

An Aquatic Environmental Chemistry Student's Experiment: Influence of Human Activity on Water Sources

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ABSTRACT

This work presents a lab designed to study the influences of human activity on the surface water in the environment. Students sampled and performed measurements on water from nine sites that were influenced by various human activities: relatively natural sources (an environmentally impacted spring and stream), agriculture (water from a fish pond, and leachates from cow manure deposit and henhouses), industry (leachate from a tractor and machinery garage), recreational, and regular urban activity (water from a small recreational pond, a treated sewage reservoir, and discharge water from a washing machine). Measurements included a wide range of environmental physical and chemical parameters, and a broad screening for metals using a simultaneous inductively coupled plasma (ICP) emission spectrometer.

ONE OF THE MAIN PURPOSES of an undergraduate aquatic environmental chemistry course is to demonstrate to the students the crucial impact of human activity on water sources. During the years we developed a lab that focused on enlightening the different anthropogenic contributions to the water in the environment. To do that we choose several water sources in the same region, and performed a series of measurements.

When we started performing such experiments (during fall 2001) we let the students bring water samples of their interest. This approach led to large similarity between water samples, since environmental sciences students usually brought water samples from springs, streams, and ponds surrounding their living areas. A year later, we improved the experiments by choosing samples from the same geographical area, but subjected to different human activity. During fall 2003 we performed an experiment with nine different water samples. Five of the sampled sites surrounded the same geographical location: Yiron Plateau, in the northern Galilee. Four additional samples were taken to emphasize other aspects and influences of human activity.

Yiron plateau (33°4'35" N lat; 35°27'16" E long) was extensively studied for archaeological purposes, revealing prehistoric tools from Acheulean origin (Ohel, 1986a, 1986b). It is about 1 by 4 km, sloping from 808 m in the western side (across the Israel-Lebanon border) to 650 m in the east, above the deep gorge of Dishon Stream. The eastern part of the plateau is covered by a basaltic layer (see Fig. 1a). Prehistoric tools found in the layers below the basalt led to the conclu-

sion (Lamdan and Ronen, 1983) that it is relatively young and it belongs to the Quaternary system. Below the basalt, there is a deep layer of calcite from the Eocene (Bar Kokhba and Timrat formations, Avedat Group). In part of the plateau, 1- to 2-m paleosols are found in the contact between the two layers (Fig. 1). The upper layer of the paleosols shows a "roasted" layer of clay soil that was exposed to very high temperature (Fig. 1b). In studies performed on volcanic conduits of the basalt (see Fig. 2) in an artificial cut of the plateau (Matmon and Ron, 1999) a temperature of about 500°C was deduced, based on petrographic analysis. The area has a Mediterranean weather, with mild and very wet winters (average temperature of 7°C) and warm and very dry summers (25°C). The average total amount of precipitation is 780 mm, completely concentrated in 5 months (mid-October to mid-April). The upper neogenic basalts of the Upper Galilee are considered a phreatic aquifer, whereas the lower layers of clay and gravel underneath are the base of the aquifer (Wakshall, 1983). The lower layer of the basaltic soil has very low permeability (Ravikovitch, 1992), and rain that falls during winter months over the plateau infiltrates through the upper soil and flows along the slightly inclined plateau from northwest toward southeast. In the southeastern corner of the plateau, between the basalt and the soil layers below, there is a small water source named Yiron Spring (Fig. 2), which was one of the sampling sites. During years with relatively low precipitation, the source dries completely during the summer. However, in most years it drips a small amount of water the whole year round. The purpose of this sampling site was to give the picture of relatively unpolluted "pure" water in this region.

The second sampling site was a recreational natural pond placed in the center of the plateau (Fig. 2). The "lake" is a small depression in the basalt layer, exposing water from the aquifer described above, and forming a small pond of about 5000 m² and 2 m deep. About 30 years ago people from the village transformed the natural pond and its surroundings into a small zoo, and during the last 10 years it was extensively developed and opened to the public as a scenic attraction (Fig. 3a), which includes pedal boats, numerous birds, and several other animals (deer, sheep, alpacas, llamas, etc.) (Agam Hai, 2004). During peak seasons (weekends and holidays) it might host up to several hundred tourists each day. Water from this site was sampled to gather information on the influence of such recreational activity on the water source.

A third spot on the area was the sewage reservoir located in the eastern part of the plateau (see Fig. 2). Although only 2 to 4% of sewage effluent is reused for irrigation in the USA,

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Abbreviations: a.s.l.; above sea level; CCL; contaminant candidate list; DO; dissolved oxygen; BOD₅; biochemical oxygen demand measured after 5 days; COD; chemical oxygen demand; DWEL; drinking water equivalent level; EC; electric conductivity; USEPA; U.S. Environmental Protection Agency; ICP; inductively coupled plasma emission spectroscopy; ICPS; International Programme on Chemical Safety; MCL; maximum contaminant level; SAR; sodium adsorption ratio; TDS; total dissolved solids; TSS; total suspended solids; WHO; World Health Organization.

