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Using ^{222}Rn to identify and quantify groundwater inflows to the Mundo River (SE Spain)

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ABSTRACT

Groundwater discharge to the Mundo River (SE, Spain) has been investigated from 2011 to 2013 by means of ^{222}Rn activities in river water and groundwater. Starting nearby the river source, some 50 km of river channel have been studied. The Mundo River is located in the water stressed region of the Segura River Basin. Identifying and quantifying groundwater discharge to rivers is essential for the Hydrological Plan of the Segura Basin Authority. Four main areas of groundwater discharge to the river have been identified by means of ^{222}Rn. Moreover, groundwater fluxes have been quantified using radon activities and, when possible, have been validated with chloride mass balances. The uncertainty range ($\pm 2\sigma$) of all water balances has also been assessed. Groundwater discharge (Q_{GW}) values estimated by radon mass balances (RMB) and chloride mass balances (CMB) were similar in the river tracts and/or dates in which surface inputs from tributaries were null or negligible. This adds confidence to the Q_{GW} values estimated by RMB in the reaches were CMB could not be performed due to the existence of ungauged surface inputs, as is the case of the upper basin of the Mundo River, as well as to the applicability of the method to similar situations. Quantification of groundwater discharge allowed identifying Ayna zone as the main gaining reach of the studied area, with up to $29{,}553 \pm 8667$ m^3 day^{-1} in year 2011. Overall, the total Q_{GW} estimated by means of RMB for the studied area was 8–16% of the total river flow. The results are coherent with the meteorological conditions of the study period (average rainfall around 450 mm/y) and also with the undisturbed situation of the aquifers discharging to the Mundo River in the considered area.

1. Introduction

Groundwater discharge into a river system plays an important role in the hydrological and ecological functions of the river, especially in arid or semiarid regions where perennial streamflow is mainly sustained by aquifer-derived flow. Surface water and groundwater have been often considered two separate entities and investigated separately (Kalbus et al., 2006); however, understanding the processes regulating the complex interactions between rivers and adjacent groundwater systems is critical to water resources management, and they have to be considered components of a unique hydrologic system (Andreu and Solera, 2002; Sahuquillo, 2004; Custodio, 2007; Pulido-Velázquez et al., 2007). In the European Union (EU) water management policies take this issue into account by means of the European Water Framework Directive [2000/60/CE] and the Groundwater Directive [2006/118/EC]. The EU legislation aims for an integrated management of surface water and groundwater. Quantifying the relationship between these resources and the locations of groundwater discharge to surface waters is fundamental for developing conceptual models of water systems at catchment scale.

Groundwater contribution to rivers can occur as either discrete flow from springs or diffuse seepage through the river bed. A variety of physical, chemical and numerical methods have been developed to estimate groundwater discharge to a river. However, the heterogeneities and the problems of integrating measurements at different scales are still a challenge to determine and quantify water interactions (Sophocleous, 2002; Kalbus et al., 2006; McCallum et al., 2012).

Natural chemical tracers can be useful tools to identify and quantify groundwater fluxes to rivers as they can provide an integrated view of a large area over a long period of time. The possibility to use chemical tracers depends mainly on the contrast between the concentrations of the tracer in groundwater and surface water. The accurate characterization of tracer's sources and sinks is also essential to identify the groundwater component for adequate mass balance calculations. Furthermore, factors such as the spatial variability and the potential for the tracer to change by evaporation, precipitation, radioactive decay, degassing, or biochemical reactions also play an important role (Unland et al.,

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2013). Major ions (for example Cl^-), stable isotopes and radioactive isotopes such as ^{14}C, ^{3}H, ^{222}Rn, ^{226}Ra, $^{238}U/^{234}U$, and $^{87}Sr/^{86}Sr$ are often used to investigate river–groundwater interactions. ^{222}Rn (hereinafter referred to as radon if otherwise not needed) has proven to be an excellent tracer in river–groundwater interactions and its use has increased in the past decade as the ease of measurement has improved (Ellins et al., 1990; Genereux and Hemond, 1990; Genereux et al., 1993; Cable et al., 1996; Corbett et al., 1997; Cook et al.;, 2003, 2006; Lamontagne et al., 2008; Spizzico, 2005; Dulaiova and Burnett, 2006; Lamontagne and Cook, 2007; Mullinger et al., 2007; Stellato et al., 2013; Burnett et al., 2010; Peterson et al., 2010; Cartwright et al., 2011; Gilfedder et al., 2012; Smerdon et al., 2012; McCallum et al., 2012; Guida et al., 2013; Unland et al., 2013).

Radon is a naturally occurring radioactive noble gas whose concentration is 2–3 orders of magnitude greater in groundwater than in surface waters (Burnett et al., 2001). Natural radon consists of several short-lived radioactive isotopes. Due to their half-lives, the isotopes with some interest for environmental applications would be ^{210}Rn [2.4 h], ^{211}Rn [14.6 h], ^{220}Rn [55.6 s], ^{222}Rn [3.8235 day], and ^{224}Rn [1.8 h], but due to its half-life ^{222}Rn is the most useful and commonly used for groundwater studies. ^{222}Rn decays through a long chain of alpha and beta processes involving short-lived radioisotopes into stable ^{206}Pb. The ^{222}Rn decay is an alpha process producing first ^{218}Po (3.10 min half-life), whose accumulation is used to measure ^{222}Rn concentration.

The source of ^{222}Rn in groundwater is ^{226}Ra, also the longest-lived of radioactive radium isotopes, with a half-life of 1601 years. ^{226}Ra derives from uranium decay and is ubiquitous in sediments and sedimentary rocks. Thus, the amount of ^{222}Rn present is primarily determined by the lithology and geochemical composition of the aquifer material (Cecil and Green, 2000; Sakoda et al., 2011) as well as by the time from release into groundwater and the sampling moment. Radon tends to concentrate in areas of tectonic disturbance, and in faulted areas in general, as a result of intense degassing fluxes due to the local high permeability of the bedrock and soil (Ellins et al., 1990; Etiope and Martinelli, 2002; Ioannides et al., 2003). Moreover, as a result of its relative high solubility (Ball et al., 1991), in fractured aquifers radon can be transported long distances from its point of emanation by fast water flow before decaying. Thus, anomalous activities can be present in areas without uranium and radium enriched rocks. Similarly, radon activity can be higher than expected in aquifer areas where thermodynamic conditions induce uranium and/or radium concentration changes by adsorption or precipitation in mineral phases (as secondary or trace components). Hence, the presence of clayey sediments may induce increasing of radon activity at aquifer scale through the accumulation of uranium and radium. These processes have to be considered to use radon in groundwater flow studies, but are less relevant when using it to identify and quantify groundwater discharge to rivers.

The activity of radium in rain water is negligible. Its occurrence in surface waters is derived mostly from groundwater discharge, but due to a relatively short half-life of ^{222}Rn and the rapid gas exchange to the atmosphere, high radon activities are only present in river locations where there is active groundwater discharge. Although radon surveys are performed on a local approach, the technique provides information at a regional scale, being a good tool for water management (McCallum et al., 2012). Additionally, radon data combined with river discharge and physical dimensions can be used to quantify groundwater discharge by means of radon mass balances. On the other hand, quantifying groundwater discharge rates involves many parameters that are often difficult to measure. Consequently, the associated uncertainty needs to be calculated and made explicit to understand the meaning of the estimated flows.

The aim of this work is to determine and quantify the relationship between groundwater and surface water in the Mundo River using radon activity. The Mundo River is located in the upper Segura River Basin, a water stressed region in SE Spain. Since three decades ago the region receives temporary imported water resources to supply the high water demand areas in the middle and lower parts of the Segura River Basin. Thus, identifying and quantifying groundwater discharge to rivers, and especially to the Mundo River, which is under natural flow conditions, is essential for the water action plan (Hydrological Plan) of the Segura River Basin. The contribution of this tool and its results would also help in making decisions and adopting policies of sustainable water use for the 2015–2020 Environmental Strategic Plan of the Segura River Water Authority (www.chsegura.es).

To this purpose, three main objectives were established: i) to identify preferential groundwater discharge areas in the Mundo River, ii) to check the performance of radon as a tracer to quantify groundwater discharge to rivers in karstic areas, and iii) to quantify groundwater flows using radon mass balances, among other techniques, as far as using a multi-technique approach to provide more robust information on groundwater–surface water studies.

2. Site description

The Mundo River is a perennial stream with a 2400 km^2 catchment area located in SE Spain. The river originates from a spring in the mountain plateau Calar del Mundo, forming a 300 m high waterfall known as Los Chorros del río Mundo. The river flows NE for 107 km, being the main tributary of the larger Segura River, which flows from W to E into the Mediterranean Sea. The studied area encompasses 50 km of the Mundo River and extends from the gauging station n° 100 in Fig. 1, 2.09 km downstream the headwater, to station n° 117, 42.76 km from the headwater and 5 km upstream of the Talave Reservoir, where the Mundo River receives water transferred from the Tajo River Basin, in NE Spain, through a 250 km aqueduct.

Following SGOP (1988), the studied river tract is mainly fed by groundwater discharge from two Mesozoic carbonate-rock aquifers, the Pliegues Jurásicos del Mundo and Alcadozo (Fig. 2), and from several tributaries: De la Vega, Salado, Celada, Provencio, Vadillos, Bogarra, Cañadas, and Talave creeks, joining the Mundo River at 3.3, 3.5, 7, 10, 20, 22, 33, and 45 km downstream the river source, respectively (Fig. 1). Only the Bogarra creek is permanent. The De la Vega and Celada creeks are fed mainly by small springs from the Calar del Mundo and Cujón aquifers and by rainfall (Rodríguez-Estrella, 1979; IGME, 2009). The Salado, Provencio, Vadillos, Cañadas, and Talave creeks flow only during and after intense rainfall events.

