

# GROUND-WATER POLLUTION DETERMINED BY BORON ISOTOPE SYSTEMATICS



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**Abstract**-Boron isotopic systematics as related to ground-water pollution is reviewed. We report isotopic results of contaminated ground water from the coastal aquifers of the Mediterranean in Israel, Cornia River in north-western Italy, and Salinas Valley, California. In addition, the B isotopic composition of synthetic B compounds used for detergents and fertilizers was investigated. Isotopic analyses were carried out by negative thermal ionization mass spectrometry.

The investigated ground water revealed different contamination sources; underlying saline water of a marine origin in saline plumes in the Mediterranean coastal aquifer of Israel ( $\delta^{11}\text{B}=31.7\text{‰}$  to  $49.9\text{‰}$ , B/Cl ratio  $\sim 1.5 \times 10^{-3}$ ), mixing of fresh and sea water (25‰ to 38‰, B/Cl  $\sim 7 \times 10^{-3}$ ) in saline water associated with salt-water intrusion to Salinas Valley, California, and a hydrothermal contribution (high B/Cl of  $\sim 0.03$ ,  $\delta^{11}\text{B}=2.4\text{‰}$  to  $9.3\text{‰}$ ) in ground water from Cornia River, Italy. The  $\delta^{11}\text{B}$  values of synthetic Na-borate products ( $-0.4\text{‰}$  to  $7.5\text{‰}$ ) overlap with those of natural Na-borate minerals ( $-0.9\text{‰}$  to  $10.2\text{‰}$ ). In contrast, the  $\delta^{11}\text{B}$  values of synthetic Ca-borate and Na/Ca borate products are significantly lower ( $-15\text{‰}$  to  $-12.1\text{‰}$ ) and overlap with those of the natural Ca-borate minerals. We suggest that the original isotopic signature of the natural borate minerals is not modified during the manufacturing process of the synthetic products, and it is controlled by the crystal chemistry of borate minerals.

The B concentrations in pristine ground-waters are generally low ( $<0.05$  mg/l) while contaminant sources (e.g., domestic waste water) are enriched in boron; hence boron isotopes can be used to evaluate the impact of anthropogenic boron on the environment. Moreover, the isotopic composition of contaminated ground-water can reveal the sources of pollution since different sources are characterized by distinguishable isotopic ratios. Sea water ( $\delta^{11}\text{B} = 39\text{‰}$ ), salt-water intrusion and marine-derived brines (40‰ to 60‰) are sharply different from hydrothermal fluids ( $\delta^{11}\text{B} = -10\text{‰}$  to  $10\text{‰}$ ) and anthropogenic sources (sewage effluent:  $\delta^{11}\text{B} = 0\text{‰}$  to  $10\text{‰}$ ; boron-fertilizer:  $\delta^{11}\text{B} = -15\text{‰}$  to  $7\text{‰}$ ). Some differences (up to 15‰) may exist between domestic waste water and boron-fertilizer.

## 1. INTRODUCTION

Boron is biologically an essential element but is toxic to many plants at high concentrations (> 1ppm). Thus many crops (e.g., orange, lemon, apple) are sensitive to high B levels in irrigation water. High boron levels in drinking water can be also toxic to humans, affecting fertility and pregnancy [1]. The World Health Organization [2] guideline value for boron is 0.3 mg/l and has been considered as the drinking-water standard of the European Community. Nevertheless, in many water resources worldwide, boron concentrations in ground- and surface water exceed this value rendering such water unacceptable according to the European standards. Hence, there is a need for understanding the sources, sinks and mobility of boron in ground-water. Boron can also be used diagnostically in delineating sources of dissolved material and water flow in aquifer systems.

In addition to concentration determinations, boron isotope analyses have been increasingly used in hydrogeological studies during the last decade. This growth has resulted from the recognition of large variations in the natural isotopic composition of boron (at least 90‰), and the development and refinement of mass spectrometric techniques [e.g., 3-7]. The wide range in isotopic composition of the boron sources in water resources, both natural (e.g., sea water, fossil brines, hydrothermal fluids) and anthropogenic (sewage effluents, boron fertilizers, fly ash leachate, landfills effluents), as well as the reactivity of boron with the aquifer matrix make boron a useful natural isotopic tracer for delineating sources of pollution in ground-water systems.

In the present paper, the basic concepts of boron isotopes and analytical techniques are reviewed. The results of the boron isotopic composition of anthropogenic boron and contaminated ground water from different coastal aquifers from Israel, Italy, and California, USA are presented and discussed.

## 2. BASIC CONCEPTS OF BORON ISOTOPE SYSTEMATICS

Natural boron has two stable isotopes,  $^{11}\text{B}$  and  $^{10}\text{B}$  which occur in a natural abundance ratio of approximately 4. Variation in the ratio of the two isotopes is expressed in the  $\delta^{11}\text{B}$  notation, defined as:

$$\delta^{11}\text{B} = [ (^{11}\text{B}/^{10}\text{B})_{\text{sample}} / (^{11}\text{B}/^{10}\text{B})_{\text{NBS 951}} - 1 ] \times 1000.$$

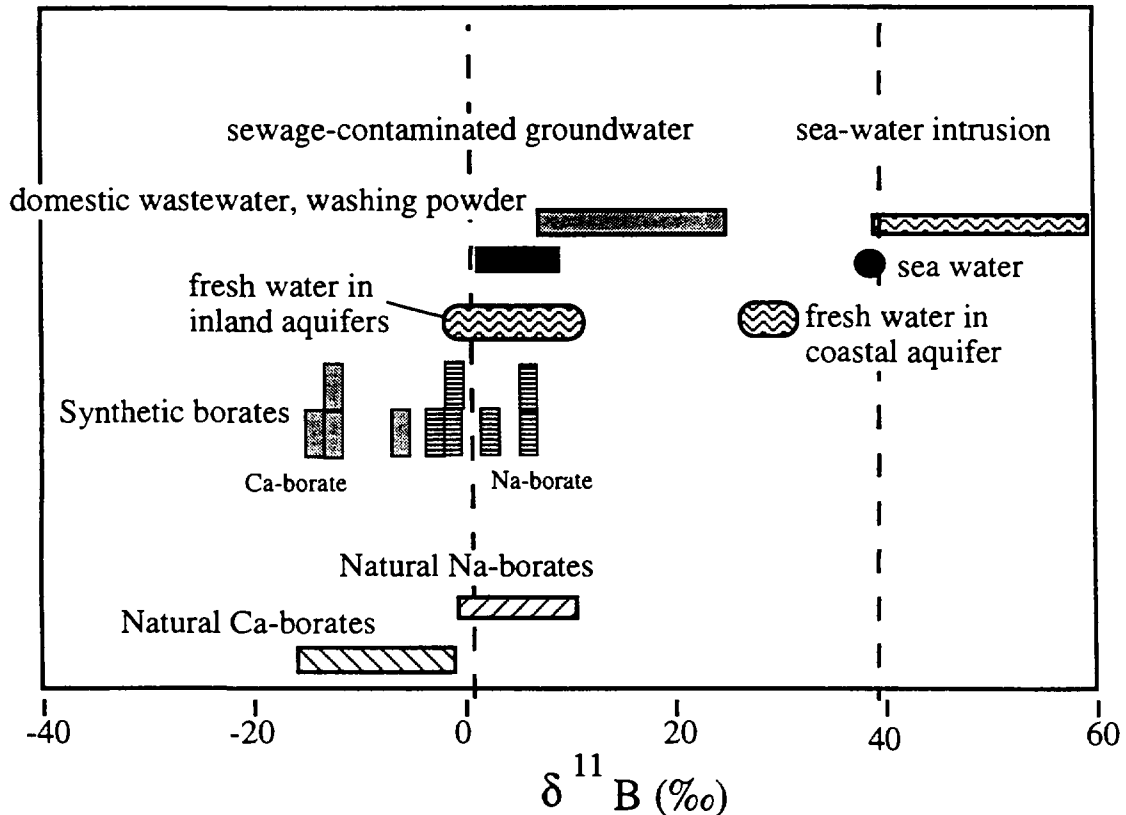
where the SRM-NBS 951 boric acid serves as a standard.

Boron is present in aqueous solutions as  $\text{B}(\text{OH})_4^-$  ion, undissociated boric acid  $\text{B}(\text{OH})_3^0$ , polyborate ions and borates  $[(\text{Na-Ca-Mg})\text{B}(\text{OH})_4^+]$ . The distribution of these species is controlled by the pH, salinity and specific cation concentrations.