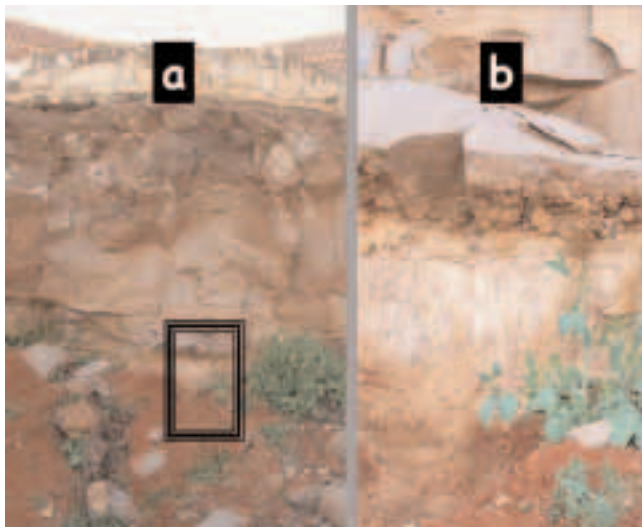


Fig. 1. (a) Basalt layer over a paleosol on the eastern part of Yiron Plateau, (b) magnification of the inset at the left, showing the roasted layer between the paleosol and the newer basalt above it.

Israel reused about 65% of the country's sewage for irrigation (Manahan, 2000, p. 259; Cikurel et al., 2003). On Yiron Plateau there is a small village (Kibbutz Yiron) of about 600 inhabitants. Extensive agriculture on the plateau includes orchards, a vineyard, a nursery for ornamental trees, and several henhouses. Sewage from all the urban activity is piped to an operational reservoir where it undergoes treatment and is pumped afterward to the open sewage reservoir mentioned above (Fig. 3b). The treated wastewater is then used for irrigation of orchards and vineyards. Water was sampled from the reservoir and analyzed to obtain information on the influence of normal urban activity and level of purification of such small and local sewage treatment plant.

Another sampling site was a garage located beside the village (Fig. 2). The agricultural equipment of the village is treated, washed, and stored at this garage. Water is drained from a washing platform (Fig. 3c) of the garage to a borehole. Workers wash tractors, sprayers, and all kinds of agricultural machinery in the platform. This site was chosen to bring data on the influence of machinery and mechanical devices, and regular treatment of such equipment on the water source.

The last sampling point in Yiron Plateau was near the henhouses (Fig. 2). Four to five times during each year the henhouses are emptied, and chickens are delivered to the slaughterhouse. After that henhouses are cleaned and disinfected

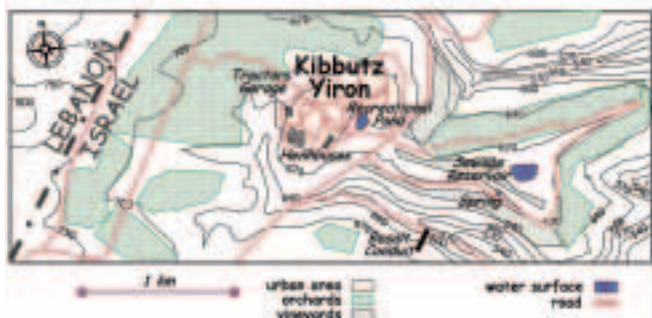


Fig. 2. Schematic map of the area surrounding Yiron Plateau, Upper Galilee, Israel.

from the manure accumulated during the growing season. The waste is mounded outside the site, and disposed of afterward. During the sampling period (December 2003) rain percolated through the mounds of chicken manure and created puddles (Fig. 3d). Water from the puddles was sampled to analyze how raising chickens influences the water that infiltrates through its residues.

Additional sampling spots were:

1. Water percolating through bovine manure mounds, accumulated near Sa'sa Village (about 10 km west of Yiron Plateau).
2. Water from Gush Halav Stream, mainly from natural springs, might contain occasional sewage outflows from G'ish Village (12 km south west of Yiron Plateau) and washes fields heavily pastured by cows.
3. Water from fishponds in the Hulah Valley, 20 km east of Yiron Plateau.
4. Rinse water from a washing machine.

All nine samples were tested for several analyses, as described in the experimental section. The main purpose of the study is to illustrate to the students how water that interacts closely with different human activities is influenced and affected.

In general, students are usually less experienced than laboratory workers. This results in less accurate quantitative results. In some cases results are missing in the tables due to analytical problems during the experimental procedures, related to inexperienced operators. Even with these limitations, the involvement in the process is part of the learning experience in an aquatic environmental chemistry course, and the enthusiastic students might still obtain clear qualitative results on the anthropogenic effects on water sources.