The basin has a strong topographic gradient from W to E, with heights varying from around 1600 m asl at the western part to around 300 m asl at the eastern sector. The precipitation also displays a regional gradient with average values from around 600 mm/y to around 300 mm/y in the same places (CHS, 2014). Fig. 3 shows the yearly precipitation during the study period at the Bogarra station (AEMET, 2013), located at the central part of the upper basin. The sampling surveys were performed in dry months. Years 2011 and 2012 were quite dry; some significant rainfall took place only in the 2012 winter. There was no rainfall in the area 48 h prior and during all field surveys, except for July 9th 2013, when a small rainfall event of 3.2 mm was measured in the Bogarra station (CHS, 2013).

Stream flow data at the lower part of the Mundo River studied area comes from the only automated gauging station existing in the river (station 116 in Fig. 1). The recorded yearly flow varied during the study period from around $121 * 10^6$ m^3 year^{-1} in 2011 to $96 * 10^6$ m^3 year^{-1} in 2012, and to $233 * 10^6$ m^3 year^{-1} in 2013 (Fig. 3).

The studied area comprises carbonated and detrital rocks of Triassic, Jurassic and Cretaceous ages. The area is characterized by a complex geologic structure and consists of a succession of folds and thrusts with NE–SW direction and verging towards the NE (García-Palomero, 1969). The tectonic complexity facilitates both diffuse and concentrated groundwater discharge to the river and induces the existence of several aquifers in the area. The Pliegues Jurásicos del Mundo and Alcadozo aquifers are mainly formed by Jurassic limestones and dolostones overlying Triassic sandstones and clays containing evaporites, mostly gypsum and anhydrite, with a minor presence of halite (IGME, 1974a, 1974b, 1975a,

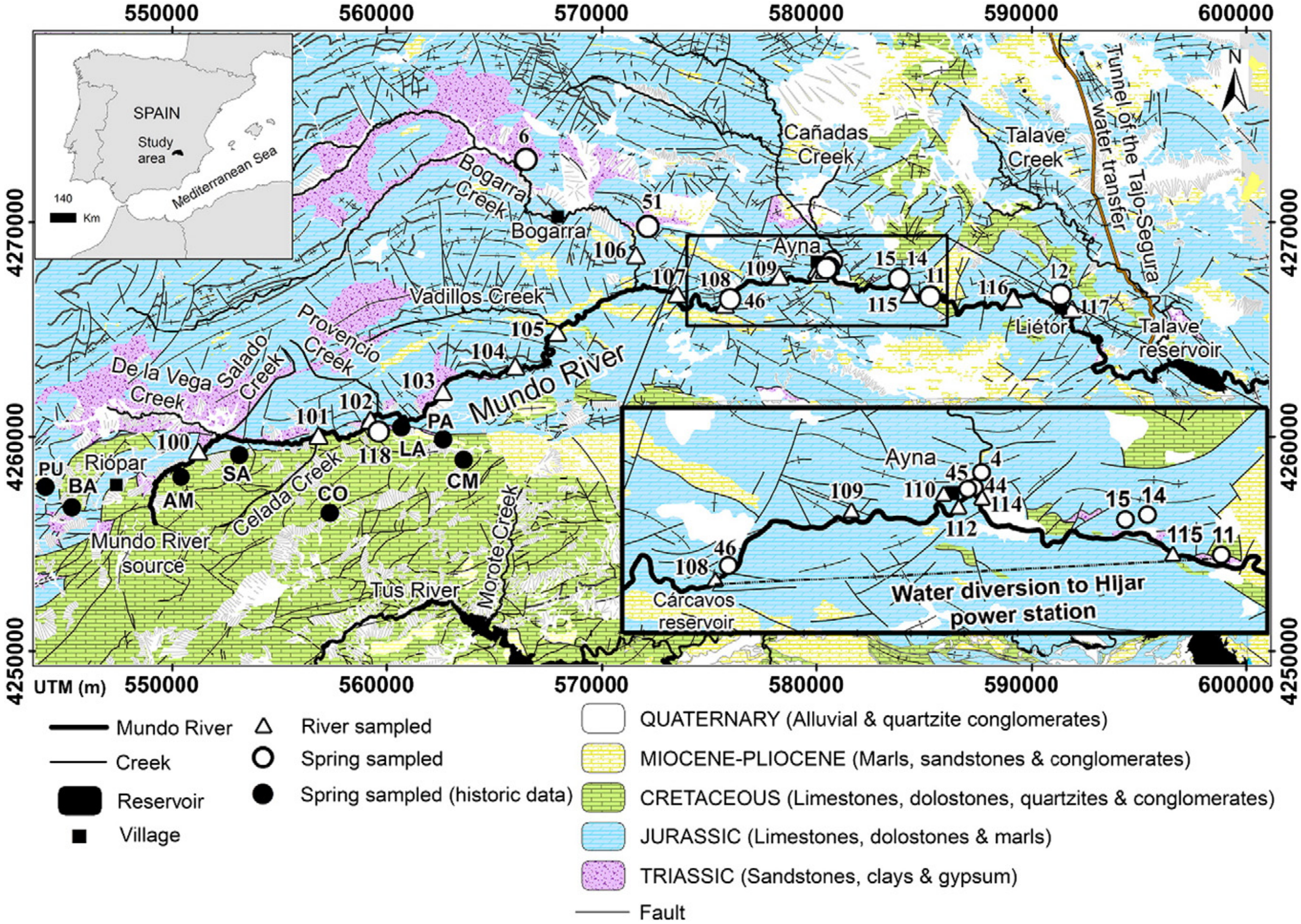

Fig. 1. Simplified geology of the Mundo River basin (modified from IGME, 1974a, 1974b, 1975a, 1975b, 1978, 1980) showing the sampling locations in rivers and springs.

1975b, 1978, 1980; Ortí et al., 1996). The Calar del Mundo and the Cujón aquifers, formed by Cretaceous limestones overlying the Jurassic formations, are also known to contribute to the Mundo River upper basin, but to a lesser extent (Rodríguez Estrella, 1979).

3. Materials and methods

Groundwater discharge to the Mundo River was studied by means of ^{222}Rn activity balance, chloride (Cl^-) content mass balance, and river flow changes.

3.1. Field surveys, water sampling, radon activity, and river discharge measurement

Three in field radon measurement and chemical sampling campaigns were conducted on approximately 50 km of the Mundo River during October 2011, May 2012 and July 2013 at 17 sampling/measurement locations (Fig. 1), 16 of them in the Mundo River (n° 100 to 112 and 114 to 117 in Fig. 1), and one in the Bogarra Creek (n° 106). River sample/measurement locations were selected at regular intervals, although some of them were conditioned by the accessibility. A denser

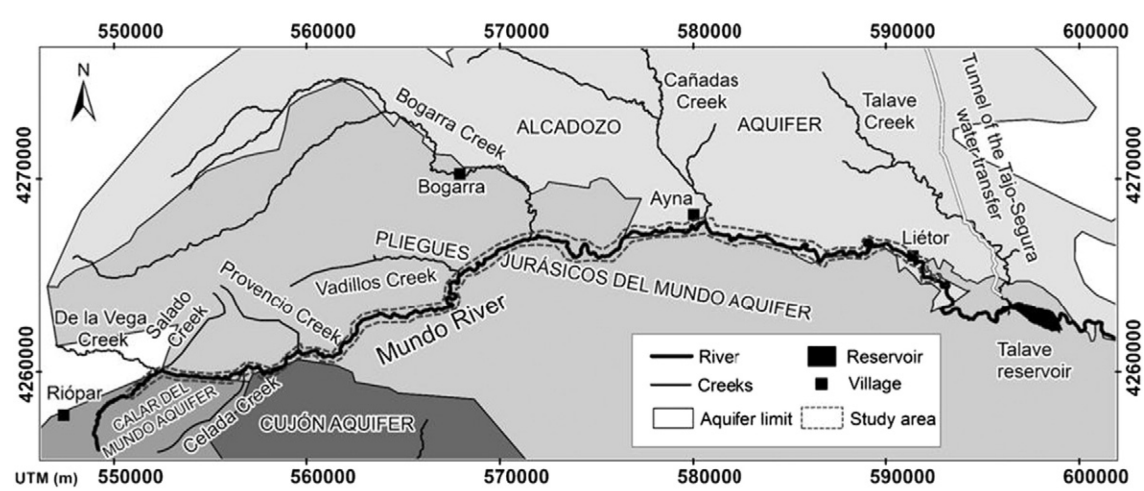

Fig. 2. Location and limits of the aquifers existing in the study area.

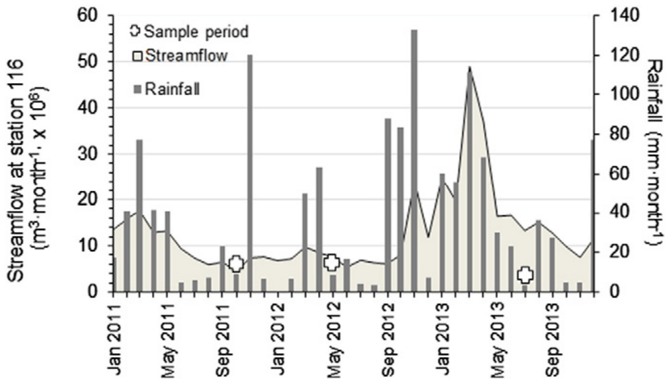

Fig. 3. Monthly rainfall at Bogarra village and streamflow in the Mundo River station 116 during years 2011, 2012, and 2013. The crosses indicate the sampling surveys. River flow data were taken from www.chsegura.es, and rainfall data were taken from http://www.aemet.es.

surveying was planned and carried out at the Ayna village site, where several permanent, large springs concentrate in less than 1 km length (Fig. 1). All the surveys were planned to be carried out at base flow conditions, though this was not fully achieved in the 2013 survey.

Groundwater radon measurement and sampling for chemical analysis was also conducted. Radon measurement and sample collection were performed in ten springs (n° 4, 6, 11, 12, 14, 44, 45, 46, 51 and 118 in Fig. 1), most of them located very close to the river channel, albeit not all springs were sampled in every survey.

