isolated pockets in the aquifer. Instead, the young ages and the aging inland  
415 imply active, current, hydraulic connectivity between the aquifer and the Mediterranean Sea.  
416 Moreover, and from a practical aspect, if the saline water was identified as old, it would have  
417 been considered to contain finite volume of storage. The opposite is true if the age is young and  
418 the seawater mass in the aquifer is connected to the current sea. In the former case, pumping of  
419 the old saline water may be conducted in order to use this water for desalination and decrease the  
420 potential risk of increased salinization of the fresh water volume by this problematic water. Such  
421 action will have no chance of success in the case of connection with the sea since the water head  
422 is permanent and stable (sea level) regardless of the rate of pumping. Consequently, according to  
423 our findings over pumping of fresh water in the eastern confined portion of the YTB would draw  
424 more saline water from the infinite reservoir of Mediterranean Sea. This important water  
425 resource needs to be managed accordingly in order to sustain its quality. Moreover, the fresh-  
426 saline water interface may rise in the future in response to the anticipated sea level rise.

427

#### 428 **4. Summary and conclusions**

429 This work demonstrates that noble gas radionuclides are better than other tracers for  
430 determining the rate of seawater intrusion. The multi-tracer approach of these more reliable  
431 isotopes provides effective assessments of age structures for both seawater and fresh water  
432 components that mixed in the coastal aquifer. Having such new tools will encourage more

433 similar hydrogeological studies in which new drillings and dating of coastal saline groundwater  
434 will enable determination of the connection between the sea and the adjacent aquifer and  
435 estimation of the risk of seawater intrusion.

436 Our results change previous perceptions and indicate that the age of the saline water in  
437 the western part of the aquifer is relatively young, and its origin is from active seawater intrusion  
438 into the deep confined portion of the aquifer during the Holocene. These young ages imply that  
439 pumping of fresh water should be carefully managed due to the risk of salinization by  
440 accelerated seawater intrusion, and that the fresh-saline water interface may rise in response to  
441 the anticipated sea level rise.

442

443

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453 and production wells.

454

455

456

457 Figure captions

458 Figure 1. Location map of the western Mountain aquifer (Yarkon-Tananim Basin - YTB) and the  
459 sampled wells. Blue arrows denote main directions of fresh groundwater flow. The southern part  
460 of the aquifer (Sinai and northern Negev) is outside the chart. Note the black line which denotes  
461 the western boundary of the YTB Aquifer with the impermeable TalmeYafe group. The green  
462 full circles denote locations of sampled wells, seven of which are given in Table 1 and the rest  
463 taken from previous study of Burg et al. (2006).

464 Figure 2. Schematic cross-section from the Samaria Mountains in the east to the Mediterranean  
465 Sea in the west (see location in Figure 1). Some of the wells are projected onto the cross-section.  
466 The fresh-saline water interface is very close to horizontal. The red broken line denotes possible  
467 seawater intrusion from the sea through openings in the TalmeYafe group.

468 Figure 3. Radiocarbon values versus Cl concentrations, showing the values (blue points) in  
469 groundwater in the studied area as well as the possible values of the fresh and saline end  
470 members. The colored lines are mixing lines according to different values of the initial  
471 concentration (  $A_0$  ) of the fresh water component. Data are from Table 1 (triangles) and from  
472 previous studies (circles, Burg and Talhami, 2013, Burg et al.,2006).

473 Figure 4.  $\delta^{18}\text{O}$  versus Cl concentrations, showing simple mixing line of fresh water with  
474 seawater, implying one source of saline water. Data from Table 1 and from previous studies  
475 (Burg and Talhami, 2013, Burg et al.,2006).

476 Figure 5. Age ranges of saline and fresh groundwater determined by  $^{39}\text{Ar}$  and  $^{81}\text{Kr}$  data. The  
477 gray areas indicate possible ages based on the  $^{81}\text{Kr}$  data and the mixing equation 1b. The  
478 bandwidth is defined by the analytical uncertainty as calculated by the unified approach using a  
479 68% confidence limit. The red areas define constraints from the  $^{39}\text{Ar}$  data including the  
480 analytical uncertainties and a range for underground production between 0-10% modern (Eq 1a).  
481 Age ranges that fulfill the constraints for both tracers correspond to the shaded areas. The  
482 presence of tritium for Bet Eliezer is only consistent with the assumption that the freshwater  
483 component is younger than the saline water (case C1). The criterion  $t_f < t_s$  is therefore included for  
484 each plot by the green line. The final concluded age bands for the saline (violet numbers) and  
485 freshwater (orange numbers) are also given.

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