MATERIALS AND METHODS

Sampling Procedure

Water samples were collected during the second week of December 2003, in two 1-L clean plastic bottles from each site. Dissolved oxygen (DO) was measured in situ, at the sampling site, whereas all other measurements except metals concentrations (see the Metals section) were conducted within the



Fig. 3. Sampling sites surrounding Yiron's Plateau during December 2003: (a) Agam Hai recreational pond; (b) sewage reservoir; (c) tractor's garage washing platform; (d) puddles around henhouses.

same day. Another sampling was performed on four of the nine sites during the end of April 2004 to compare and confirm part of the measured parameters.

Chemical and Physical Measurements

Total Suspended Solids

The total suspended solids (TSS) were determined by filtering 200 to 500 mL of the sample water (depending on the apparent turbidity) through a pre-weighed (± 0.001 g) 55-mm Macherey-Nagel filtering paper in a Buchner funnel. The filters were then placed in an oven at 110°C for 90 minutes and then allowed to cool off in a desiccator and weighed again using an analytic scale. The TSS was calculated from the weight gain of the filter (Boehnke and Delumyea, 2000). The total dissolved solids (TDS) were also estimated by the procedure presented in Boehnke and Delumyea (2000). However, due to inaccuracies in the procedure arising from lack of experience, results are not presented.

Buffer Capacity, Alkalinity, pH, and Electrical Conductivity

The electrical conductivity was measured with a specific electrode (LF 323 set, WTW Germany), whereas the pH was determined using a Cyberscan 500 pH electrode. For determination of buffer capacity and the potentiometric alkalinity, 1-mL increments of 0.01 M HCl were added into a 250-mL beaker filled with 100 mL of sample water, while stirring continually with a magnetic stirrer. The pH was recorded after each increment until reaching pH 4. In cases where the pH declined too slowly, a 0.1 M HCl solution was used. The buffer capacity was calculated as the moles of acid required for a 1 unit pH decline of a liter of sample and the potentiometric alkalinity as the moles of acid required for adjusting the pH of a liter sample to pH 4 (Boehnke and Delumyea, 2000). Alkalinity was also measured using the indicator methyl orange. The procedure was the same as in the potentiometric alkalinity, but the endpoint of titration was set by the color change of the indicator, which changes its color at pH 4.3.

Dissolved Oxygen, Biochemical Oxygen Demand₅, and Chemical Oxygen Demand

Dissolved oxygen was measured in situ using a specific electrode (M.R.C Oxygen Meter DO-5508) and confirmed with Aquamerck Oxygen Test (see the Additional Chemical Measurements section). The biochemical oxygen demand (BOD) was measured by preparing approximately 1:10 and 1:50 dilutions, and subtracting the DO of the samples after 5 days of storage in the dark from the initial DO. Initial and diluted samples were brought to saturation in relation for oxygen by stirring during approximately 2 hours.

Chemical oxygen demand (COD) measurements were performed only on four samples taken during April 2004, using COD digestion vials (HACH 21258-15 pk/150) shaken and placed in a Spectroquant TR 420 (Merck) for 2 hours at 148°C. Digestion samples were allowed to cool off and the COD was determined by a HACH DR/2000 at 420 nm, a vial with distilled water was used as blank.

Metals

For determination of metals 20 mL of each sample were filtered through 0.45 μm Whatman paper filter, acidified to pH 2 by addition of concentrated nitric acid and measured using an ICP– Spectroflame simultaneous emission spectrophotometer.

Additional Chemical Measurements

The concentrations of nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and phosphate (H_2PO_4^-) were measured using the Aquamerck Compact Laboratory for Water Testing kit (Merck 1.11151.0001). To increase the sensitivity and accuracy in PO_4^{2-} measurements, we slightly modified the procedure: reagents were taken from the Aquamerck kit, but the final determination was performed by measuring the optical density using a Spectronic 20 Genesys spectrophotometer at the absorption peak of 882 nm with a 5-cm path length cuvette.

RESULTS AND DISCUSSION

The large amount of data obtained might be presented in several ways, according to the points of interest of the students or the lecturer. We divided it in the following tables, trying to focus on the influence the different anthropogenic activities have on the values measured:

- Dissolved oxygen, and oxygen related parameters (DO, temperature, percentage of oxygen saturation, BOD₅, COD)
- Sodicity related parameters (Na, Ca, Mg, SAR)
- Major nutrients (nitrate, nitrite, ammonium, phosphate, P, K)
- Elements listed in the USEPA Inorganic Contaminants List and National Secondary Drinking Water Regulations (USEPA, 2004) (As, Ba, Cr, Cu, Hg, Pb, Sb, Se, Al, Fe, Mn, Zn, total S)
- Other measured elements (Ni, B, Co, Si, Sr, V)
- Physical parameters (TDS, pH, alkalinity, buffer capacity, EC)

Dissolved Oxygen and Oxygen Related Parameters

The oxygen content of water varies with temperature, salinity, turbulence, the photosynthetic activity of algae and plants, and atmospheric pressure. The maximum solubility of oxygen in water decreases as temperature and salinity increase. Maximum values at sea level ranges from 15 mg L⁻¹ at 0°C to 8 mg L⁻¹ at 25°C. Variations in DO can occur during the day in relation to temperature and biological activity (i.e., photosynthesis and respiration). Since respiration processes utilize oxygen, waste discharges high in organic matter and nutrients can lead to decreases in DO concentrations as a result of the increased microbial respiration occurring during the degradation of the organic matter. Concentrations less than 5 mg L⁻¹ may adversely affect the functioning of biological communities and less than 2 mg L⁻¹ may lead to death of most fish species (Chapman and Kimstach, 1992).