Sampling for radon measurement and chemical analysis was carried out using a small submersible water pump situated approximately 10 cm above the river bed. Special care was taken to avoid river sections where the water velocity was low and thus river water was not well mixed. Groundwater sampling was also conducted using a submersible water pump situated at the springs's outlet. All springs, except number 45, discharge above the river water level. Spring 45 also discharges above the river surface, but it can only be measured in the border of the river channel. This is the only measure that could entrain some dilution by mixing with river water. However the two radon values available, measured in October 2011 and May 2012, are identical (1896 ± 218 and 1848 ± 216 Bq m^{-3}), which suggests that dilution did not occur.

Water samples for chemical analysis were collected at each location after measurement of radon activity (1 h pumping; see below) in air-tight polyethylene bottles, and preserved refrigerated over a 1–2 day period. The concentrations of major and some minor and trace ions were determined by ion chromatography at the Geological and Mining Institute of Spain (IGME, Madrid). The accuracy of the chemical analyses was checked by calculating their ionic balance error (ε); all the analyses had ε ≤ 5%. In addition, in situ measurements of electric conductivity (EC), pH, total alkalinity, water and air temperature (°C) were performed. EC and pH were measured using calibrated EC and pH meters. Total alkalinity was measured in 100 mL water samples filtered through 0.45 μm filters and titrated with H_2SO_4 using a Hach 16900 digital titrator. Water temperature was measured using a digital thermometer that recorded data every 1 min, whereas air temperature was measured with a mercury thermometer.

Radon activity was measured at each location using a RAD7 portable radon monitor (Durridge Co., MA-USA) and its accessory RADAQUA, which brings radon in the air and in water into equilibrium. This equilibrium is temperature dependent, thus temperature measurements were made using a temperature probe inserted in the RADAQUA chamber and recorded using a data logger. The response time of the measurement is controlled by several factors, including: i) the half-life of ^{218}Po (daughter of ^{222}Rn), of 3.1 min (Dulaiova et al., 2005); ii) the water flow that passes through the RADAQUA; a volume of approximately 40 L is required to deliver the radon to the air loop before it reaches equilibrium (thus, a water flow rate of Q L/min will take at least 40/Q minutes to deliver radon activity in water to the air loop; Durridge, 2013); and iii) the velocity of radon transfer from water to air, which in turn depends on the size of the water drops in RADAQUA and on the aeration efficiency (Burnett et al., 2001). Taking these factors into account, radon measurements were conducted during 1 h for both surface and groundwater at Q = 26 m^3 day^{-1}. Results are shown in Tables 1 and 2, reported in Bq m^{-3}.

River discharge was gauged at each radon measurement station using the velocity–area method (Custodio and Llamas, 1983; Sauer and Meyer, 1992), which consists of a discrete integration of flow velocity measured at different points over a channel cross-section divided into smaller sections:

$$Q = \sum_{i=1}^{N} Q_i = \sum_{i=1}^{N} B_i D_i V_i \tag{1}$$

where Q is the river flow passing through a particular gauging river cross section, i is each of the segments in which the control section is split, N is the total number of segments, and B_i, D_i and V_i are the mean width, depth and perpendicular water velocity of each segment, respectively. B_i and D_i were measured using a graduated tape, whereas V_i was measured using an impeller flowmeter OTT-FAT Z400.

3.2. Water mass balances in a river reach

Let us consider the mass balances in a river reach between two gauged sections assuming steady state conditions (the change in the water volume is negligible in the measuring time interval) during the balance time interval, and negligible or known surface runoff input from tributaries. The steady water mass balance (WMB) in the reach per unit time interval (here a day) can be expressed as (Fig. 4):

$$Q_{Ro} + Q_{GW} + P - E = Q_{Rx} \tag{2}$$

where Q_{Ro} is the stream flow at the upstream gauging section (m^3 day^{-1}), Q_{GW} is the groundwater inflow (m^3 day^{-1}) within the river reach, P is the direct precipitation on the reach (m^3 day^{-1}), E is the evaporation rate (m^3 day^{-1}) in the reach, and Q_{Rx} is the stream flow at the downstream gauging section (m^3 day^{-1}). The net groundwater inflow rate in such a river reach can be calculated rearranging Eq. (2) as:

$$Q_{GW} = Q_{Rx} + E - Q_{Ro} - P. \tag{3}$$

Q_{GW} includes other possible unknown surface inputs in the reach. In this study, groundwater inflow rates (Q_{Gw} in Fig. 4) were estimated per unit surface area (m^3 day^{-1} m^{-2}) of the river bed and converted to total flow (m^3 day^{-1}) for the whole bed surface of each river reach.

3.3. Radon mass balances in a river tract

Groundwater discharge into a river can also be estimated by means of a radon mass balance (RMB) using in-river field radon activities measurement. Considering steady-state conditions, a radon mass balance within a differential portion of the river of length dx (m), with mean width w (m) and stream depth b (m), and assuming i) constant concentration or specific activity (hereinafter simply called activity), in which river outflow has the reservoir concentration C_R (Bq m^{-3}) and inflow has a concentration differentially distinct, dC_R (Bq m^{-3}), ii) no rainfall during and in the days before the survey in order to approach the assumed steady state, and iii) good mixing inside the river volume, can be expressed as (Fig. 4):

$$\begin{aligned} &Q_{Ro}(C_R - dC_R) + q_{Gw}C_{Gw}wdx + F_h wdx + \lambda_{222}Ra^{226}\text{wbdx} \\ &= (Q_{Ro} + q_{Gw}wdx - \text{Ewdx})C_R + \text{Ewdx}C_E + F_A wdx + \lambda_{222}\text{wbdx}C_R \end{aligned} \tag{4}$$

Table 1
River station, measured flow rate (Q_R), ^{222}Rn activity and other chemical parameters relevant for this work measured at the Mundo River and the Bogarra Creek stations during the study. See location in Fig. 1.

River station	Sampling date	Distance (km)[a]	Height (m asl)	Q_R (m^3 day^{-1})	±2σ (m^3 day^{-1})	^{222}Rn (C_R) (Bq m^{-3})	±2σ (Bq m^{-3})	$Cl^-{}_R$ (mg L^{-1})	±2σ (mg L^{-1})	$Br^-{}_R$ (mg L^{-1})	rCl/rBr (r = meq/L)
100	03/05/2012	2.09	950	41,575	3086	190	89	2.3	0.6	0.003	1751
100	02/07/2013			20,777	2419	217	33	3.6	0.9	0.008	1009
101	02/07/2013	7.68	909	119,216	9532	529	105	8.7	2.1	0.011	1774
102	02/07/2013	10.16	879	116,753	6305	536	100	8.8	2.1	0.011	1799
103	02/07/2013	13.57	836	113,938	4104	150	53	5.4	1.3	0.007	1723
104	21/10/2011	16.82	805	-	-	180	75	14.5	3.5	0.027	1210
104	03/05/2012			134,730	12,934	117	70	-	-	-	-
104	03/07/2013			116,249	11,160	140	56	11.1	2.7	0.013	1924
105	03/05/2012	18.77	795	142,453	12,251	267	92	12.5	3.0	0.011	2557
105	03/07/2013			131,947	5277	247	71	9.2	2.2	0.014	1484
106	21/10/2011	22.46	790	-	-	161	71	38.6	9.3	0.053	1642
106	03/07/2013			88,163	18,338	116	49	30.7	7.4	0.032	2162
107	03/07/2013	24.48	714	220,110[b]	-	37	28	18.5	4.4	0.019	2199
108	09/07/2013	26.72	698	1128	26	67	34	16.8	4.0	0.017	2221
109	10/07/2013	29.14	600	-	-	236	93	17.8	4.3	0.018	2229
110	13/10/2011	30.86	645	3528	268	490	113	38.8	9.3	0.108	811
110	03/05/2012			11,356	863	604	125	-	-	-	-
110	04/07/2013			15,462	1205	707	112	28.4	6.8	0.064	999
112	13/10/2011	31.23	636	-	-	688	131	34.8	8.4	0.098	801
114	13/10/2011	31.48	644	33,578	2398	1319	176	25.0	6.0	0.081	696
114	03/05/2012			30,712	2150	1316	177	-	-	-	-
114	04/07/2013			35,916	2729	1527	184	24.2	5.8	0.065	840
115	10/07/2013	34.82	622	-	-	117	46	19.3	4.6	0.028	1553
116	03/05/2012	41.22	561	296,266[c]	-	-	-	-	-	-	-
116	02/07/2013	41.22	561	318,309[c]	-	46	30	20.5	4.9	0.028	1649
117	21/10/2011	42.76	500	-	-	125	64	27.4	6.6	0.051	1211

-: Not surveyed.
[a] From Mundo River source.
[b] Calculated as $Q_{105} + Q_{106}$.
[c] After an automatic station of the Segura River Water Authority.

Table 2
Spring number and characteristics, geology, ^{222}Rn activity and other chemical parameters relevant for this work measured in springs during the study. See location in Fig. 1.