The isotopic fractionation of boron is due to the differences in the interatomic boron/oxygen vibrational energy and symmetry differences between the trigonal boron species (undissociated boric acid  $\text{B}(\text{OH})_3$ ) and the tetrahedral anions ( $\text{B}(\text{OH})_4^-$ ).  $^{11}\text{B}$  is preferentially partitioned into  $\text{B}(\text{OH})_3$  (the dominant dissolved boron species at normal pH), while  $^{10}\text{B}$  is preferentially incorporated into the  $\text{B}(\text{OH})_4^-$  which enters the solid phase. The isotopic fractionation factor between the two aqueous boron species at 25°C was estimated as 0.981 [8]. As a result, the large (~90‰) isotopic variation which is recognized in natural reservoirs

(see in Fig. 1) makes boron isotopic ratios a potential candidate for tracing the origin of dissolved salts in ground waters.

Previous studies have emphasized the differences between two distinct end-members: (1) marine-derived sources with high  $\delta^{11}\text{B}$  values (e.g., sea water = 39‰; Dead Sea = 57‰; [9]); and (2) rock-derived sources with relatively low  $\delta^{11}\text{B}$  values (e.g., Sea of Galilee,  $\delta^{11}\text{B}$  = 24‰, [10]; salt lakes from Qaidam Basin, China,  $\delta^{11}\text{B}$  = -1‰ to 12‰; [11]).



**Fig. 1.**  $\delta^{11}\text{B}$  values and range. Note the large difference between sea water and fresh ground water; also  $^{11}\text{B}$  depletion in Ca-borate versus Na-borate. Industrial products mimic the isotopic composition of their parent raw materials.

Boron in the atmosphere exists in gaseous and particulate forms. The gaseous boron makes up 97% of total boron in the troposphere. It has been argued [12] that boron in the atmosphere is mainly derived from sea-salt degassing and fumarole gases with a boron residence time of approximately one month. A large isotopic variation is expected in the atmosphere since the isotopic compositions of the source materials are different: the ocean has  $\delta^{11}\text{B}$  = 39‰, volcanic gases boron with  $\delta^{11}\text{B}$  = 1.5 to 6.5‰ [13], and boron leached from clay particles with  $\delta^{11}\text{B}$  = -6.6‰ to 15‰ [14, 15]. Indeed such a variability is reflected in a wide range of  $\delta^{11}\text{B}$  values (0.8 to 35 ‰) reported by Spivack [16] in 4 rainwater samples over the Pacific Ocean. Recently, Eisenhut and Heumann [17] reported a B content of 2.3 mg/l and  $\delta^{11}\text{B}$  value of 13.1‰ for rainwater from Germany.

The behavior of boron isotopes in the unsaturated zone has been evaluated only partially. Vengosh et al. [18] have shown that adsorption onto clay minerals during the migration of fluids through the vadose zone (calcareous sandstone of the coastal aquifer of

Israel) may modify the original composition of the solution towards higher  $\delta^{11}\text{B}$  values and lower B/Cl ratios (preferential adsorption of  $^{10}\text{B}$ ).

The  $\delta^{11}\text{B}$  values of low-B fresh groundwater (<0.1 mg/l) is determined by a mixture of leached boron derived from the host aquifer rocks (usually with low  $\delta^{11}\text{B}$ ) and boron supplied from marine aerosols with a high  $\delta^{11}\text{B}$ . In coastal zones the weight of the marine end-member will be larger, whereas further inland, the low  $\delta^{11}\text{B}$  fraction becomes more important. Thus, uncontaminated groundwater from the coast of Israel yielded a narrow range of  $\delta^{11}\text{B}$  of  $\sim 30\%$  [18], reflecting clearly a marine influence. In contrast, fresh water lakes in the Alps show relatively low  $\delta^{11}\text{B}$  values (0.9‰ to 6.2‰; [19]) as do ground waters from the Great Artesian Basin in Australia ( $\delta^{11}\text{B} = -16\%$  to 2‰; [20]).

### 3. ANALYTICAL TECHNIQUES

Boron concentrations in ground water can be determined spectrophotometrically using the reagent Azomethine-H [21]. ICP, atomic emission spectroscopy, ICP-MS [22], and isotope-dilution mass spectrometry were also used for B determination [3,4, 6]. The sensitivity of the two later techniques is significantly higher (a detection limit of  $\sim 0.05$  mg/l in spectrophotometric technique versus a few ng/l in ICP-MS).

McMullen et al [23] developed a thermal ionization mass spectrometric technique in which  $\text{Na}_2\text{BO}_2^+$  ions were detected (in the mass ratio of 89/88 for  $^{11}\text{B}/^{10}\text{B}$ ) using a solid-source mass spectrometer. This technique was successfully applied in numerous studies [e.g. 8, 24, 25]) with a precision of  $\sim 2\%$ . Spivack and Edmond [5] refined this method by substitution of  $^{133}\text{Cs}$  for  $^{23}\text{Na}$  and producing  $\text{Cs}_2\text{BO}_2^+$  ions which significantly improved the precision to  $\sim 0.3\%$ . Alternatively, the thermal ionization mass spectrometer has been used, in which  $\text{BO}_2^-$  negative ions (a mass ratio of 43/42) are measured in a reverse polarity solid-source mass spectrometer, The negative thermal ionization technique is highly sensitive (i.e., a few ng of B sample versus mg B in positive thermal ionization), independent of chemical purity, enables direct loading without B separation and has a precision of  $\sim 2\%$  [3,4,6,7,19]. Several attempts have been made to measure the B isotopic ratios by ICP-MS [22], but the poor reproducibility, matrix effects, and low precision (4-7‰), makes this technique only useful for reconnaissance studies.

The separation of B for isotopic analyses has been carried out by using a boron-selective resin, Amberlite IRA-743 [7, 21]. Alternatively, boron can be separated by a standard anionic-exchange resin which reduces possible contributions of impurities [5]. Vengosh et al., [6] have shown that some geological materials (sea water, brines, saline ground water, carbonates) can be loaded directly onto a mass spectrometer filament without chemical separation and analyzed by negative thermal ionization mass spectrometry.

The data presented in this paper were analyzed by negative thermal ionization mass spectrometry. Groundwater samples were separated by B-specific resin, mixed with salts ( $\text{MgCl}_2$  and  $\text{Ba}(\text{OH})_2$ , or B-free seawater, i.e., seawater from which all the B was removed in a B-specific column) to enhance ionization, loaded onto Re single filaments, and measured by a reverse polarity Finnigan MAT-261 mass spectrometer Germany at the laboratory of Professor Heumann, University of Regensburg, [7,18,19]. Some samples from the coastal aquifer of Israel were measured in a VG-331 mass spectrometer at University of North Carolina at Wilmington, NC. Borate compounds and groundwater samples from California

were measured by a NBS solid-source mass spectrometer at the University of California, Santa Cruz. The mode of filament loading and mass spectrometry procedures were strictly repeated with samples and NBS-SRM standards in order to minimize the variability of mass spectrometer induced isotopic discrimination. A standard deviation of less than 2‰ was determined by NIST SRM-951 and seawater replicates. The mean of the absolute  $^{11}\text{B}/^{10}\text{B}$  ratios of NIST SRM-951 replicates, analyzed along with the samples was  $3.9935 \pm 0.008$  at Regensburg,  $4.015 \pm 0.005$  at Wilmington, and  $4.013 \pm 0.003$  at Santa Cruz.

#### 4. RESULTS

Contaminated ground water from three different coastal aquifers in Israel, Italy and California have been investigated for their boron isotopic variations. In addition borate compounds that are used for different industrial applications were analyzed for their B isotopic ratios.

##### **Israel:**

Salinization of ground water is the main contamination feature of the Mediterranean Coastal Plain aquifer of Israel (Fig. 2). Over-exploitation (up to  $450 \times 10^6 \text{ m}^3$  a year) beyond the natural replenishment ( $\sim 340 \times 10^6 \text{ m}^3$ ) had caused a continual drop in piezometric levels between the 1950's to mid-1980's and formation of deep hydrologic depressions, associated with increases in salinity. Since the middle of the 1980's pumping rates have been reduced and water levels have consequently increased. Nevertheless, salinity continues to increase despite the restoration of the water levels. Saline plumes have developed in the central parts of the aquifer (e.g., Be'er Toviyya; [26]) and in its eastern margins (e.g., Revadim; Fig. 2). The investigated brackish ground water from saline plumes in the inner parts of the aquifer yielded Cl variations of 200 mg/l to 1400 mg/l, B content of 0.1 to 0.7, and  $\delta^{11}\text{B}$  values in the range of 25‰ to 50‰ (Table 1). The brackish waters are also characterized by high Ca, low Na/Cl (lower than sea water values), marine Br/Cl and  $\text{SO}_4/\text{Cl}$  ratios [19].