Analysis of DO values performed during December 2003 (Table 1) show relatively high saturation values at the spring, fishponds, and stream waters. The sewage reservoir presents also a relatively high value, indicating relatively efficient treatment. Drainage from bovine manure and henhouse pud-

Table 1. Temperature (T), dissolved oxygen (DO), oxygen saturation level, and biochemical oxygen demand in 5 days (BOD₅).

Site	December 2003				April 2004		
	T	DO	Satura- tion	BOD ₅	DO	BOD ₅	COD
	°C	mg L ⁻¹	%	mg L ⁻¹			
Yiron Spring	17.6	7.5	78.7	3.9	7.9	0.6	0
Sewage reservoir	14.4	7.5	73.5	45.1	5.8	12.9	41
Cow manure drainage	13.6	2.3	22.1	56.7			
Gush Halav stream	12.7	9.4	88.7	36.5			
Henhouse puddles	17.6	4.3	45.3	134.2			
Garage drainage	15.3	0.4	4.0	172.9	4.4	36.2	88
Recreational pond	12.6	11.8	111.3	18.0	9.1	10.3	109
Washing machine	20.0	5.5	60.6	178.9			
Fish ponds	13.0	9.5	90.4	30.0			

dles show low DO values. The recreational pond is oversaturated with oxygen, indicating large photosynthetic activity in the pond's waters. Garage water is almost anoxic, leading to interesting correlated results in the iron in solution (see Table 4), due to reducing conditions.

Table 1 also presents biochemical oxygen demand after 5 days (BOD₅). The BOD₅ test was developed more than 100 years ago to determine the strength of waste water discharged into rivers. The 5-day time period was arbitrarily chosen based on the time of flow of the Thames River between London and the sea. The test is considered imprecise and errors may reach 20% (Logan et al., 2000). Despite the disadvantages, the technique is widely used to determine the pollution strength of wastewater and the quality of receiving waters (Radojevic and Bashkin, 1999, p. 197). Unpolluted water typically has BOD of 2 mg L⁻¹ or less, whereas water in contact with wastewater may have values up to 10 to 15 mg L⁻¹. Raw sewage can have BOD of up to 600 mg L⁻¹, whereas treated sewage effluent has BOD values that range from 20 to 100 mg L⁻¹ depending on the level of treatment applied. Some industrial wastes may have BOD values as high as 25 000 mg L⁻¹ (Chapman and Kimstach, 1992).

When we analyze December 2003 measurements considering those guidelines, we see that values measured at Yiron Spring are considered "polluted" as for surface quality classification. Water from the sewage reservoir at the same date fall into the range mentioned above for its category but are well above the Israeli standard for irrigation water that is set to 10 mg L⁻¹ (Cikurel et al., 2003), indicating a low-level treatment. Garage water during December 2003 show a very high value that may arise from machinery oils and other related organic compounds. High values in the washing machine water may be ascribed to biochemical degradable detergents. All other samples show highly polluted values related to contact with human or animal waste: the cow manure drainage, henhouse puddles, the stream (which has intensive grazing by pasture animals, and might even have some wastewater contribution), and the recreational lake (with a large amount of animals around it).

Measurement performed again on four of the sites during April 2004 show considerable lower values of both DO and BOD. The spring and the sewage reservoir values in April were within normal values. We ascribed the differences to the sampling date and weather influence: December measurements reflected mainly the end of the summer, since November and the beginning of December 2003 were relatively dry

Table 2. Measured concentrations of Na, Ca, and Mg, and evaluation of the sodium adsorption ratio (SAR).

Site	Na	Ca	Mg	SAR
	mg L ⁻¹			mM ^{0.5}
Yiron Spring	38.9	47.0	17.0	1.3
Sewage reservoir	55.8	64.1	30.1	1.5
Cow manure drainage	162.9	84.6	57.8	3.5
Gush Halav stream	54.7	97.7	18.0	1.4
Henhouse puddles	35.0	94.4	52.8	0.7
Garage drainage	35.3	85.7	30.3	0.9
Recreational pond	61.6	47.3	36.0	1.7
Washing machine	224.3	12.6	20.0	9.6
Fish ponds	11.0	52.2	7.7	0.4

months. April's measurements reflect the winter situation, since January and the beginning of February were rainy, and the total precipitation was above average, raising the flux of the spring. Differences in the oxygen concentrations in the garage might depend on the type of machinery or equipment washed lately, leading to large fluctuations. However, part of the decrease in BOD may be ascribed to the fact that the washing platform and adjacent drainage puddle (see Fig. 3c) was covered with concrete and rearranged during February 2004. In the process all the sediments accumulated were cleaned and removed, and the drainage is now piped to a concrete covered borehole.