Spring	Sampling date	Distance (km)[a]	Height (m asl)	Assumed geology	^{222}Rn (C_{GW}) (Bq m^{-3})	±2σ (Bq m^{-3})	$Cl^-{}_{GW}$ (mg L^{-1})	±2σ (mg L^{-1})	$Br^-{}_{GW}$ (mg L^{-1})	rCl/rBr (r = meq L^{-1})
4	26/10/2011	31.52	700	J[b]	1912	204	13.9	3.3	0.068	462
4	25/09/2012				-	-	19.0	4.6	-	-
4	10/07/2013				-	-	12.0	2.9	-	-
6	03/11/2011	17.52	909	T_G[c]	1797	206	12.7	3.1	0.090	319
6	06/09/2012				-	-	12.3	2.9	0.073	379
6	08/07/2013				-	-	10.0	2.4	0.073	309
11	03/11/2011	36.13	600	J[b] + T_H[d]	2096	212	66.2	15.9	0.089	1676
11	06/09/2012				-	-	62.0	14.9	0.067	2087
11	09/07/2013				-	-	59.0	14.2	-	-
12	13/10/2011	42.76	646	J[b]	2337	224	28.9	6.9	-	-
12	26/09/2012				-	-	30.0	7.2	0.132	512
12	09/07/2013				-	-	25.0	6.0	-	
14	08/11/2011	34.69	600	J[b]	1751	193	36.9	8.8	0.131	634
14	25/09/2012				-	-	39.0	9.4	-	-
14	10/07/2013				-	-	33.0	7.9	-	-
15	08/11/2011	34.91	589	J[b]	-	-	36.9	8.9	-	-
44	13/10/2011	31.48	640	J[b]	2069	219	18.6	4.5	0.079	530
44	03/05/2012				2247	227	-	-	-	-
45	20/10/2011	31.31	640	J[b]	1896	218	20.8	5.0	0.087	539
45	03/05/2012				1848	216	-	-	-	-
45	10/07/2013				-	-	18.0	4.3	-	-
46	12/01/2012	26.85	670	J[b]	4776	329	24.1	5.8	0.057	952
46	09/07/2013				-	-	23.0	5.5	-	-
51	19/01/2012	24.69	909	T_G[c]	-	-	10.5	2.5	0.165	144
51	16/07/2013				-	-	15.0	3.6	-	-
118	02/07/2013	10.01	889	C[e]	3628	287	3.7	0.9	0.015	560

-: Not surveyed.
[a] From Mundo River source.
[b] Jurassic limestones and dolostones.
[c] Triassic sandstones, clays and evaporites (gypsum dominated).
[d] Triassic sandstones, clays and evaporites (halite dominated).
[e] Cretaceus limestones.

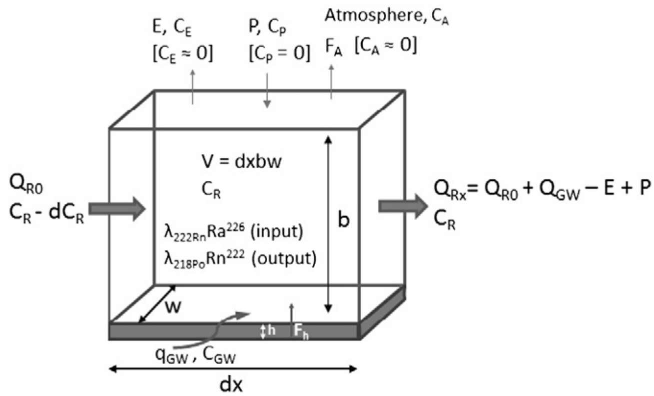

Fig. 4. Illustration of water and radon mass balance components for a river tract having a differential length.

where the terms of the balance, all of them in Bq day^{-1}, and their components are:

- $Q_{Ro}(C_R - dC_R)$ = radon inflow through the upstream section (at x = 0). Q_{Ro} = stream flow at x = 0 (m^3 day^{-1}).
- $q_{Gw}C_{Gw}wdx$ = radon inflow with inflowing groundwater in the river differential volume. q_{Gw} = groundwater inflow rate (m^3 day^{-1} m^{-2}); C_{Gw} = radon activity in inflowing groundwater (Bq m^{-3}).
- F_hwdx = radon diffusive inflow from the hyporheic zone (the layer beneath the stream bed) to the river differential volume, at a rate of F_h (Bq m^{-2} day^{-1}).
- $\lambda_{222}Ra^{226}wbdx$ = radon generation rate in the river differential volume from decay of ^{226}Ra dissolved or contained in suspension particles in the river water (Bq m^{-3}). If secular equilibrium between ^{226}Ra and ^{222}Rn is assumed due to the great half-life difference and a time lapse greater than several ^{222}Rn half-lives, then $\lambda_{222}{}^{222}Rn = \lambda_{226}{}^{226}Ra$, the chemical symbols indicating number of atoms, λ indicating the respective decay constants (λ = ln2/half-live; λ_{222} = 0.181 day^{-1}, and $\lambda_{226} = 1.187 \cdot 10^{-6}$ day^{-1}) and the products indicating activities (A, in Bq m^{-3}). Following Bateman (1910), when the half-life of the parent (p) is much greater than that of the daughter (d) the ingrowth of the last follows this equation: $A_d(t) \approx A_p(1 - e^{-\lambda_d t})$.
- $(Q_{Ro} + q_{Gw}wdx - Ewdx)\, C_R$ = radon outflow leaving the river differential volume, considering total outflow (inflow plus groundwater contribution minus evaporation at rate E (m day^{-1}), with radon activity C_R (Bq m^{-3}) from a well-mixed reservoir.
- $EwdxC_E$ = radon outflow due to evaporation in the river volume. C_E = radon specific activity in leaving vapor (Bq m^{-3}). C_E is very difficult to know. Since it refers to a dissolved gas and not to a part or the water molecule (as is the case of oxygen and hydrogen isotopes) it is safely taken $C_E = 0$ and the transfer effect is assumed included in F_A.
- F_Awdx = flux of radon diffused to the atmosphere through the river surface boundary layer. The diffusion rate is $F_A = D\,(C_R - C_A)/z$, where D = diffusion coefficient (m^2 day^{-1}) through a boundary layer of thickness z (m); C_R and C_A are radon concentrations in actual, well-mixed river water and in water in equilibrium with radon in the atmosphere at ambient temperature. D and z can be estimated using empirical formulas that are introduced later in the text.
- $\lambda_{222}wbdxC_R$ = decay of radon contained in the river volume.

The equation can be simplified assuming that under common circumstances: i) the contribution to radon concentration by ^{226}Ra decay in the river volume is minor (i.e. $\lambda_{222}Ra^{226} \approx 0$), ii) the atmospheric concentration of radon is negligible, so in the corresponding equilibrium concentration in water ($C_A \approx 0$), and iii) the radon concentration in evaporating water vapor (C_E) is minor, thus assumed to be negligible ($C_E \approx 0$).

Radon concentration C_R changes with distance (x) along a stream receiving groundwater inflow, so it is C_{Rx} (C_{Rx} = radon activity at x, Bq m^{-3}). Noting that $Q_{RX} = Q_{R0} + q_{GW}xw - Exw$ and assuming that Q_{Gw} and E are constant along the tract, the change of radon activity within a river volume can be deduced from the previous radon balance under the simplifying conditions:

$$\frac{Q_{Rx}}{w}\frac{dC_R}{dx} = q_{GW}(C_{GW} - C_R) - F_A - \lambda_{222}bC_R + F_h. \tag{5}$$

This formula has been used in the past decade by several authors to estimate groundwater fluxes to rivers (Cook et al., 2006; Mullinger et al., 2007; Cartwright et al., 2011; McCallum et al., 2012; Unland et al., 2013). It can be rearranged to make groundwater discharge inflow rate (m^3 day^{-1} m^{-2}) the subject as:

$$q_{Gw} = \left(\frac{Q_{Rx}}{w}\frac{dC_R}{dx} + F_A + \lambda_{222}C_Rb - F_h\right) \cdot (C_{GW} - C_R)^{-1}. \tag{6}$$

3.4. Estimation of the radon diffusive inflow from the hyporheic zone

In stream areas where groundwater discharge inflow rate or the activity (concentration) of radon are small, the magnitude of F_h might be significant (Cook et al., 2006; Lamontagne and Cook, 2007; Cartwright et al., 2011). In the Mundo River, the hyporheic zone is assumed to be a single well-mixed reservoir (i.e. homogenous radon activity) with the same width as the stream. Following Cook et al. (2006), if a continuous water exchange is assumed between the river and the hyporheic zone and the residence time in the hyporheic zone approaches zero, with zero net water flux and no significant lateral flow within it, the solute mass balance within this hyporheic zone can be summarized as:

$$q_hc_R - q_hc_h + \gamma h\theta - \lambda_{222}h\theta c_h = 0 \tag{7}$$

where q_h is the water inflow from the river into the hyporheic zone, which is equal to the outflow from the hyporheic zone to the river (m^3 day^{-1} m^{-2}); C_R is the radon activity in river water (Bq m^{-3}); C_h is the activity of radon in the hyporheic zone (Bq m^{-3}); γ is the radon production rate in the water within the hyporheic zone (Bq m^{-3} day^{-1}); h is the mean thickness of the hyporheic zone (m), and θ is the porosity of the hyporheic zone (dimensionless); the other variables have been described above.

If γ is assumed to be zero and radon decay negligible, the radon activity in the hyporheic zone will be the same as that in the stream water. Although C_h can be measured in the field, resolving for q_h requires conducting field experiments involving tracer injections (Unland et al., 2013). However, F_h can alternatively be calculated using measurements in river reaches where the activity of radon does not change with distance (i.e. $dC_R / dx = 0$) and there is no groundwater discharge (i.e. $Q_{GW} = 0$), or it is negligible but C_{GW} is very different from C_R, as it is commonly the case (Cartwright et al., 2011). Under these conditions, and assuming (see above) $C_E \approx 0$, the net flux of radon from the hyporheic zone can be calculated as:

$$F_h = F_A + \lambda_{222}bC_R. \tag{8}$$

3.5. Estimation of radon changes due to diffusion to the atmosphere

For constant river flow (Q_R), in the absence of other sources and sinks of radon, including that coming from the hyporheic zone, decay and generation from ^{226}Ra decay, the change of radon activity in a differential river tract of length dx, is:

$$dC_R = (Dw/(Q_R z)/(C_R - C_A)dx. \quad (9)$$

Integrated between an inflow section (u) and an outflow section (d), it results:

$$L = \frac{\frac{Q_R z}{Dw} ln(C_u - C_A)}{C_d - C_A} \quad (10)$$

where L is the length of the tract, C_d is radon activity in the outflow section (Bq m^{-3}) and C_u is the radon activity in the inflow section (Bq m^{-3}). This solution coincides with that used by Elsinger and Moore (1983) and Ellins et al. (1990) when C_A is assumed negligible and Q_R is changed by $Q_R = v\, b\, w$, where v is river water average velocity (m day^{-1}) and b water depth (m), resulting in:

$$C_d = C_u \exp^{(-(D/zbv)L)}. \quad (11)$$

If the radon concentration difference is known and there is no groundwater discharge inside the control reach, z can be calculated as:

$$z = \frac{\frac{LD}{bv\ \ln C_u}}{C_d} \quad (12)$$

and following Peng et al. (1979), the molecular diffusivity of radon (m^2 s^{-1}) can be estimated as:

$$\log D = \frac{-1010}{T} + B \quad (13)$$

where T is the absolute temperature (°K) in the river water, and B is a constant depending on the gaseous species (Himmelblau, 1964). Based on Róna's (1917) measurements, the value of B for radon is −1.475.