##### **Italy:**

The quality of ground water in the coastal aquifer of Cornia River (Fig. 3) in north-western Italy has been degraded due to increase in salinity (in some locations  $>1000 \text{ mg/l}$ ) and high boron levels. D'Avino and Spandre [27] reported high concentrations of boron (up to 8 mg/l) which exceed irrigation water standards and WHO guidelines. The brackish water are enriched in Ca, Mg, K, and B and depleted in Na relative to sea water, with slightly higher Br/Cl ratios ( $2 \times 10^{-3}$  relative to  $1.5 \times 10^{-3}$  in sea water). The investigated samples yielded Cl concentrations between 38 to 687 mg/l, boron from 1.3 to 5.35 mg/l, and  $\delta^{11}\text{B}$  values of -2.4‰ to 9.3‰ (Table 2).

##### **California:**

The Salinas Valley, California, is one of the largest coastal agricultural centers in the U.S. It is the headwaters of one of the nation's largest submarine canyons beneath Monterey Bay. This combination presents severe challenges for sustainable agriculture because both anthropogenic effects of cultivation and seawater intrusion through submarine canyon walls have degraded the quality of regional groundwater on which agriculture depends. Extensive water withdrawal associated with the developed agriculture of the north-west of the Salinas Valley (Fig. 3), has caused a significant drop in piezometric levels and intrusion of salt-water into the 180' and 400' aquifer systems. Early signs of salinization were recorded already

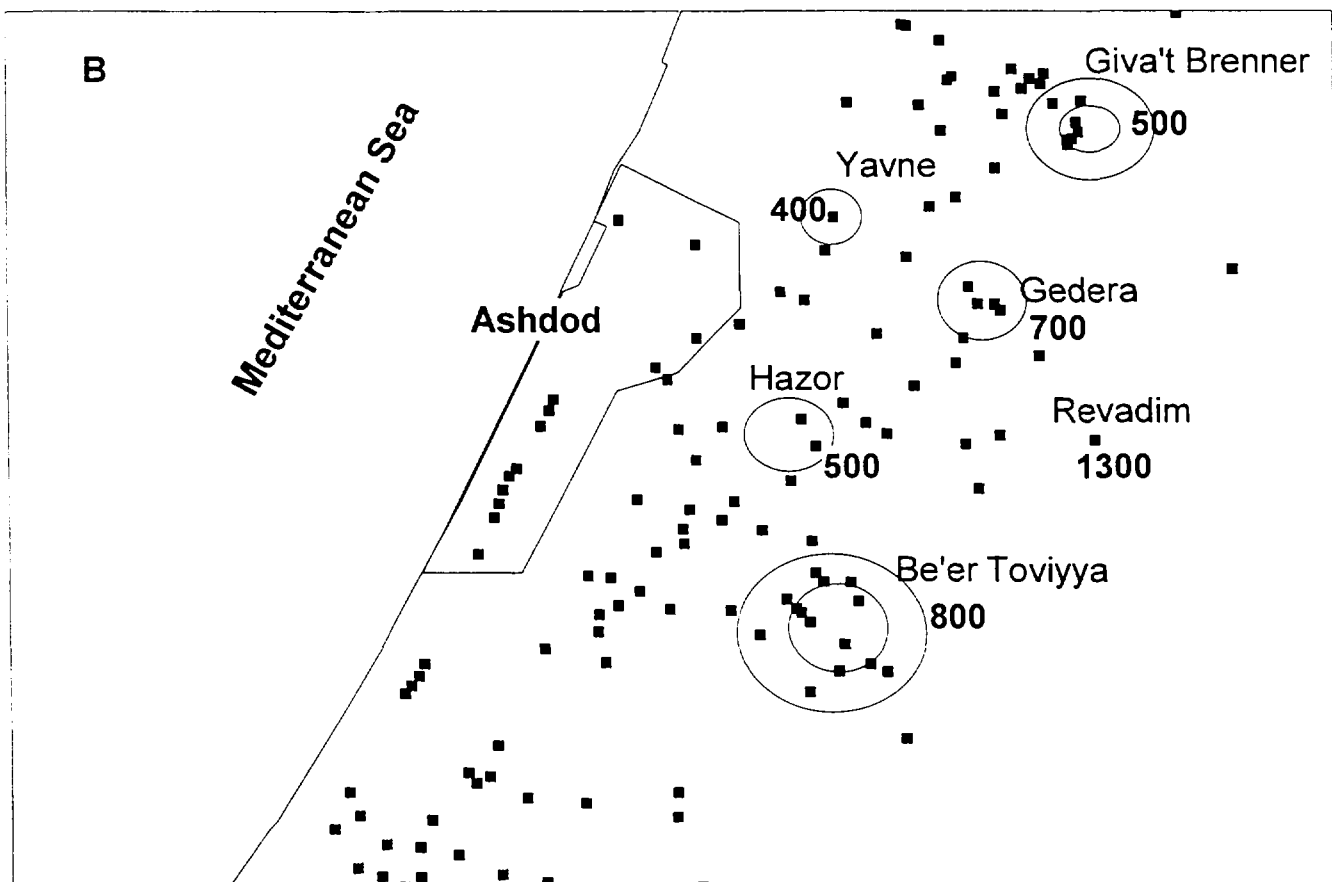
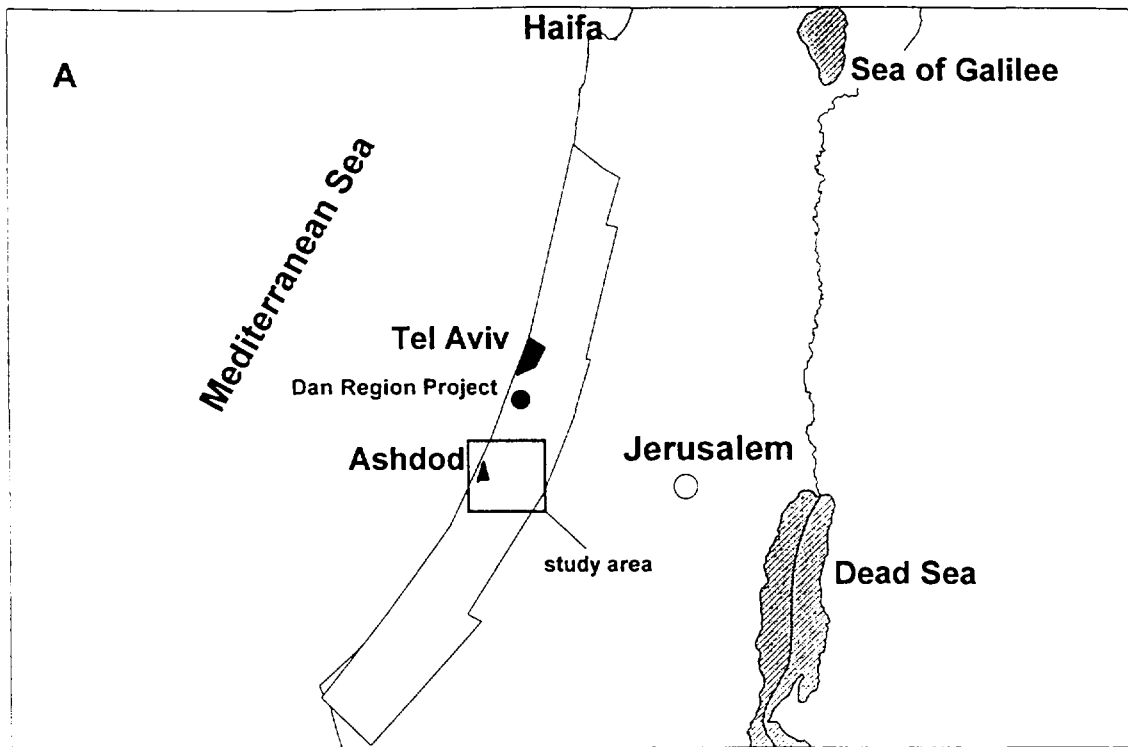


Fig. 2. General map of the Mediterranean coastal aquifer of Israel (A) and the study area in its central part (B). The squares in map B are the locations of the wells. The main saline plumes are marked with circles with the highest Cl concentrations (for 1995).

**Table 1:** Boron isotopic results of brackish ground water from the Coastal aquifer of Israel.  $\delta^{11}\text{B}$  values are reported in ‰, chloride and boron in mg/l, and B/Cl ratios are molar.