We should emphasize that due to the lack of experience, and the dilutions needed for BOD determination, relatively low analytical errors might be considerably amplified. As mentioned before, large errors are observed in this measurement even when performed at optimal conditions.

It is interesting to compare BOD₅ and COD results for April 2004 measurements. The COD is a measure of the oxygen equivalent of the organic matter susceptible to oxidation by a strong oxidizing agent. The main difference between BOD and COD is that while the first determines biologically natural processes, the latter measures chemical oxidation, including nitrite, sulfite and ferrous iron (Radojevic and Bashkin, 1999, p. 202–206). Thus, COD of wastewater is generally higher than BOD (Chapman and Kimstach, 1992). This trend is observed in Table 1, except for Yiron's spring sample, where no chemically oxidizable pollutants are observed. The large difference in the recreational pond water (COD > 10 × BOD) might be ascribed to organic matter nonsusceptible to oxidation by biological processes.

Sodicity Related Parameters

Table 2 presents concentrations of Na, Ca, and Mg in mg L⁻¹, and evaluation of the sodium adsorption ratio (SAR), which is defined as the ratio between the soluble Na⁺ concentration to the square root of the sum of Ca²⁺ and Mg²⁺ concentrations, where all the parameters are measured in mM.

Sodium appears in the USEPA list of drinking water contaminant candidates (USEPA, 1998), since high levels of salt intake can be associated with hypertension in some individuals. This led USEPA to suggest a drinking water equivalent level (DWEL) of 20 mg L⁻¹. All of the samples except fish-pond water, present levels that were higher than that limit. Guidelines in other countries present values that range between 150 and 200 mg L⁻¹ (Radojevic and Bashkin, 1999, p. 451). The very low value suggested by the USEPA was strongly crit-

Table 3. Measured concentrations nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺), total phosphorus (P), phosphate (PO₄³⁻), and potassium (K).

Site	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	mg L ⁻¹		
				P	P from PO ₄ ³⁻	K
Yiron Spring	0.00	25	0.0	0.1	0.0	1.0
Sewage reservoir	0.70	5	4.0	4.2	1.5	84.1
Cow manure drainage	0.03	10	5.0	11.8	4.6	165.2
Gush Halav stream	0.05	0	0.1	1.7	1.1	24.6
Henhouse puddles	0.00	0	0.6	42.4	16.6	97.5
Garage drainage	0.20	0	0.1	93.2	9.6	16.7
Recreational pond	0.08	0	0.3	0.2	0.8	42.3
Washing machine	0.40	10	0.2	81.6		42.1
Fish ponds	0.00	0	0.1	0.6		3.3

icized, primarily due to their determination that sodium in drinking water is not a public health concern because of its extremely low level in drinking water and its small contribution to overall sodium intake. The argument was that food, which is the major source of sodium, is allowed to average 440 mg day⁻¹ under a “salt-restricted” medically supervised diet, and that controlling sodium content in food would address salt-restriction more directly. Furthermore, studies from 1996 published by the American Medical Association (Midgley et al., 1996) showed a lack of association between sodium and blood pressure, except for older individuals with existing hypertension. Finally, USEPA decided to include sodium on the contaminant candidate list (CCL) primarily as a vehicle to reexamine and correct the current, outdated guidance (USEPA, 2002). Therefore, sodium is listed, not as a Regulatory Determinations Priority, but as a Research Priority to allow time to evaluate and revise this specific USEPA regulation. When this is completed, USEPA will reevaluate whether sodium merits retention on the CCL for any further action. However, even USEPA publications denote that sodium levels in drinking water from most public water systems are unlikely to be a significant contribution to adverse health effects (USEPA, 1998).

Sodium in irrigation water may lead to swelling effects of the clay particles in soil, causing decreased permeability and severe problems of drainage in the soil (Stumm and Morgan, 1996). Such effect is known as “sodicity” or sodic soils. The SAR is considered as a crucial parameter for that matter: Irrigation waters with SAR > 13 mM^{0.5} are considered to cause severe permeability problems to the soil (Sparks, 1995). Thus, this parameter is of high interest in reused water, as for the case of the sewage reservoir. Israel proposed new Israeli standards for treatment of sewage effluent for unrestricted irrigation and discharge to streams, limits SAR < 5 mM^{0.5} (Cikurel et al., 2003). It can be seen that in our case, SAR values are generally low. However, it is interesting to denote the SAR in the washing machine water: due to the shortage of water in Israel, people with high environmental awareness sometimes use washing machine outflow for irrigation and gardening. The SAR value measured in the rinsing water (9.6 mM^{0.5}) is almost twofold the new Israeli standard, and might lead to sodification of the soil. Thus, even though this practice arises from very good intentions, it might have environmentally negative implications.