3.6. Chloride mass balances

To check the results obtained using the RMB, groundwater inflow rate to the Mundo River was also estimated using chloride mass balances (CMB) when it was possible. Since Cl^- is a conservative, non-volatile tracer, it is neither lost by degassing to the atmosphere nor decayed. Thus, estimating groundwater inflow rate in a river reach by the CMB is rather simple. Under steady state conditions, the CMB in a river reach of length L (m) can be expressed as:

$$Q_{Ro}Cl_{Ro} + Q_{Gw}Cl_{Gw} = (Q_{RL} + Q_{Gw} - E)Cl_{RL} \quad (14)$$

where Q_{Ro} is the stream inflow (m^3 day^{-1}) in the river reach from upstream ($x = 0$); Cl_{Ro} is the concentration of Cl^- (mg L^{-1}) in the stream water at $x = 0$; Q_{Gw} is the groundwater inflow (m^3 day^{-1}) into the river reach; Cl_{Gw} is the concentration of Cl^- (mg L^{-1}) in the inflowing groundwater; Q_{RL} is the stream outflow (m^3 day^{-1}) from the river reach at x = L; E is the evaporation rate (m day^{-1}); w is the mean width of the stream within the reach (m), and Cl_{RL} is the concentration of Cl^- (mg L^{-1}) in the stream water at x = L. Rearranging Eq. (13) to estimate groundwater inflow rate gives:

$$Q_{GW} = \frac{Q_{RL} \cdot Cl_{RL} - Q_{Ro} \cdot Cl_{Ro}}{Cl_{Gw} - Cl_{RL}} - ECl_{RL}. \quad (15)$$

In the present work the Eqs. (1), (3), (6), (8), (11), (12), (13) and (15) have been used to estimate the values of different variables used in the mass balances performed, except the value of E (evaporation from the river), which was taken from the web site of the Segura River Basin Water Authority (www.chsegura.es). Eqs. (2), (4), (5), (7), (9), (10) and (14) are shown just to complement the explanations.

3.7. Uncertainty evaluation

Estimating groundwater discharge rates using mass balances involves many parameters, some were measured in the field and some others were predicted using empirical models. The effect of field measurements uncertainties on the estimated mass balances is an important aspect for the interpretation and the confidence of the results. In this paper, the statistical propagation error method (Eq. (15)) (Tellinghuisen, 2001; Alcalá and Custodio, 2008) is used to determine uncertainty in groundwater inflow values calculated by RMB and CMB:

$$\sigma^2_{QGW} = \sum_{i=1}^{k} \left(\sigma_{X_i} \frac{\partial f}{\partial X_i} \right)^2 \quad (16)$$

where X_i is each of the i variables (up to k) used to calculate Q_{GW}; and σ is the standard deviation of each variable, which are assumed normally distributed.

With respect to the water mass balance (WMB) uncertainty, the overall uncertainty of velocity values estimated with the velocity–area method is due to a combination of many error sources, including errors in measuring the cross-sectional area (depth and width determination), in measuring the mean velocity at a given time and in space (vertically and transversally), including current meter errors, and differences in the discharge computation procedure. In this work the expression proposed by Sauer and Meyer (1992) to calculate the uncertainty in a single discharge measurement using the velocity–area method has been used:

$$S_Q = \sqrt{\frac{\left(S_d^2 + S_t^2\right)}{N} + S_i^2 + S_S^2 + S_h^2 + S_V^2 + 0.75} \quad (17)$$

where S stands for standard error of the respective following components and subscripts: flow, Q; depth measurement, d; pulsation of velocity, t; instrument error, i; vertical distribution of velocity, S; oblique flow, h; and horizontal distribution of depth and velocity, V. N is the number of vertical profiles.

As regards to the RMB uncertainty, the standard deviation of radon measurements (C_R and C_{GW}) was calculated by the RAD7 software. Since radioactive decay obeys Poisson statistics, $\sigma = \sqrt{N}$, where N is the number of counts. However, as Poisson statistics underestimates the uncertainty at very low counting, RAD7 uses $\sigma = 1 + \sqrt{N+1}$ to compensate for this.

Neither the decay constant not the evaporation was included in the calculation of the RMB uncertainty, λ because it is assumed accurate (i.e. σ = 0), and E because its values ranged between 10^{-2} and 10^{-3} m day^{-1}, so their impact on the radon mass balance is negligible.

With respect to the Cl^- concentrations measurement in water samples, the laboratory reported a relative uncertainty of 12%.

4. Results and discussion

4.1. Identification of groundwater discharge areas with radon

Radon activity measured in river water was rather constant for each control location during the study period, but they changed spatially between 37 ± 28 Bq m^{-3} and 1527 ± 184 Bq m^{-3} (Table 1). The evolution of radon activity along the river (Fig. 5a) allows to identify areas with very low radon activities (<100 Bq m^{-3}, uncertainty included), which are primarily assumed to be zones where groundwater discharge is minimum or even inexistent, and areas with high (in relative terms) radon activities (400 to 1700 Bq m^{-3}, uncertainty included), which are assumed to be zones where groundwater discharge is significant.

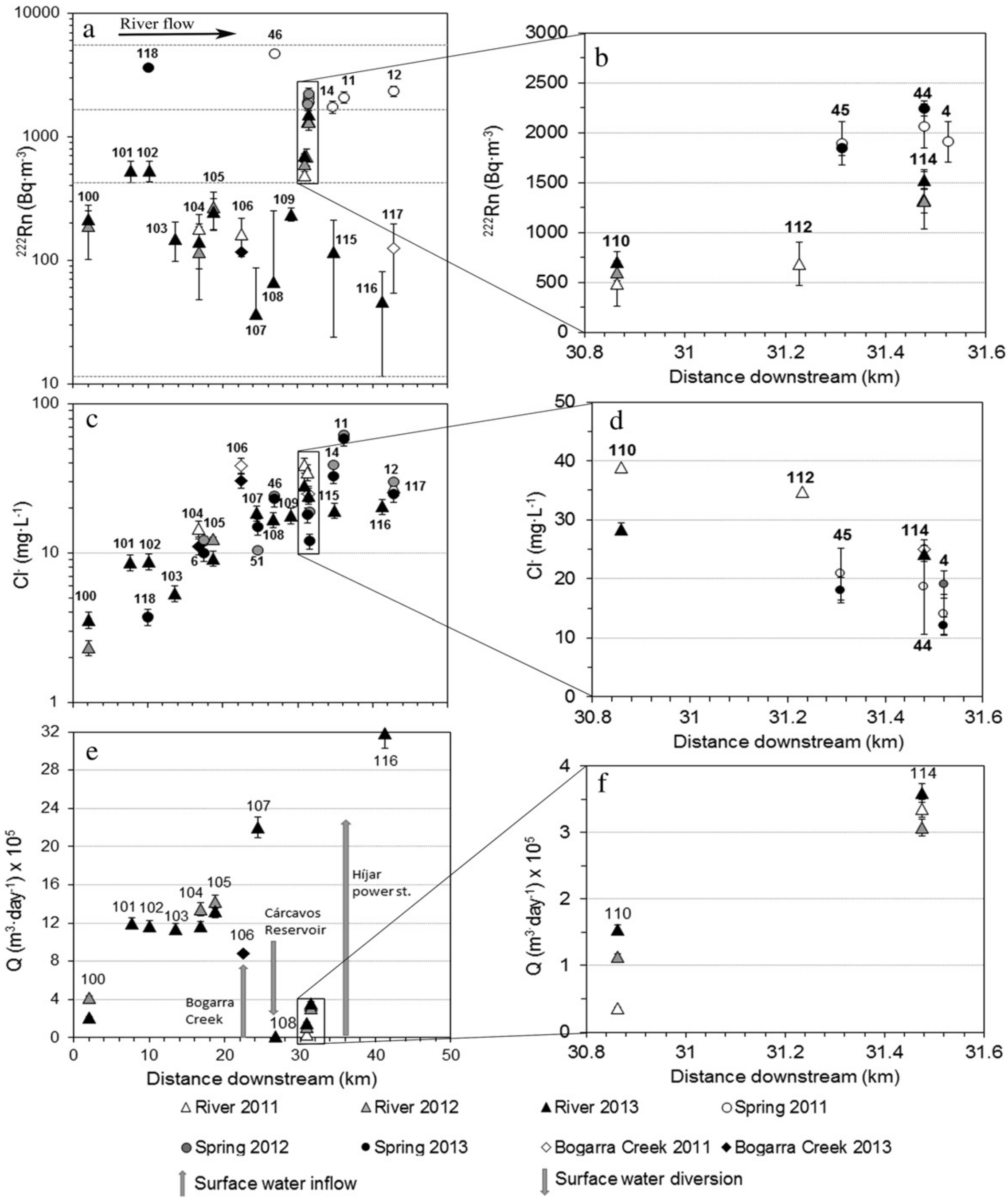

Fig. 5. Field data measured at the Mundo River from the river source, at the Bogarra Creek (station 106) and at several springs from the Cujón, Alcadozo and Pliegues Jurásicos del Mundo aquifers during 2011, 2012 and 2013. a) Radon activities in the whole studied area; b) Radon activities in Ayna; c) Cl^- concentrations in the studied area; d) Cl^- concentrations in Ayna; e) Stream flow measured in the studied area, and f) Stream flow measured in Ayna.