WELL	I.D.	B #	Date	$\delta^{11}\text{B}$ (‰)	B	Cl	B/Cl ( $\times 10^{-3}$ )	MS *
<b>Be'er Toviyya saline plume</b>								
Kefar Varburg A	12512401	120	12/7/92	45.6	0.26	457	1.88	
Be'er Toviyya 5	12612402	32	13/7/92	46.2	0.18	404	1.48	
Be'er Toviyya 3	12612403	31	13/7/92	47.6	0.26	715	1.17	
Be'er Toviyya 6		202	1/7/93	49.9	0.32	711	1.48	
Be'er Toviyya 7		203	1/7/93	40.3	0.24	544	1.45	
Kefar Varburg D		204	1/7/93	41.4	0.14	257	1.80	
<b>Central saline plumes</b>								
Hazor kibbutz B	13112301	119	20/7/92	32.6	0.20	303	2.13	
Hazor Kibbutz A	13212302	118	19/7/92	31.7	0.16	508	1.03	
Hazor Kibbutz A	13212302	344	1/8/95	35.3	0.29	489	1.94	*
Hazav 1	13312602	117	16/8/92	34.9	0.20	333	2.01	
Ashdod 5	12711701	94	16/7/92	31.9	0.10	410	7.60	
Ashdod 6	12811902	21	16/7/92	33.7	0.33	325	3.33	
Ashdod 2	12911801	20	16/7/92	37.5	0.39	345	3.71	
Ashdod 10	13012001	22	16/7/92	36.6	0.42	333	4.14	
Yavne 13	13712401	91	1/7/92	30.2	0.12	135	2.94	
Yavne 10	13712601	90	1/7/92	34.4	0.20	221	2.94	
Yavne 2	13812401	88	1/7/92	32.9	0.11	405	8.91	
Yavne 3	13812701	89	1/7/92	34.6	0.17	363	1.54	
Yavne 3	13812701	356	1/8/95	43.6	0.16	407	1.29	*
Yavne c	13512203	46	1/7/92	35.6	0.18	221	2.64	
Yavne A	13512301	47	1/7/92	32.9	0.21	227	2.96	
G.Brenner Siman Tov	14013102	6	17/7/92	38.3	0.19	343	1.77	
Giva't Brenner	14213001	11	17/7/92	48.4	0.12	405	0.96	
Berkovitz								
Giva't Brenner	14013104	7	17/7/92	28.8	0.19	412	1.52	
Levinson								
G. Brenner Levinson	14013104	353	18/10/95	37.2	0.18	414	1.43	*
Giva't Brenner A	14113103	9	17/7/92	29.6	0.13	328	1.25	
G. Brenner M	14113104	10	17/7/92	24.8	0.14	218	2.05	
Kevuzat Shiler C	14213002	8	17/7/92	48.5	0.10	251	1.35	
Kevuzat Shiler B	14112902	12	17/7/92	44.9	0.13	258	1.67	
Gedera Moa'za	13512901	205	24/5/93	35.1	0.25	463	1.77	
Gedera Moa'za	13512901	208	23/5/93	35.1	0.24	471	1.67	
Gedera Moa'za	13512901	350	31/8/95	39.9	0.20	479	1.37	*
Gedera Gan Mordechai	13512902	207	23/5/93	43.2	0.28	731	1.26	
Gedera Gan Mordechai	13512902	400	6/7/94	34.4	0.32	772	1.36	*
Gan Hadarom A	13412102	207	6/6/93	38.0	0.19	705	0.88	
Gan Hadarom A	13412102	209	6/6/93	30.6	0.18	576	1.02	
Gan Hadarom A	13412102	210	6/6/93	32.1	0.19	640	0.97	
Revadim kibbutz	13113201	295	15/7/94	38.2	0.67	1409	1.56	
Revadim kibbutz	13113201	337	1/8/95	38.5	0.62	1352	1.50	*

MS\* VG-336 (Wilmington, North Carolina)

**Table 2:** Boron isotope results of ground water from Cornia River in north-western Italy, and Salinas Valley, California.  $\delta^{11}\text{B}$  values are reported in ‰, chloride and boron in mg/l, and B/Cl ratios are molar.

Name	$\delta^{11}\text{B}$	Cl	B	B/Cl
<b>Cornia, Italy</b>				
Coltie	-	86	1.3	0.050
C. Olmo	-0.71	687	5.4	0.026
C. Olmo	2.95	402	4.3	0.035
Franciana	0.73	82	4.1	0.164
Salcio	3.14	415	4.1	0.033
Gera	-2.40	46	3.4	0.241
Roviccione	9.25	44	3.5	0.261
Casalpiano	-0.57	68	3.0	0.143
C. di Cornia	2.29	38	3.3	0.278
Macchiaita	2.82	40	3.2	0.256
<b>Salinas Valley, California</b>				
				( $\times 10^{-4}$ )
Monterey Bay sw	38.4	19000	4.6	7.94
13S/2E -34M2	31.1	726	0.1	5.38
14S/2E-14L2	25.3	650	0.1	5.22
14S/2E-20B1	32.6	1670	0.2	3.99
14S/2E-15L2	24.0	973	0.3	8.26
14S/2E-11C1	38.2	593	0.2	8.07
13S/2E -34N1	26.5	400	0.1	114
14S/2E -03F2	24.7	254	0.3	336

**Table 3:** Boron isotopic composition of synthetic borate products.

Material	source	company	$\delta^{11}\text{B}$ (‰)
<b>Na-borates</b>			
Na-borate	Turkey	Etibank, Turkey	7.6
Boric acid, tech. grade	Boron, Ca	US Borax	3.8
"Neobor" 2401 granular, 5 mol (penyahydrate)	Boron, Ca	US Borax	6.7
Borax 2101, granular, 10 mol (decahydrate)	Boron, Ca	US Borax	-0.4
Ammonium baborate 4351	Boron, Ca	US Borax	-2.0
Fertibor@	Boron, Ca	US Borax	-0.1
<b>Ca-borates</b>			
Boric acid (derived from Ca-borates)	Turkey	Etibank, Turkey	-13.4
CADYCAL 100 (Ca-borate)	Fort Cady, Ca	Fort Cady Minerals	-12.8
Campion Boronal ( $\text{NaCa}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ )	Chilea	Chilean Nitrate Cor.	-13.0
Boron fertilizer	Peru		-4.9



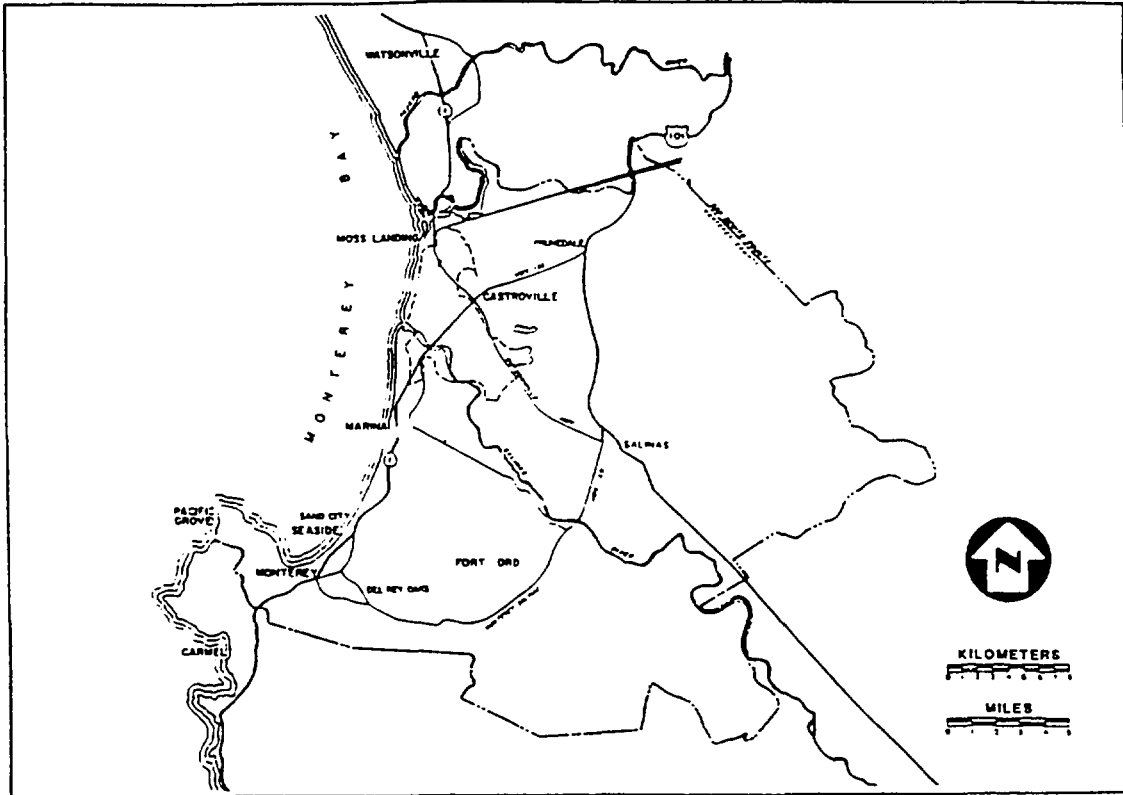


Fig. 3. Location maps of the Salinas Valley coastal area off Monterey Bay, central California, and the coastal aquifer of Cornia River in north-western Italy.

during the 1940's near the coast line of Monterey Bay [28] and the inland encroachment of salt-water has continued [29].