There is no evidence of adverse health effects specifically attributable to magnesium or calcium in drinking water. However, undesirable aesthetic and industrial effects due to the

Table 4. Measured concentrations of aluminum (Al), barium (Ba), iron (Fe), manganese (Mn), sulfur (S), and zinc (Zn).

Site	Al	Ba	Zn	Mn	mg L ⁻¹	
					S	Fe
Yiron Spring	5.2	19.6	8.8	1.0	5.04	0.008
Sewage reservoir	6.3	18.4	13.2	56.3	9.66	0.037
Cow manure drainage	22.5	14.3	23.6	71.8	14.38	0.118
Gush Halav stream	5.8	247.9	21.1	2.2	15.8	0.018
Henhouse puddles	16.0	23.1	13.6	679.0	6.74	3.530
Garage drainage	200.1	96.3	32.3	1416.0	6.33	14.190
Recreational pond	7.2	143.8	6.7	2.6	8.92	0.032
Washing machine	26.3	3.1	35.2	3.8	135.70	0.036
Fish ponds	7.0	33.3	9.2	1.7	6.48	0.020

Table 5. Measured concentrations of boron (B), cobalt (Co), nickel (Ni), strontium (Sr), vanadium (V), and silicon (Si).

Site	B	Co	Ni	Sr	V	mg L ⁻¹
						Si
Yiron Spring	18	2	0	288	5	23.4
Sewage reservoir	64	1	1	490	2	9.2
Cow manure drainage	103	7	17	202	7	15.4
Gush Halav stream	75	2	10	691	8	13.0
Henhouse puddles	186	8	17	266	7	7.6
Garage drainage	174	41	46	419	22	9.5
Recreational pond	90	2	4	389	4	0.0
Washing machine	62	3	8	35	7	39.3
Fish ponds	32	2	3	130	9	0.7

presence of calcium or magnesium in drinking water may result from its contribution to hardness.

It is interesting to notice that the high SAR in washing machine water doesn't arise merely from a Na⁺ increase, but also from a relatively low Ca²⁺ value. This results, combined with the large phosphorus (Table 3) and sulfur (Table 4) values, and the low strontium value (Table 5), might be ascribed to the activity of softening ingredients usually used in detergents, reducing the concentration of hardening cations as calcium, magnesium, and strontium.

Major Nutrients

Table 3 presents a series of chemical parameters correlated to plant nutrients in the water. Some values are missing in the table due to analytical problems in the experimental procedures.

Nitrogen is essential for living organisms as an important constituent of proteins. In the environment, inorganic nitrogen occurs in a range species as nitrate (NO₃⁻), nitrite (NO₂⁻), and the ammonium ion (NH₄⁺). Ammonia and the related ammonium ion usually comes from excretions by biota, and from discharges into water bodies by some industrial processes. It is also a component of municipal or community waste. The maximum concentrations allowed in drinking water range from 0.5 to 2.0 mg L⁻¹ in the EU and Russia, respectively (Chapman and Kimstach, 1992). In our samples high concentrations were found in water in close contact with human or animal waste, especially in the cow manure drainage and the sewage reservoir, and to lesser extent at the henhouse puddles and recreational pond.

The nitrate ion (NO₃⁻) is the common form of combined nitrogen found in natural waters. It may be biochemically reduced to nitrite (NO₂⁻) by denitrification processes, usually under anaerobic conditions. Such conditions can be observed in the anoxic waters of the garage sample, were no nitrate is

observed. Concentrations in excess of 20 mg L⁻¹ nitrate usually indicate pollution by human or animal waste, or fertilizer runoff. The World Health Organization (WHO) (Chapman and Kimstach, 1992) recommended a maximum limit for NO₃⁻ in drinking water of 50 mg L⁻¹ (equivalent approximately to 11 mg L⁻¹ N). In lakes and ponds, concentrations of nitrate in excess of 1.0 mg L⁻¹ tend to stimulate algal growth and indicate possible eutrophic conditions. High nitrite concentrations (higher than 1.0 mg L⁻¹) are generally indicative of industrial effluents and are often associated with unsatisfactory microbiological quality of water.

In all our samples concentrations of nitrate and nitrite are below the maximum levels allowed and mentioned. The relatively high value of nitrate measured in the spring water (25 mg L⁻¹ NO₃⁻, equivalent approximately to 11 mg L⁻¹ nitrogen as nitrate) might be ascribed to the intensive agriculture, irrigation, and fertilizer application over Yiron Plateau. Similar nitrate values were measured during April 2004.

Table 3 also shows results for phosphorus measured with ICP, and phosphorus measured from phosphate measurements, colorimetrically. Since values of total P > 0.02 mg L⁻¹ are considered "eutrophic" (Radojevic and Bashkin, 1999, p. 142), all our samples match those criteria. Differences between total phosphorus and phosphates might be in most cases due to problems in the experimental determination of the phosphate: the molybdate reaction that measures the phosphate ion, is efficient mainly with orthophosphates and less effective with condensed or organic phosphates; whereas ICP measurements are sensitive to all P. That explains the higher values generally obtained for total phosphorus measurement. The only case with higher values for the phosphate is the recreational pond water. Such effect might arise from the filtration procedure performed for the total phosphorus measurement with ICP, which was not performed for the phosphate-ammonium molybdate reaction.