The deduced evolution of groundwater discharge along the whole studied river length is as follows:

- In the 2013 survey radon activity increased from 217 ± 33 Bq m^{-3} at station 100 (the most upstream gauging point) to 529 ± 105 Bq m^{-3} at station 101, placed 5 km downstream the former one. Radon activity at station 102, 3.5 km downstream station 101, was 536 ± 100 Bq m^{-3}. This suggests that groundwater discharge occurs between stations 100 and 101, but probably also between stations 101 and 102, as in the absence of groundwater discharge radon activity is expected to decrease due to decay and radon transfer to the atmosphere. However, stream flow measurements (Fig. 5e) indicate that river flow was constant between stations 101 and 102, with Q_R = 119,216 ± 9532 m^3 day^{-1} and 116,753 ± 6305 m^3 day^{-1}, respectively. To check the existence of groundwater discharge between stations 101 and 102, as radon values suggest, the effects of radon decrease due to degassing were calculated using Eq. (10); results are discussed in Section 4.3.
- Radon activity decreased between stations 102 and 103, while between stations 103 and 104 it remained constant (Fig. 5a). The river flow rate did not change significantly between stations 102 and 104 (Fig. 5e). Altogether, this suggests that there is no groundwater input between stations 102 and 104.
- Small increases in radon activity and in river discharge are observed at the subsection 104–105 both in the 2012 and the 2013 surveys. As the river does not receive any known permanent tributary in this

sector, the results point to the existence of groundwater discharge in this reach.

- Radon activity decreased and river flow rate increased between stations 105 and 107. Among both stations the Mundo River receives the Bogarra Creek (station 106), whose water has a lower activity than the Mundo River at station 105. Radon activity measured at station 107, just after the confluence of the Bogarra Creek, is the lowest most measured value in the whole study area (37 ± 28 Bq m^{-3}), suggesting the absence of significant groundwater discharge between stations 105 and 107.
- Between stations 107 and 110 radon activity increases while river flow decreases, but artificially. Station 108 is in the Cárcavos Reservoir, from which most of the Mundo River flow is diverted. This water is used for hydroelectric power generation 14 km downstream, at the Híjar Power Station, where water regains the river channel. From station 108, where the flow is quite small (1128 m^3 day^{-1} in July 2013), to station 110 the flow rate increases notably (15,462 m^3 day^{-1} in July 2013; Fig. 5, e and f, and Table 1). This adds confidence to the interpretation of radon increase due to groundwater inflow.
- The radon surveys performed in 2011, 2012 and 2013 in the Ayna village area (approximately a 600 m long tract; Fig. 5b) show a gradual increase in radon activity between stations 110 and 114. Activities measured in the three surveys were rather homogenous for both stations, ranging from 490 ± 113 to 707 ± 112 Bq m^{-3} in station 110, and from 1319 ± 176 to 1527 ± 184 Bq m^{-3} in station 114. Three well known springs (44, 45 and 4 in Fig. 1) discharge into the Mundo River close to station 114. Thus, the activity of river water at this station is clearly due to a mixture of surface water and groundwater.
- Radon activities measured in the stations located downstream the Ayna area are below 125 Bq m^{-3} (Fig. 5a). The range $^{222}Rn = 30$ to 150 Bq m^{-3} has been assumed to represent the background radon activity of the Mundo River, meaning the activity of water with little or no groundwater influence.

Groundwater radon activities were measured in springs discharging to the Mundo River along the studied area. Data are shown in Fig. 5a and summarized in Table 2. The measured activities ranged from around 1700 Bq m^{-3} to around 4700 Bq m^{-3}. Albeit not all springs were measured at every sampling campaign, most of the springs from the Alcadozo and Pliegues Jurásicos del Mundo aquifers (Jurassic limestones and dolostones) had comparable activities around 2000 Bq m^{-3}, except springs 46 and 118. Spring 46, measured only in the 2013 survey, had $^{222}Rn = 4776 \pm 164$ Bq m^{-3}. The spring is located close to a fault and also to a wedge of marly sediments (Fig. 1). Both circumstances could explain its high activity compared to others springs. Spring 118, also measured only in the 2013 survey, had $^{222}Rn = 3628 \pm 143$ Bq m^{-3}. This spring, also located in a faulted area, belongs to the Cujón aquifer, a perched aquifer formed by Cretaceous limestone. The origin of the relatively high radon activity in these two springs has yet to be studied.

4.2. River water and groundwater Cl^- concentration input for the chloride mass balances, CMB

As CMB is used to validate RMB results, river water and groundwater Cl^- concentrations have been characterized. Cl^- concentrations in the Mundo River and in groundwater are depicted in Fig. 5, c and d, including their relative uncertainty as error bars, and summarized in Tables 1 and 2. The measured values were roughly constant in time for those river stations and springs sampled more than once, but they varied across the study area. Although some river stations and springs were sampled during the 3-year study, the most complete campaign was carried out in July 2013. Thus, the results discussed in this section refer mostly to the 2013 survey.

In spring water the Cl^- contents increase roughly downflow from the upper river basin. The least mineralized groundwater sample was measured in spring 118, located in Cretaceous limestones in the upper basin, with $Cl^- = 3.7$ mg L^{-1}, and the most mineralized one was from spring 11, some 36 km downflow the river source, located in Jurassic limestones, with $Cl^- \approx 65$ mg L^{-1}. Spring 11 is the only one having sodium-chloride water (information not shown here), which is assumed to be due to the local influence of halite-bearing Triassic sediments, since tectonic wedges of Triassic materials are common in the area (Ortí et al., 1996). Springs 6 and 51, located in the Bogarra Creek basin, are also nearby Triassic materials, but they have 3 to 6 times more SO_4^{2-} than Cl^- (Table 2), while Cl^- contents are similar to the expected local atmospheric supply after Hornero et al. (2013), which is 10 to 12 mg L^{-1}. These two springs are assumed to have the signature of gypsum-dominated Triassic materials.

The Cl^- contents in the Mundo River water increases downflow from values <5 mg L^{-1} nearby the river source (station 100) to values around 40 mg L^{-1} nearby Ayna village (station 110). The river is a main regional discharge area of both Alcadozo and Pliegues Jurásicos del Mundo aquifers, and it is assumed that groundwater discharge has increasing residence time and mineralization from W to E. However, the hypotheses regarding the origin of the salinity in the Mundo River also consider the existence of evaporite minerals in Triassic sediments, which crop out as small patches along the river channel and also as extended bodies in the basins of the main tributaries, such as De Celada, Salado and Bogarra creeks.

The Cl/Br molar ratio has been studied in a number of samples to determine the origin of salinity both in groundwater and in the Mundo River water (Tables 1 and 2). The relationship between the Cl/Br values and the Cl^- contents was compared to the compilation performed by Alcalá and Custodio (2008) for water having many different salinity origins. After Fig. 6, most of the springs have Cl/Br values characteristic of rain recharged at medium-high altitude inland areas and flowing through evaporite-free materials, except for spring 11 and less clearly for springs 12, 14, 44 and 45.

The Bogarra Creek station (106) is known to have influence from urban wastewater, and half of the creek basin is over Triassic outcrops (see Fig. 1). After Alcalá and Custodio (2008) urban wastewater has Cl/Br values between 900 and 1400, and leaching of gypsum containing halite has values between 1400 and 5400. The two samples available from station 106 have Cl/Br values of 1642 (year 2011) and 2162 (year 2013), which are coherent with a dominant lithological source.

The Cl/Br values of the Mundo River samples seem to split into two groups (Fig. 6), which could be related to main salinity sources: 1) Samples from stations 110, 112 and 114, all of them from the Ayna village area, with Cl^- and Cl/Br values similar to those of the springs discharging in this area (4, 44 and 45); then, the origin salinity is assumed that of the spring waters, mostly atmospheric supply, with a possible small lithological contribution. 2) The other river samples have Cl^- contents between 2 and 27 mg L^{-1} and Cl/Br ratio values >1000, which is well over the values of local atmospheric supply, which are ≈300 to 600, as also shown by groundwater. The increase of Cl^- content between stations 100 and 102 can be attributed to lithological contribution of the Triassic, as between both control stations the Mundo River receives several tributaries (De la Vega, Salado) running over Triassic sediments, and the river channel itself does. Patches of Triassic sediments also crop out between stations 109 and 115. Then, a variable contribution of Triassic sediments to river salinity in all samples with Cl/Br values >1000 can be confidently supported.

4.3. Groundwater discharge to the Mundo River after radon mass balances

Groundwater inflows to the Mundo River were estimated using RMB for the three surveys performed. All the mass balances were performed for river tracts comprised between consecutive control sections whenever it was possible. The results were discussed with respect to total

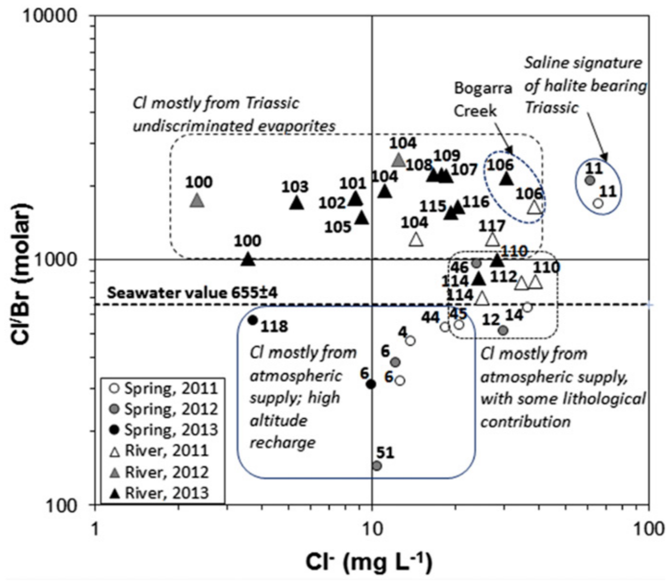

Fig. 6. Cl/Br molar ratio vs. Cl^- content (mg L^{-1}) in the springs and river water samples with indication of the most probable origin of Cl^- according to the compilation of Alcalá and Custodio (2008).

flow increases in the whole studied area calculated by differential gauging (WMB), and they were compared to CMB results available for the 2011 and 2013 surveys.