Saline water from the 180' aquifer has been investigated as part as a multi-isotope study of the salinization process of the aquifer. The saline water is characterized by low Na/Cl ratios (lower than sea water values of 0.86) and high Ca concentrations. The investigated samples yielded Cl contents of 250 mg/l to 1670 mg/l, B of 0.1 to 0.3 mg/l, and  $\delta^{11}\text{B}$  values of 25‰ to 38‰ (Table 2; [29]).

Isotopic analyses of treated domestic waste water from Riverside, California and Santa Anna River in Orange County which receives treated wastewater effluents yielded  $\delta^{11}\text{B}$  values of 0.25‰ and 1.95‰, respectively.

#### **Synthetic boron products:**

Synthetic Na-borate products of US Borate have  $\delta^{11}\text{B}$  values of -0.4‰ to 7.5‰ (Table 3). The  $\delta^{11}\text{B}$  values of synthetic Ca-borate and Na/Ca borate products from the U.S.A (CADYCAL100), Turkey (boric acid of EtiBank), and Chile (Champion Boronat) are significantly lower ( $\delta^{11}\text{B}$ =-15‰ to -12.1‰).

### 5. THE IMPACT OF ANTHROPOGENIC BORON

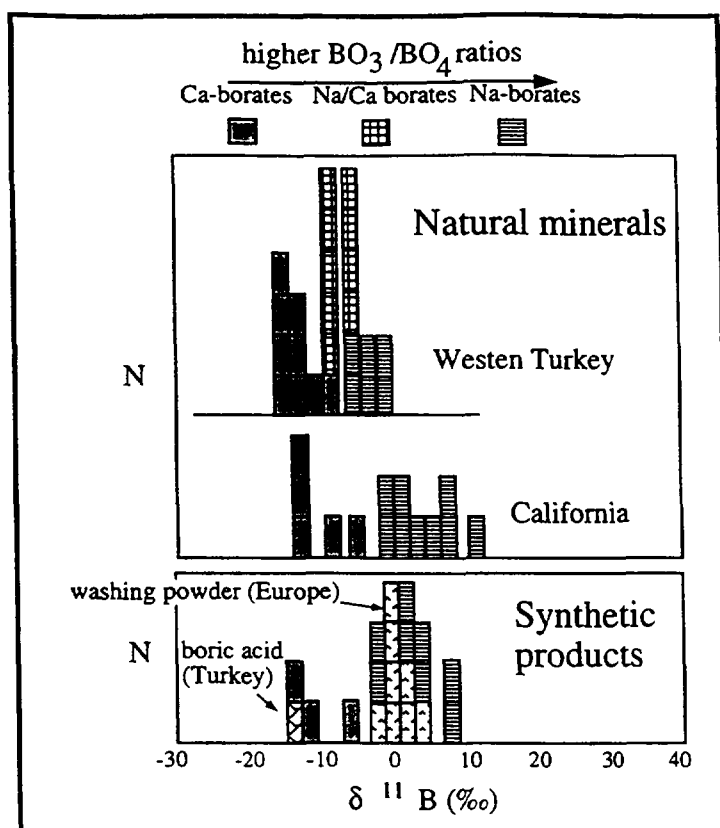
Boron compounds are widely used in various industrial applications (e.g., glass fiber, ceramics, and fertilizers) but the main industrial applications of boron that apparently affect groundwater systems are washing powders and agricultural applications of boron-fertilizers and boron-pesticides. Sodium perborate ( $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ ) is used as a bleaching agent in domestic and industrial cleaning. More than 790,000 tons of sodium perborate were used in Western Europe alone during 1985 [30,31]. Recently, sodium perborate has been introduced into "all-in-one" detergents in North America as an alternative to chlorine bleach and is used as a stain-removing agent in advanced dish washing powders. Since boron, like other inorganic ions, is not removed during waste-water secondary treatment it accumulates in domestic waste-water and consequently in natural aquatic systems [18,32]. Moreover, even during desalinization of domestic waste water using reverse osmosis techniques only 20-30% of boron is removed relative to 99% of chloride [data from 33]. The resistance of B in reverse osmosis can be related to the boron species in which the dominant species at low pH, boric acid, is not removed on the membrane.

Boron compounds are also used as fertilizers and pesticides. In areas of high precipitation and low B in irrigation water, boron fertilizers are added to increase the B content of soil fluids. In the USA the main supply of boron-fertilizers is U.S. Borate Co. which supplies Na-borate products (e.g., Fertibor, Polybor 4601, Borax 2101, Neobor). Since Na-borates are highly soluble and can be leached rapidly through the soil, Ca- and Na/Ca-borates are also used as fertilizers. The relatively lower solubility of the latter result in slow release of boron to the plants. Ca- and Na/Ca borates are produced from natural Ca-borates (Fort Cady, California, USA and Etibank, Turkey) and Na/Ca borates (Chile).

Our data (Table 3) show a clear distinction between the synthetic products of Na-borates ( $\delta^{11}\text{B}$ =-2‰ to 7‰) and those of Ca-borates ( $\delta^{11}\text{B}$ =-15‰ to -12‰). It has also been shown [34,35] that the  $\delta^{11}\text{B}$  of Na-borate minerals (borax, tincal) are higher than those of Na/Ca (ulexite) and Ca-borates (colemanite, iyoite) of the same geologic origin. The trend is

explained by the crystal chemistry of the minerals; minerals with higher  $BO_3/BO_4$  ratios have higher  $\delta^{11}B$  values. The boron isotope compositions of the investigated synthetic Na-borate, sodium perborate from California ( $\delta^{11}B = 3 \pm 1\%$ ; [7,18,19]), and washing powders from Europe (-2.9‰ to 3.1‰; [7, 36]) overlap with those of natural Na-borate minerals from California (a total range of -0.9‰ to 10.2‰; Figs 1 and 4). In contrast, the  $\delta^{11}B$  values of synthetic Ca-borate and Na/Ca borate products from the USA, Turkey, and Chile, mainly used as fertilizers, have lower  $\delta^{11}B$  results (as low as -15‰, Table 3) which mimic those of the natural Ca-borate minerals.

It appears that the boron isotopic composition is not modified during manufacturing of the synthetic products. While sodium perborate is produced solely from Na-borates and is used only in detergents, other boron compounds are used for fertilizers and are manufactured also from Na/Ca and Ca-borates. The borate compounds from Turkey (boric acid of EtiBank,  $\delta^{11}B = -13.4\%$ ), Chile (Champion Boronat; -15‰) and USA (CADYCAL100; -12.8‰) have a distinguishable lower  $\delta^{11}B$  signature which may be used to trace drainage fluids in agricultural areas in which B-fertilizers are being used (Fig. 5). Thus in some cases, boron isotope ratios may delineate different sources of anthropogenic boron (i.e., waste water versus agriculture return flow).



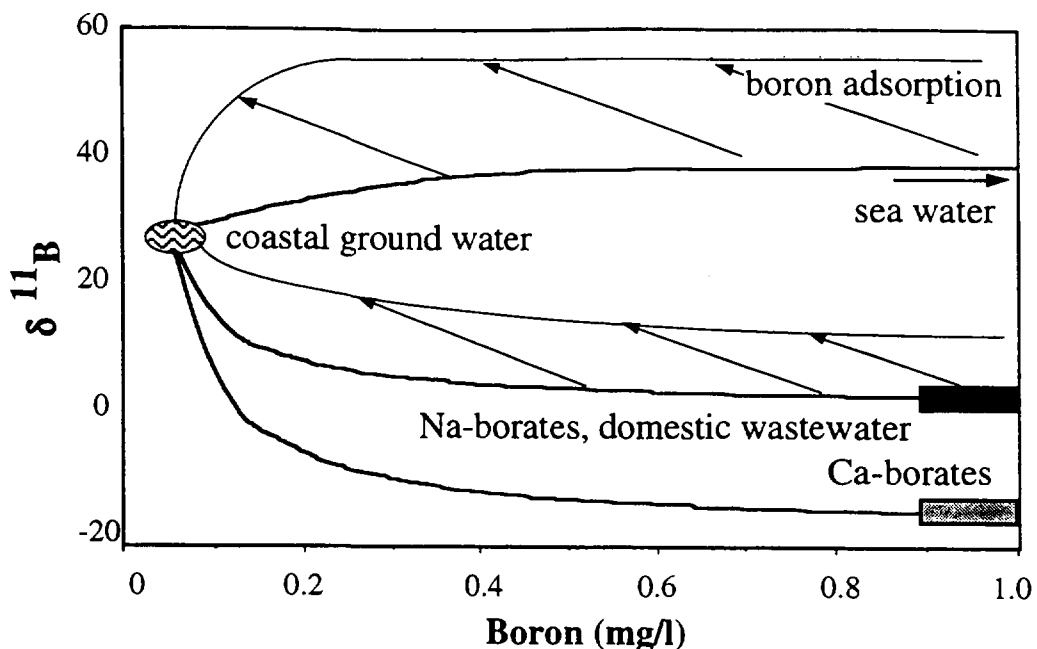
**Fig. 4.** Isotopic variations of natural and anthropogenic borates. The synthetic products reflect the isotopic composition of their sources: Ca-borates are 'lighter' than Na-borates. Values of natural minerals from [34] and [35].