The main source for phosphorus in the environment is human and animal waste, sewage, agricultural drainage, and detergents containing phosphorus (Radojevic and Bashkin, 1999, p. 238; Boehnke and Delumyea, 2000). In samples interacting with animal or human activity (sewage reservoir, stream, cow manure, lake, fish ponds) the first two sources are important. In the garage and washing machine samples, detergents are the main contribution. As for the henhouses: chicken manure may contribute; however, we assume that some of the phosphorus comes from detergents and disinfecting substances employed in the cleaning of the premises.

Measured amounts of potassium are also shown in Table 3. Potassium is needed for plants, animals, and humans, but at high concentrations it might be poisonous. Laying down a potassium standard for drinking water quality is considered obsolete. In 1992 the WHO eliminated the potassium parameter in its guidelines stating that it can be omitted, since the parameter has no relevance to water quality to the consumer (Baert et al., 1996). Older standards in Flanders were set to 12 mg L⁻¹, and changed in 1991 to 30 mg L⁻¹. In the "Blankaert" water production center of the Flemish water company, potassium contributions were mainly ascribed to industrial discharges, and only marginally to drainage from farmlands. As an example the authors mention discharge from the soybean-processing industry, which contained 1000 mg L⁻¹ K. Our "industrial" sample (garage), does not have high

potassium amounts, emphasizing that the main source of potassium in water is from organic sources. Very high values are measured in samples that were in contact with mammal or bird waste (sewage, cow manure, henhouses, recreational pond), whereas fish do not seem to contribute considerably to potassium concentrations (fish ponds). It is interesting to notice that even though basalt rock and soils contain relatively high percentage of potassium (Ravikovitch, 1992), this does not permeate to the water, and remains bound to the soil particles. Thus, increase in the amounts of potassium might indicate leakage of sewage to the water source, although no microorganisms are measured (Friedler and Green, 2001).

USEPA Inorganic Contaminants List and National Secondary Drinking Water Regulations

Table 4 includes measured concentrations of aluminum, barium, iron, manganese, sulfur, and zinc. Values measured for other USEPA inorganic contaminants (As, Cd, Cu, Cr, Hg, Pb, Sb, Se) were below the limits of detection of the instrument, and were omitted.

Aluminum is the third most ubiquitous element in the earth crust. However, due to the insolubility of the parent minerals, the concentration in the water is rarely more than 1000 µg L⁻¹ (Butcher, 1988). Aluminum is not considered to be toxic in water at normal pH, but increasing amounts are leached as the pH decreases, leading to fish deaths, although the mechanism is still not fully resolved (Radojevic and Bashkin, 1999, p. 263). Considering those facts, British Columbia guidelines for freshwater aquatic life limit the maximum aluminum concentration for water in pH > 6.5 to 100 µg L⁻¹, whereas for lower pH, where aluminum solubility increases, an equation is given to evaluate the limiting value (Butcher, 1988). A secondary maximum contaminant level (MCL) was set by the USEPA to 50 to 200 µg L⁻¹, due to aesthetic effects of water coloring (USEPA, 1992). The main anthropogenic source of aluminum is its use as coagulant. It might be also a component in dyes, paints, disinfectants, abrasives, catalysts, and other industrial uses. Such uses may explain its relatively high value in garage drainage water, which is the only measured value slightly above the USEPA secondary MCL mentioned above.

Barium is used in making a wide variety of electronic components, in metal alloys, bleaches, dyes, fireworks, ceramics, and glass. Its MCL was set to 2000 µg L⁻¹ because USEPA believes that given present technology and resources, this is the lowest level to which water systems can reasonably be required to remove this contaminant should it occur in drinking water (USEPA, 2004). Considering the sources mentioned it is hard to explain the relatively high amounts found in Gush Halav Stream and in the recreational pond. However, low barium amounts might be correlated with high sulfate concentrations leading to the precipitation of BaSO₄ (see the Sulfur subsection). It is interesting to notice that UK guidelines for barium in drinking water (Radojevic and Bashkin, 1999, p. 451) are considerably lower (10 µg L⁻¹), and almost all of our samples would be considered barium-polluted under such standards.

Iron is a micronutrient essential for living organisms. The main sources are chemical weathering of geological materials, waste water from the textile or painting industry, and

agricultural sources. High concentrations of iron are not known to have adverse health effects (Radojevic and Bashkin, 1999, p. 255), but may lead to problems of bittersweet taste, smell, and staining in laundry. Due to such problems it is considered a secondary contaminant and its maximum level in drinking water is set to $300 \mu\text{g L}^{-1}$ (USEPA, 1992), and in irrigation water (Cikurel et al., 2003) to $2000 \mu\text{g L}^{-1}$.