RMB was performed using Eq. (6). Averaged values were used for river depth and width. The flux of radon to the atmosphere (F_A) was calculated using Eqs. (10) and (11); the obtained value ranged from 507 to 3993 Bq m^{-2} day^{-1}. The possible flux of radon from the hyporheic zone (F_h) was estimated using Eq. (8) in a river reach with streambed sediments and river morphology representative of the most common features in the whole studied area, and where $dC_R / dx = 0$, so that groundwater discharge was assumed to be inexistent. The river reach chosen was located between stations 103 (13.57 km) and 104 (16.82 km), where a rather constant radon activity was measured (C_R ~ 150 Bq m^{-3}, see Table 1). The estimated value for F_h was 713 Bq m^{-2} day^{-1}. Although the value of F_h may vary over time and location, depending on the river slope and groundwater discharge rate (Unland et al., 2013), here it has been assumed to be constant for the entire studied area. Table 3 shows an example of the parameters used to estimate groundwater flows by river tracts, in this case applied to tract 110–114 (Ayna).

All the RMB, CMB and WMB results are synthesized in Table 4 and in Fig. 7. The following main information can be deduced from these and from Fig. 5 and Tables 1 and 2:

- The observed radon activity increases suggest clearly the occurrence of groundwater discharge in tracts 100–101 (5.6 km long), 104–105 (1.95 km long), 108–110 (4.14 km long), and 110–114 (620 m long).
- In tract 100–101, the activity of spring 118 (3628 ± 286 Bq·m^{-3}; Table 2) was assumed to represent local groundwater discharge. Although this is the only groundwater sample surveyed in the present work, the assumption is based on the fact that historic chemical data from several other springs existing in the same area (PU, BA, SA, AM, CO, LA and PA in Fig. 1) and also from the Celada Creek, which joins the Mundo River from the South within this tract, have similar chemical characteristics than spring 118 (Fig. 8, a and b). The Q_{GW} calculated by the RMB is 19,392 ± 5148 m^3 day^{-1}. This value could not be checked by CMB calculations as within this tract Triassic sediments crop out in the Mundo River channel and increase the Cl^- content of river water from around 3 mg L^{-1} (control station 100) to around 10–14 mg L^{-1} in control stations 101 to 105. The last values are similar to the Cl^- contents of springs 6 and 51 (10 to 15 mg L^{-1}, Table 2 and Fig. 8b), located in Triassic sediments, which supports the hypothesis that the river can gain Cl^- just by direct contact with Triassic materials. Should the Q_{GW} calculated with the RMB be realistic, the groundwater discharge within this tract would be 14% to 25% (considering the uncertainties) of the increase of total runoff in the same tract (98,439 ± 11,813 m^3 day^{-1}). As mentioned above, this river tract receives water from three tributaries not gauged in this work (De la Vega, Salado, and Celada creeks). Several works mention a pooled average of 16,000 m^3 day^{-1} (IGME-DGOH, 2001; Moral, 2005; IGME, 2009). There is no chemical information about De la Vega and Salado (which means salty) creeks, but as both streams flow over Triassic sediments they are assumed to have Cl^- contents larger than the Mundo River in control station 101, but contributing a much smaller flow rate. Radon activities of those tributaries are expected to be low and comparable to the Mundo River value in station 100. Thus a RMB would not be able to quantify their contributions.
- In tracts 101–102 and 102–103, and taking into account the uncertainty, the river flow was quite constant, so groundwater inflow was assumed to be zero or negligible.

To check the existence of groundwater discharge between stations 101 and 102, as radon values suggest, the theoretical effects of radon decrease due to degassing were calculated using Eq. (10). Previously, the thickness of the boundary layer was calculated (Eq. (11)) to be $z = 21.9 * 10^{-6}$ m in a reach without groundwater discharge, in this case between stations 102 and 103. The calculated z value is in agreement with the ones obtained by Elsinger and Moore (1983), which ranged from $19 * 10^{-6}$ to $48 * 10^{-6}$ m, and Ellins et al. (1990), which ranged from $9.9 * 10^{-6}$ to $41 * 10^{-6}$ m. The molecular diffusivity of radon (D) at 23 °C (air temperature at the measurement time) was also calculated (Eq. (12)) to be $D = 1.04 * 10^{-4}$ m^2 day^{-1}, in agreement with the results obtained by Ellins et al. (1990). The calculated radon activity expected at station 102 after gas exchange is 264 Bq m^{-3}, which is 40–60% of the radon activity actually measured (536 ± 50 Bq m^{-3}, Table 1). Thus,

Table 3
Parameters used for estimating groundwater inflow into the Mundo River at Ayna (stations 110 to 114) by radon mass balance. Variables such as the radon radioactive decay constant (λ), the flux of radon from the hyporheic zone (F_h), the thickness of the boundary layer (z) and the radon molecular diffusivity (D) are constant or assumed to be constant in this study. Their values are: $\lambda = 0.18$ day^{-1}, $F_h = 713$ Bq m^{-2} day^{-1}, $z = 21.9 * 10^{-6}$ m, and $D = 1.04 * 10^{-4}$ m^2 day^{-1}.

Symbol	Description	October 2011	May 2012	July 2013
Q_{Ro}	River flow at station 110 (m^3 day^{-1} ± 2σ)	3528 ± 268	11,356 ± 863	15,462 ± 1205
Q_{RX}	River flow at station 114 (m^3 day^{-1} ± 2σ)	33,578 ± 2398	30,712 ± 2075	35,916 ± 2729
C_R	Radon activity of stream water (Bq m^{-3} ± 2σ)	1319 ± 289	1316 ± 302	1527 ± 296
C_{Gw}	Radon activity of groundwater (Bq m^{-3} ± 2σ)	2069 ± 219	2247 ± 227	[a]
F_A	Radon gas transfer coefficient (Bq day^{-1} m^{-2})	3929	3374	3284
w	River width (m)	4.0	5.4	7.4
b	River depth (m)	0.15	0.13	0.12
v	River velocity (m day^{-1})	56,160	43,200	35,424

[a] Not measured. Values from 2012 have been used.

Table 4
Groundwater inflows to the Mundo River calculated by the radon (RMB) and chloride (CMB) mass balances, and total water mass balances (WMB) in all the investigated tracts and the three study periods.

River tract	Tract length (m)	RMB [$Q_{GW} \pm 2\sigma$(*10^3 m^3 day^{-1})]			CMB [$Q_{GW} \pm 2\sigma$(*10^3 m^3 day^{-1})]			WMB [$Q_R \pm 2\sigma$(*10^3 m^3 day^{-1})]		
		2011	2012	2013	2011	2012	2013	2011	2012	2013
100–101	5588	–	–	19.4 ± 5.1	–	–	[a]	–	–	98.4 ± 11.8
101–102	2475	–	–	−1.9 ± 3.3[b]	–	–	[a]	–	–	−2.5 ± 0.2
102–103	3415	–	–	−3.8 ± 4.4[b]	–	–	[a]	–	–	−2.8 ± 0.2
103–104	3247	–	–	−2.7 ± 1.8[b]	–	–	[a]	–	–	2.3 ± 0.2
104–105	1951	–	6.2 ± 6.7	5.4 ± 4.7	–	–	[a]	–	7.7 ± 0.8	15.7 ± 1.6
105–107	5708	–	–	[c]	–	–	[c]	–		[c]
108–110	4148	–	–	10.8 ± 0.6	–	–	16.8 ± 8.2	–	–	14.3 ± 1.1
110–114	612	29.5 ± 8.7	20.0 ± 7.0	23.5 ± 9.3	32.6 ± 14.9	–	19.9 ± 14.6	30.1 ± 2.1	19.3 ± 1.4	20.4 ± 1.6

- : Not surveyed.
[a] Unable to perform CMB.
[b] Q_{GW} is assumed = 0 m^3 day^{-1}
[c] Field conditions prevented to perform flow gauging or CMB.

although the differential flow gauging between stations 101 and 102 suggests that there is no input of groundwater in the reach, radon measurements show that an input cannot be discarded. The RMB results could not be checked by CMB due the above mentioned Cl^- contribution to the river by Triassic outcrops.