The nature of anthropogenic boron contamination in groundwaters have been studied in different environmental settings, and is summarized below.

### Domestic waste water

Anthropogenic boron in waste water is isotopically distinct from natural boron in groundwater, particularly in coastal aquifers, and thus can be utilized to identify the source of contamination. The  $\delta^{11}\text{B}$  values of raw and treated sewage effluents from the Dan Region Sewage Reclamation Project in Israel ( $\delta^{11}\text{B}=5.3\text{‰}$  to  $12.9\text{‰}$ ) overlap with those of natural non-marine Na-borate minerals ( $-0.9\text{‰}$  to  $10.2\text{‰}$ ) but differ significantly from those of regional uncontaminated groundwater ( $\sim 30\text{‰}$ ) and sea water ( $39\text{‰}$ ) [18]. Groundwater contaminated by recharge of treated sewage yields a high B/Cl ratio with a distinctive anthropogenic isotopic signature ( $7\text{‰}$  to  $25\text{‰}$ ). Elemental B and  $\delta^{11}\text{B}$  variations reflect both mixing of sewage effluents with regional groundwater and boron isotopic fractionation associated with boron removal by adsorption onto clay minerals. The distinctive isotopic signature of anthropogenic boron was recognized, however, in most samples and was significantly different from those of natural sources such as marine-derived saline groundwater ( $35\text{‰}$  to  $60\text{‰}$ ; [18]).

Our results of treated waste water from Riverside and Santa Anna River in Orange County, California also demonstrate that boron isotopes can be used as a sensitive tracer to detect the impact of waste water on fresh water resources. The  $\delta^{11}\text{B}$  values of Santa Anna River ( $\delta^{11}\text{B}=2\text{‰}$ ) and treated waste water from Riverside ( $0.3\text{‰}$ ) are similar to Na-borate compounds used in detergents but significantly different from fresh water from coastal areas with higher  $\delta^{11}\text{B}$  values. In addition, Bassett et al. [37] used the distinctly different isotopic composition of injected treated waste water and irrigation-affected water ( $\delta^{11}\text{B}>40\text{‰}$ ) to trace the affect of injection into an alluvial aquifer near El Paso, Texas.



**Fig. 5.**  $\delta^{11}\text{B}$ -B mixing lines between uncontaminated boron in ground water and possible contaminants: sea water, Na-borates, and ca-borates. Note that: (1) the difference between marine and anthropogenic contamination remains detectable in spite of adsorption modifications; and (2) differences between various anthropogenic sources may be detectable.

### **Fly ash leachate**

Boron is also enriched in coal, resulting in high concentrations of boric acid in fly ash leachate (up to 14 ppm). Davidson and Basset [38] showed that fly ash leachates have a wide range of  $\delta^{11}\text{B}$  values (-19.2‰ to 15.8‰) which differ from those of local ground-waters.

### **Landfills**

Eisenhut and Heumann [17] demonstrated high B contents (up to 6.7 mg/l) and low  $\delta^{11}\text{B}$  values (-5.7‰ to 9.6‰) in seepage water from different landfills in south-east Bavaria, Germany. It was suggested that washing powder ( $\delta^{11}\text{B}=-2.9‰$  to 3.1‰) was one of the main boron source in the landfills although other sources with lower  $\delta^{11}\text{B}$  were also identified. The distinctive high B and low  $\delta^{11}\text{B}$  signals of the seepage water was different from those of local groundwater and thus were used to track contaminates flows in the local aquifer [17]. High concentrations of boron are also expected in runoff from feedlots, paper mills, and mining operation that can be used for identifying contaminant sources [38], yet their isotopic signatures have not been constrained.

## **6. SALT-WATER INTRUSION IN COASTAL AQUIFERS: THE CASE STUDIES OF CALIFORNIA AND ISRAEL**

In many coastal aquifers salt-water intrusion frequently occurs due to extensive withdrawals of ground water and reduction of fresh water piezometric levels. Chemical changes in modern sea water composition upon its entry into an aquifer can be caused by mixing with fresh ground water as well as water-rock interactions. In many cases the saline ground water associated with salt-water encroachment in coastal aquifers are enriched in Ca and have low Na/Cl ratios relative to modern ocean water. High salinity near the coast is typical to salt-water intrusion yet other sources with high salinity (e.g., connate brines, agriculture return-flows [39]) can cause salinization, each requiring separate management strategies. We propose the use of boron isotope composition of saline water as an indicator of the origin of salinization. Two specific cases are presented: that of saline ground water from the coastal aquifer of Salinas Valley, California (Table 2) and from the Mediterranean coast of Israel (Fig. 6):

- (1) Conservative behavior of boron in which the B concentrations and isotopic ratios reflect mixing between sea water and fresh water with lower  $\delta^{11}\text{B}$  values. This case was demonstrated in the 180' aquifer of the Salinas Valley with  $\delta^{11}\text{B}$  values of 25‰ to 38‰ (Table 2) reflecting mixing of regional uncontaminated ground water ( $\delta^{11}\text{B}=16‰$ ) with sea water.
- (2) Non-conservative behavior of boron in which water-rock interactions, in particular B adsorption resulted in high  $\delta^{11}\text{B}$  values and lower B/Cl ratios relative to seawater values. This case was demonstrated in saline water from the salt-water intrusion zone of the Mediterranean coastal aquifer of Israel with  $\delta^{11}\text{B}$  values of 35‰ to 60‰ and B/Cl ratios  $< 7 \times 10^{-4}$  [18]. The  $^{11}\text{B}$  enrichment and total B depletion of the intruded sea water suggest boron removal, in which  $^{10}\text{B}$  was adsorbed preferentially onto clay minerals in the aquifer. The magnitude of  $^{11}\text{B}$  enrichment relative to the original sea water is up to 20‰ and is similar to the isotopic shift recorded in other marine brines (e.g., Dead Sea, [9]).

We conclude that salt-water intrusion originated initially from sea water may have a marine or higher  $\delta^{11}\text{B}$  values and marine or lower B/Cl ratios. This  $\delta^{11}\text{B}$  signal is different from non-marine brines (e.g., salt-lakes in Qaidam Basin with  $\delta^{11}\text{B}$  of 0‰ to 10‰; [11]),

hydrothermal fluids, and anthropogenic boron (see above). Thus we suggest that the boron isotopic systematics can be used to monitor early signs of salt-water intrusion into coastal aquifers.

## 7. INFLUENCE OF HYDROTHERMAL FLUIDS: THE CASE STUDY OF CORNIA RIVER, ITALY

The boron isotope composition of hydrothermal fluids reflects contributions from the sources rocks, typically with a low  $\delta^{11}\text{B}$  signal and high B/Cl ( $\gg$  sea water values) ratios, and uptake into secondary phases. In oceanic environments the water-rock interaction with basalt and sediments modified the B isotopic composition of sea water [40-42]. In non-marine settings the geothermal fields are also characterized by low  $\delta^{11}\text{B}$  values (e.g., Salton Sea, California,  $\delta^{11}\text{B}=-2.6\text{‰}$  to  $-1.1\text{‰}$ ; Yellowstone National Park,  $\delta^{11}\text{B}=-9.3\text{‰}$  to  $4.4\text{‰}$ ; [43,44]), reflecting the isotopic compositions of the source rocks. The influence of seawater boron with a higher  $\delta^{11}\text{B}$  in geothermal systems has been traced in central Japan ( $\delta^{11}\text{B}=-5.8\text{‰}$  to  $27.1\text{‰}$ ; [45]) and Iceland ( $\delta^{11}\text{B}=-6.7\text{‰}$  to  $30.7\text{‰}$ ; [46]). Experiments at elevated temperatures on seawater-sediment interaction have shown that whereas boron is leached from sediments at  $T>150^\circ\text{C}$ , it is adsorbed onto the clay mineral at lower temperatures [42]. The clear distinction between the B isotopic composition of rocks and sea water enables us to trace the impact of hydrothermal fluids on fresh water.