- Groundwater fluxes estimated by RMB in tract 103–104 were negligible, as radon concentration in the stream remained almost constant (C_{R103} = 150 ± 53 Bq m^{-3} and C_{R104} = 140 ± 56 Bq m^{-3}). A CMB could not be performed for the same reasons than in the former tracts. The increase of river flow rate calculated by WMB was 2311 ± 231 m^3 day^{-1}. This increase in river flow while radon activity remains constant suggests the existence of ungauged inputs of surface water along the tract, which is supported by the fact that in this sector many small, narrow and vegetated creeks merge, whose flow is not easy to see.
- Tract 104–105 was surveyed during the years 2012 and 2013. The Q_{GW} value calculated with RMB for May 2012 (6170 ± 6690 m^3 day^{-1}) is compatible with the WMB result in the same date (7723 ± 772 m^3 day^{-1}), and is coherent with the fact that the 2011–2012 autumn–winter seasons were very dry and thus significant unaccounted lateral surface contributions were not expected. The Q_{GW} value calculated for July 2013 (5410 ± 4749 m^3 day^{-1}) is comparable to that of year 2012, but is approximately 65% lower than the increase of surface flow (15,697 ± 1570 m^3 day^{-1}). This is also coherent with the fact that the 2012–2013 autumn and winter seasons were humid, so that the 2013 WMB data probably include unaccounted lateral inputs with low radon activities.
- Groundwater flows in tract 105–107 (station 106 correspond to the Bogarra tributary) were not estimated because flow gauging at station 107 could not be performed. Within this tract the Bogarra Creek joins the Mundo River, and the flow rate shown for station 107 in Fig. 4e corresponds to the sum of the rates measured at stations 105 (Mundo River) and 106 (Bogarra Creek, nearby the junction). Radon activity in the Mundo River decreases between stations 105 and 107 due to the Bogarra Creek inflow (88,163 ± 18,338 m^3 day^{-1}).
- In station 108 there is the water diversion to the Híjar Power Station (station 116). Most of the river flow is diverted and only 4% of river water is allowed to flow in the Mundo River channel downstream. This prevented to perform water flow measurement and also the RMB and CMB. However, the radon activity measured in station 108 is larger than that of station 107 (see Fig. 5), which means that there is groundwater discharge to this reach.
- In tract 108–110 (the field conditions prevented to measure river flow at station 109), the Q_{GW} value estimated in 2013 by RMB (10,836 ± 616 m^3 day^{-1}) is smaller than the Q_{GW} value estimated by CMB (16,766 ± 8181 m^3 day^{-1}). On the other hand, both estimates including their uncertainty are similar to the increase in river flow estimated by WMB (14,335 ± 1147 m^3 day^{-1}). Besides the RMB estimations were lower than CMB ones, the fact that the river flow rate was small at the upstream station (Q_{R108} = 1128 ± 26 m^3 day^{-1}) gives confidence to the RMB results and suggests that Cl^- increase in the river water (see Fig. 5) may be contributed by surface water in contact with outcrops of Triassic materials.
- Tract 110–114, located in the Ayna village, is the main gaining sector of the whole studied area. The tract is only 620 m long. There are no surface water inputs but three well-known permanent springs (4, 44, and 45) in both rims. As mentioned previously, radon measurements performed at spring 45 could have potentially entrained some dilution by mixing with river water into the sample, though the identical radon values measured in this spring in October 2011 and May 2012 suggest that there was no mixing. The radon activity of the groundwater end-member (C_{GW}) was considered to be represent by spring 44, whose source is closer to the Mundo River than spring 4, although the radon activities of all three are very close to each other (see Fig. 1 and Table 2). In years 2011 and 2013 both the RMB and CMB could be performed, while in year 2012 only the RMB could be done. The Q_{GW} values obtained by the RMB and CMB were quite similar in 2011 and 2013, and they both were similar to the WMB values. The Q_{GW} values obtained by the RMB in 2012 were also very similar to the WMB values (Table 4 and Fig. 7). The estimated Q_{Gw} for this tract was accounted for 88%, 65%, and 66% of total river flow during 2011,

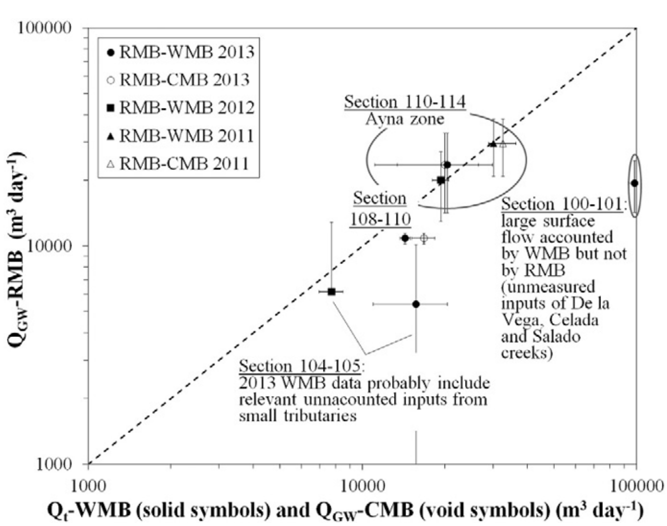

Fig. 7. Groundwater discharge estimated for different river sections by radon mass balances (Q_{GW}-RMB) compared to values estimated by chloride mass balances (Q_{GW}-CMB), and to total river runoff mass (water) balances (Q_t-WMB) during the study period.

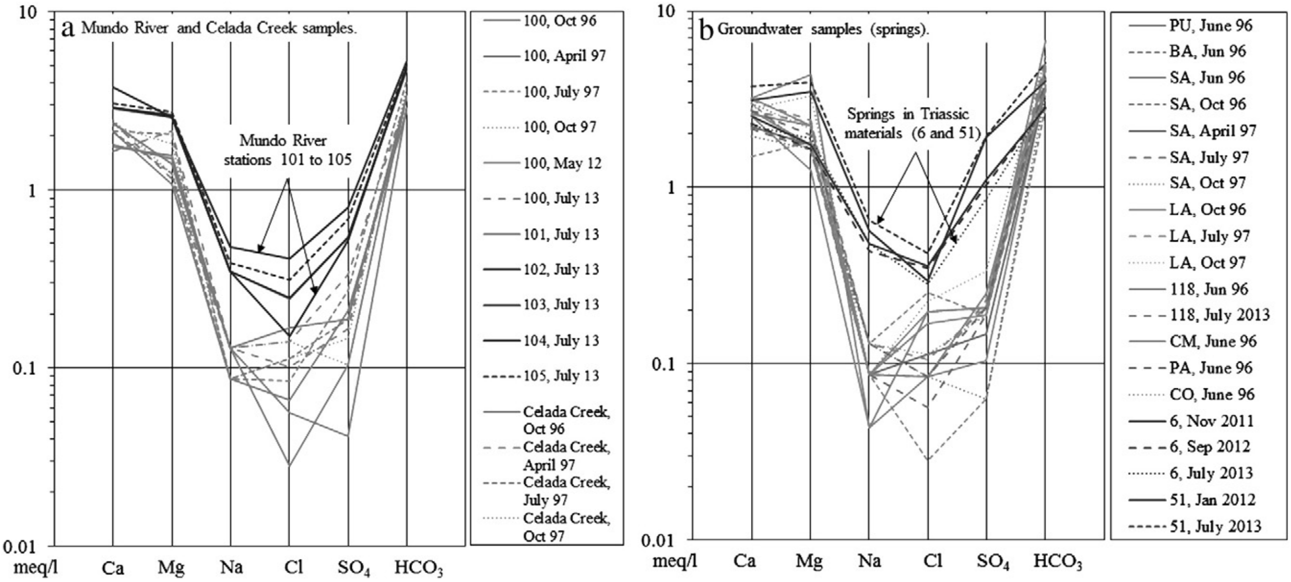

Fig. 8. Vertical logarithmic (Schoeller–Berkaloff) diagrams of surface water and groundwater in the upper part of the Mundo River basin. Data from this work (July 2013) and historic (IGME-DGOH (2001, data from years 1996 and 1997). a) Samples from Mundo River at control stations 100 to 105 (this work and historic data), and of the Celada Creek (historic data). b) Samples from springs in the carbonated aquifers Calar del Mundo and Cujón (historic data) and from two springs (6 and 51) located in Triassic outcrops within the Pliegues Jurásicos and Alcadozo aquifers (this work).

2012, and 2013 respectively. This tract offers the best field conditions for monitoring, which helps to perform accurate measurements.

- In tract 114–116 radon measurements were performed at stations 114, 115, and 116, but river flow was only gauged at station 114, while flow data at station 116 are from an automated gauging station. Moreover, at the Híjar Power Station (a few km downstream station 115) some 220,000 m^3 day^{-1} enter the Mundo River (private communication of the operating company). Thus, a RMB could not be performed, neither between stations 114 and 115 nor between stations 114 and 116. As depicted in Fig. 4a, radon activity at station 116 is very low. If there was any groundwater discharging within tract 114–116, results were probably masked by the dilution produced by the discharge at the Power Station Plant.

5. Conclusions

The measurement of radon activity in the field has been proven to be a very good tool to identify river reaches of diffuse groundwater discharge along the almost 50 km of the Mundo River studied during low water level conditions, which correspond to the conditions of the surveyed periods. The observed increases in radon activity point to the occurrence of significant groundwater discharge in four tracts of the whole studied river reach, specifically in tracts 100–101 (5.6 km long), 104–105 (1.95 km long), 108–110 (4.14 km long) and 110–114 (620 m long). Quantitatively assessed groundwater discharge by means of RMB allowed to determine Ayna tract (110–114) as the main gaining reach of the studied area, with a groundwater discharge of 29,553 $\pm$ 8667 m^3 day^{-1} (88% of total river flow) in October 2011, 20,011 $\pm$ 7054 m^3 day^{-1} (65% of total river flow) in May 2012, and 23,553 $\pm$ 9350 m^3 day^{-1} (66% of total river flow) in July 2013. Overall, the total groundwater discharge estimated by RMB to the studied reach of Mundo River was 59,191 $\pm$ 19,863 m^3 day^{-1} during July 2013, which is approximately 8–16% of the total river flow.

Moreover, when Q_{GW} values estimated by RMB were compared to Q_{GW} values estimated by CMB they showed a good similarity in tracts and/or dates where surface inputs were null or very small, which suggests that the RMB technique is useful to estimate groundwater discharge when surface inputs are negligible with respect to Q_{GW}. This adds confidence to the Q_{GW} values estimated by RMB in those tracts where CMB could not be performed due to the existence of surface inputs from ungauged tributaries. In summary, it suggests that the RMB technique is a robust tool to quantify Q_{GW} under the conditions of the Mundo River basin, which adds confidence to the calculations performed in the whole study area.

Additional confidence was gained through the estimation of the integrated uncertainty (2σ) associated with Q_{GW} by RMB and CMB, and to the WMB calculated by differential gauging. Based on this confidence, the contrast of RMB Q_{GW} values with CMB Q_{GW} and with WMB flow increases for the different surveyed tracts allowed to deduce information about the possible contribution of unaccounted (and not viewed) lateral, diffuse or concentrated surface contributions, as well as to the role of Triassic outcrops nearby or within the river channel in the increase of Cl^- contents in the river water.

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