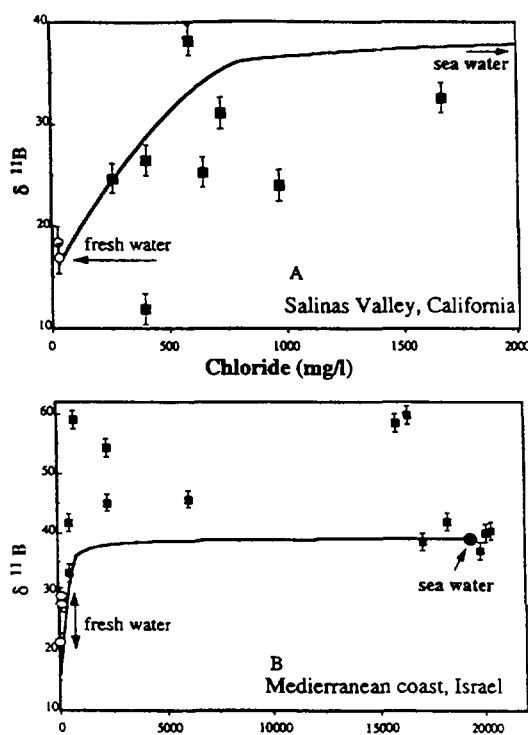


Fig. 6. Chloride versus  $\delta^{11}\text{B}$  values of saline water associated with salt-water intrusion from and Salinas Valley, California (A) and the Mediterranean coast of Israel (B). The lines represent conservative mixing between sea water and fresh water with lower  $\delta^{11}\text{B}$  values.

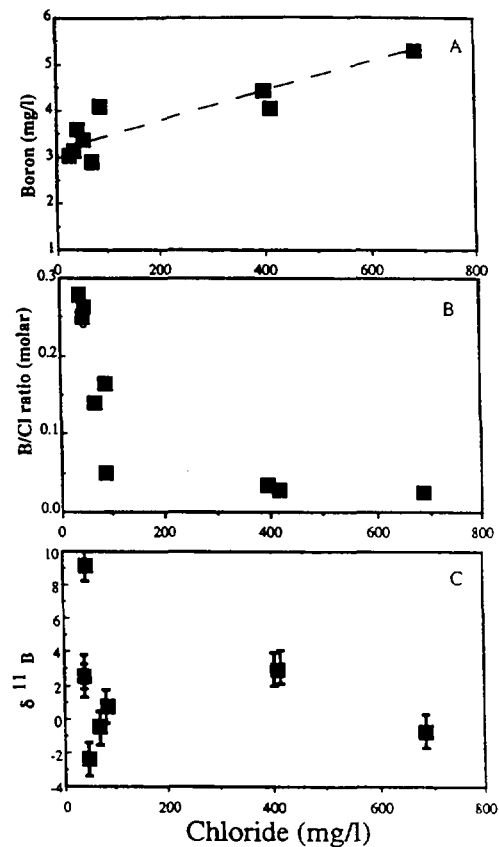


Fig. 7. Chloride concentrations versus boron contents, B/Cl, and  $\delta^{11}\text{B}$  values of ground water from Cornia River aquifer, Italy.

The saline water from the coastal aquifer of Cornia River (Fig. 3, [27]) in north-western Italy represent a good example of the application of B-isotopes. The high salinity (>1000 mg/l), and the close vicinity to the sea (Fig.3) would suggest inland encroachment of sea water. Yet the chemical composition (high Ca, low Na/Cl ratios), high B/Cl ratios, and low  $\delta^{11}\text{B}$  values of -2.4‰ to 9.3‰ rule out this mechanism. The linear correlation between boron with chloride (Fig. 7), suggests a single source for both elements. Thus, we argue that the high salinity and low  $\delta^{11}\text{B}$  signature (Fig. 7) reflect contamination by underlying hydrothermal fluids that mixed with the local ground water and caused degradation of the quality of ground water in the coastal aquifer of Cornia River .

#### 8. TRACING THE ORIGIN OF SALINITY IN SALINE PLUMES FROM THE COASTAL AQUIFER OF ISRAEL

The origin of saline plumes in the inner parts of the Mediterranean coastal aquifer (Fig. 2) of Israel is yet unresolved. The potential sources of salinity in this phreatic aquifer are anthropogenic (e.g., imported water from the Sea of Galilee via Israel's National Water Carrier, irrigation or leakage of waste water effluents) or natural sources from underlying saline water. Since each of these sources may have a distinctive isotopic ratio we investigated the chemical and B isotopic ratio of the brackish groundwater from several saline spots in the aquifer.

The boron-chloride relationships in most of the investigated ground water (Fig. 8) suggest that boron, like most of the dissolved ions, behaves conservatively in the aquifer. The B/Cl ratio decreases with salinity, but the saline ground water has a B/Cl ratio of  $1.5 \times 10^{-3}$  that is slightly higher than that of sea water ( $0.8 \times 10^{-3}$ ). In contrast to fresh ground water (Cl < 100 mg/l) with lower  $\delta^{11}\text{B}$  values (21.2‰ to 32.4‰), the  $\delta^{11}\text{B}$  values of the investigated brackish water vary from 31.7‰ to 49.9‰ (Fig.8). Based on the  $\delta^{11}\text{B}$  variations two types of brackish groundwater are identified: (1) brackish water with high  $\delta^{11}\text{B}$  values (>40‰), typical of the saline plumes of Be'er Toviyya and Kevuzat Shiler (Fig. 3); and (2) brackish ground water from the other saline plumes in the central aquifer and from the eastern part of the aquifer (Revadim) with a  $\delta^{11}\text{B}$  range of 30‰ to 40‰ (Table 1). The  $\delta^{11}\text{B}$  values of the latter group correspond to mixing between a saline source with a marine  $\delta^{11}\text{B}$  signature and fresh ground water. Similarly, the  $\delta^{11}\text{B}$  variations of brackish water from Be'er Toviyya saline plume correspond to mixing between a saline source with a high  $\delta^{11}\text{B}$  signature (> 50‰) and fresh ground water (Fig.8).

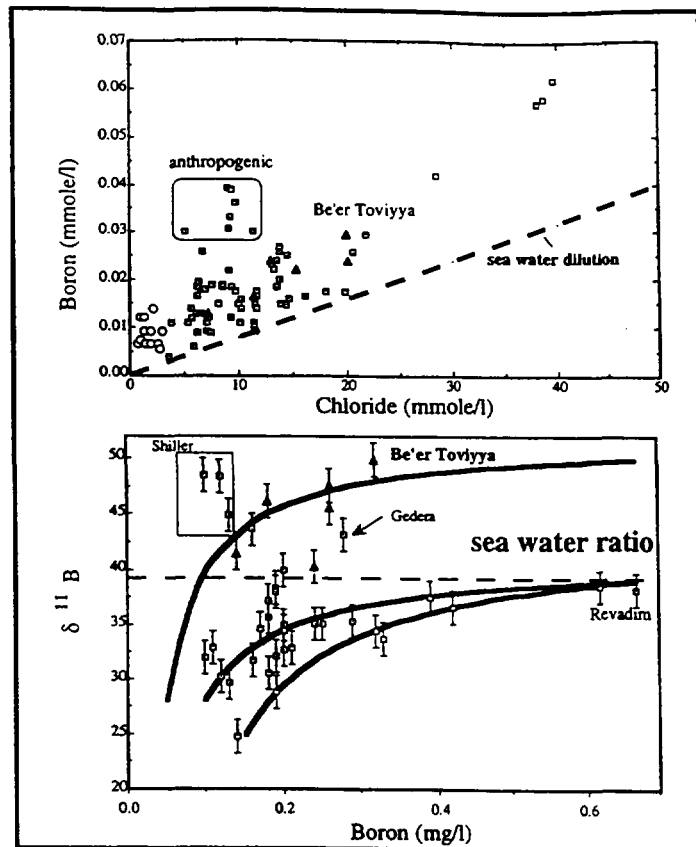
The boron isotope compositions of the brackish ground water are significantly different from those of anthropogenic sources, such as sewage effluent ( $\delta^{11}\text{B}=0-10‰$ ) or contaminated ground water (10-25‰; [18]), and thus rule out salinization from leakage or irrigation with sewage effluents. The high  $\delta^{11}\text{B}$  values are similar, however, to those of saline water associated with salt-water intrusion in the western part of the aquifer [18]. Consequently, the  $\delta^{11}\text{B}$  values suggest that the brackish ground water is derived from a marine source with a high  $\delta^{11}\text{B}$  value.

The relatively high B/Cl ratios and  $\delta^{11}\text{B}$  values of the brackish ground water rule out simple mixing between fresh water (low  $\delta^{11}\text{B}$  and high B/Cl) and Mediterranean sea water (Cl=22,000 mg/l). The high B content of sea water relative to B in freshwater would dominate the composition (e.g., B/Cl~ $0.8 \times 10^{-3}$ ) of any mixture. Moreover, mixing of fresh

water with saline water that is associated with salt-water intrusion and has higher  $\delta^{11}\text{B}$  and lower B/Cl ratios [17] would result in even lower B/Cl ratios ( $<0.8 \times 10^{-3}$ ) in order to account for the high  $\delta^{11}\text{B}$  results. Therefore, we suggest that diagenetic modifications may have modified the entrapped sea water, probably by slight contribution of B from clay minerals in the rocks.

We suggest that most of the saline plumes are derived from a modified-diluted sea water, and that the salinization process is a result of continuous mixing with the saline end-member. The original sea water was modified by adsorption processes (as reflected by high  $\delta^{11}\text{B}$  values in Be'er Toviyya and Shiler saline plumes), desorption or leaching of B from rocks (as inferred by the relatively high B/Cl ratios), and dilution with fresh water. The boron isotope results are consistent with other geochemical tracers ( $\delta^{18}\text{O}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ , Br/Cl), which also show that the main salinization in the Coastal Plain aquifer is a result of flow of underlying natural, marine-derived saline water [47].

These findings enabled the establishment of a suitable water-quality monitoring program in the Hydrological Service of Israel [48]. In addition, it has been argued that utilization of the brackish water and the underlying saline sources for desalination can reduce the operating cost and energy required, compared to desalination of Mediterranean sea water, and can be an important component in an overall fresh water conservation program in the Israeli Coastal Plain aquifer. The combination of brackish groundwater desalting and groundwater management would result in the production of usable quantities of fresh water and a long-term improvement of the water quality of the aquifer [49].



**Fig. 8.** Brackish water from saline plumes in the coastal aquifer of Israel. Mixing lines represented in B-Cl and  $\delta^{11}\text{B}$ -B spaces. Note the linear mixing of B-Cl relative to hyperbolic mixing of  $\delta^{11}\text{B}$ -B.



## 9. DISCUSSION AND CONCLUSIONS

Any strategy aimed at counteracting the harmful effects of the groundwater contamination requires a better understanding of the sources and causes of pollution. The variety of the contamination sources makes this task difficult, however. For example, the increase in the salinity of groundwater in coastal aquifers can be a result of “natural” causes such as sea water intrusion, dissolution of soluble salts in the unsaturated zone, flows of saline water from adjacent or underlying aquifers, or alternatively, anthropogenic contamination such as seepage, irrigation of sewage effluent, and agriculture return flows. Each of these salinization sources may be characterized by a distinguishable elemental and isotopic signature. Hence the use of different geochemical, including isotopic, tracers might provide additional tools for evaluation and identification of the sources of contaminated groundwater.

Boron can be used as a tracer in ground-water because of its high solubility in aqueous solution, natural abundance, and the lack of effects by evaporation, volatilization, and oxidation-reduction reactions [37]. Since boron concentrations in pristine ground-waters are generally low (<0.05 mg/l) and contaminant sources are usually enriched in boron (e.g. sea water, 4.5 mg/l; domestic waste water, 1 mg/l; fly ash leachate, 14 mg/l) the  $\delta^{11}\text{B}$  of ground-water is highly sensitive to the impact of contamination. The large isotopic variation of the potential sources can be used to trace the origin of the contamination and to reconstruct mixing and flow paths. The main end-members with distinguishable isotopic signals are (Fig. 9):

- (1) Salt-water intrusion in coastal aquifers and entrapped marine-origin brines with  $\delta^{11}\text{B}$  values of  $\geq 39\text{‰}$  and  $\text{B/Cl} \leq 8 \times 10^{-4}$ ;
- (2) Non-marine brines entrapped in non-flushed areas in aquifers and aquitrads with  $\delta^{11}\text{B}$  values of  $\sim 0\text{‰}$  and  $\text{B/Cl} > 8 \times 10^{-4}$ ;
- (3) Hydrothermal fluids in hydraulic connections to fresh water aquifers with  $\delta^{11}\text{B}$  values of  $\sim 0\text{‰}$  and high  $\text{B/Cl}$  ( $\gg$ marine ratio).
- (4) Contamination by domestic water water and other anthropogenic sources (e.g., fertilizers, pesticides, landfills) in which anthropogenic boron is derived from Na-borates with  $\delta^{11}\text{B}$  values of  $0\text{‰}$  to  $10\text{‰}$  and high  $\text{B/Cl}$  ( $>$ marine ratio).
- (5) Contamination by fertilizers originated from Ca-borates with low  $\delta^{11}\text{B}$  values as  $-13\text{‰}$  and high  $\text{B/Cl}$  ( $>$ marine ratio).

These variations show that marine and Ca-borate sources are well resolved whereas some overlaps may exist between the other contamination sources, hence additional constraints are required to distinguish between these sources. For example, high concentrations of boron have been identified in some surface freshwater (lakes and rivers) in the River Po watershed in Northern Italy [50]. The strong correlation between boron concentration and that of total dissolved phosphorus as well as anionic detergents suggest that the high boron concentrations are related to anthropogenic contamination. On the other hand, the high correlation between boron and chloride (Fig. 7), high Cl contents, and low  $\delta^{11}\text{B}$  values ( $-2.4\text{‰}$  to  $9.3\text{‰}$ ) in ground-water from the coastal plain of the Cornia River near Pisa, Italy [Table 2; 27], suggest a hydrothermal source .

Mixing of regional ground-water boron with anthropogenic boron is the major factor which determines the distribution of  $\delta^{11}\text{B}$  in contaminated ground-waters. Typically higher B concentrations in the contaminant end-member result in nonlinear (hyperbolic) boron -

$\delta^{11}\text{B}$  mixing curves (e.g., Figs 5 and 6) that enable identification, and in some cases even quantification, of the contaminants in ground water [38]. The  $\delta^{11}\text{B}$  of ground-water boron can be modified, however, by adsorption onto clay minerals in the aquifer, in particular in clay-rich aquifers and high salinity which enhance B adsorption. The isotopic shift associated with boron retention is a  $^{11}\text{B}$  enrichment of about 20‰ and thus contaminated ground-water may have higher  $\delta^{11}\text{B}$  values relative to the original source.

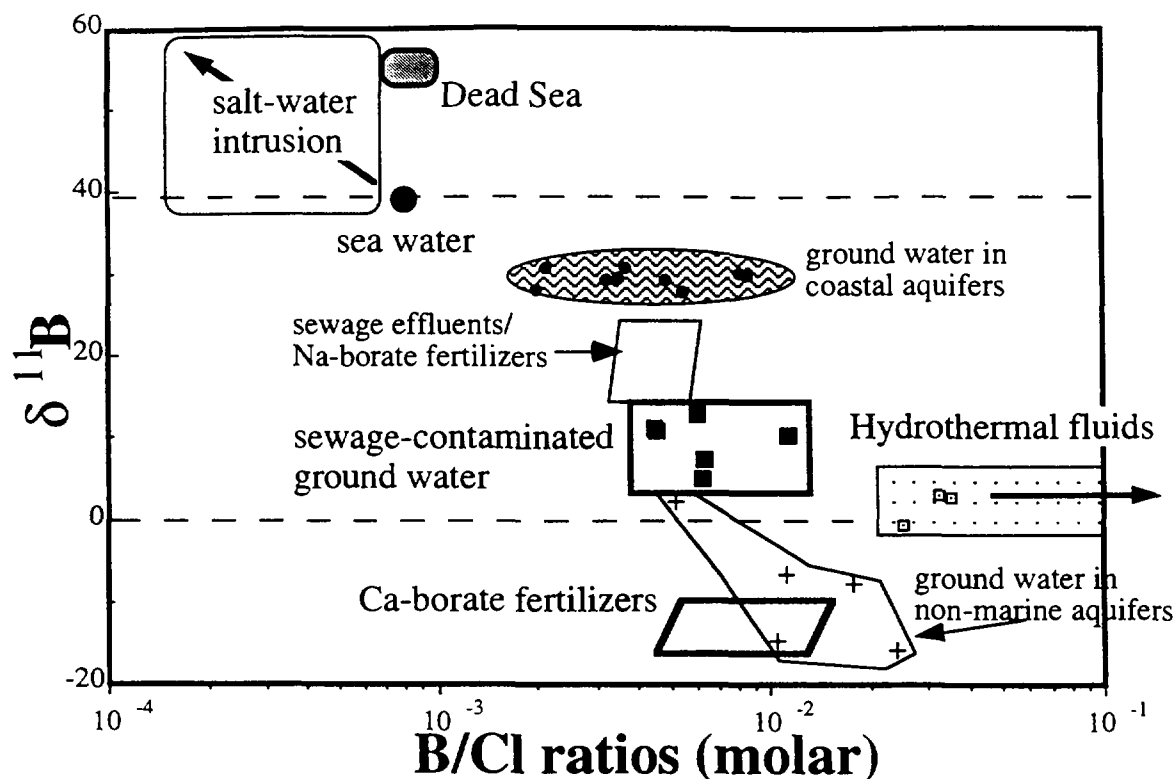


Fig. 9. Variations of B/Cl and  $\delta^{11}\text{B}$  values of potential contamination sources.

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