It should be mentioned that the pipelines that lead the water to the sewage reservoir are made of iron. In the recreational lake there are several iron sources in direct contact with the water (piers, boats, fences, etc.). Thus, if the release of iron was correlated directly with the amount of metal that comes in contact with the water, we should expect high iron concentrations in those samples. However, results for both samples were low, whereas very high concentrations were measured in the garage and the henhouse samples. We ascribed part of the garage results to residues of paints and other industrial materials, which make more influence than mere contact with ferrous pipeline. But the most important aspect that should be considered for the garage sample is the oxygen amount in the water. In most samples the dissolved oxygen saturation levels are relatively high, but in the garage water it is almost zero (see Table 1). Such conditions might lead to reduction of iron(III) to iron(II), which is considerably more soluble at the pH values measured (Howard, 1998). Under such conditions, the amount of dissolved iron in water is considerably high, as can be seen in Table 4.

Manganese is considered a problem due to aesthetic effects of metallic taste, black staining, and dark coloring of the water (USEPA, 1992). The secondary maximum contaminant level for drinking water is set to $50 \mu\text{g L}^{-1}$. Thus, samples from the sewage reservoir, cow manure, garage, and henhouses are above those levels. Levels measured on the latter two samples are even above quality criteria for irrigation water on coarse-textured soil, which is $200 \mu\text{g L}^{-1}$ (Radojevic and Bashkin, 1999, p. 454). However, the water that is indeed used for irrigation (sewage reservoir) meets this demand.

When considering the reasons for the very high level of manganese in garage waters, we should mention that its compounds are frequently used in various industrial processes and consumer products, including manufacturing and production of alloys of several metals as steel, aluminum, and copper; as an ingredient of alkaline batteries, electrical coils, welding rods, glass, dyes, and paints; as dryers for paints, varnishes and oils, fertilizers, disinfectants, and animal foods; and as an anti-knock gasoline additive for internal combustion engines (Nagpal, 2001). The high concentration in henhouse samples can be related to the income from residues of disinfectants and animal food, which accumulated in the waste removed from the henhouse floor before and during their cleaning. But the combination of high iron and manganese concentrations in both garage and henhouse samples might be ascribed to reducing conditions that increase the solubility of both metals (Howard, 1998, p.69).

The main natural source of sulfur is the weathering and dissolution of sulfur-containing minerals, predominantly gypsum (Radojevic and Bashkin, 1999, p. 251). Direct anthropogenic sources include industrial and municipal wastes, and agricultural drainage. In our samples, we can observe a very high concentration in washing machine water samples, while all other

samples are in the same order of magnitude, and when transformed to sulfate concentrations ($15\text{--}50 \text{mg L}^{-1}$) are similar to usually reported values for unpolluted water. It is interesting to present a criticism for one of the usual methods for determination of sulfate—the turbidimetry technique (Radojevic and Bashkin, 1999, p. 252). This method is based on BaSO_4 precipitation. Since K_{sp} of the salt is about 1×10^{-10} , very low concentrations of sulfate might be usually discovered by reaction with Ba^{2+} salts. In general, a calibration curve is prepared, where the amount of Ba^{2+} solution added is correlated to the sulfate concentration. However, our measurements demonstrate (Table 4) that barium concentration in sampling waters varies considerably, and might reach levels of 1mM (e.g., about 0.15mg L^{-1} in the recreational pond water). Such level would cause precipitation of sulfate concentrations of 9mg L^{-1} , even with no barium added. Thus, measuring SO_4^{2-} concentration against lab-prepared standard samples, without testing the concentration of barium in the samples may lead to errors.

Zinc is a trace constituent in most rocks, and many minerals contain zinc as a major component from which the metal may be recovered. The mean zinc levels in clay minerals and basalt rocks may reach 100mg kg^{-1} . Since it is an essential element, environmental assessment must be conducted on a site-specific basis. Zinc is unlikely to be leached from soil owing to its adsorption on clay and organic matter (ICPS INCHEM, 2001).

Recommended guidelines for Zn indicate an instantaneous maximum of $5000 \mu\text{g L}^{-1}$ for drinking or recreational water, $2000 \mu\text{g L}^{-1}$ for livestock watering, and $1000 \mu\text{g L}^{-1}$ for irrigation use (Nagpal, 1999). As seen in Table 4, all measured values are well below those limits. Anthropogenic sources of Zn include printing processes, construction materials, zinc-covered metals, zinc-containing fertilizers or pesticides, batteries, and animal manure (Radojevic and Bashkin, 1999, p. 365). Considering those sources, we may explain the slightly higher values found in the washing machine water (contact with galvanized metal) and the garage water (batteries, metal, pesticides, and fertilizers).

Additional Measured Chemical Elements

Table 5 shows concentrations of boron, cobalt, nickel, strontium, vanadium, and silicon in the different samples, as measured by ICP.

Boron in environment usually appears as borax, or as minerals combined with magnesium, calcium, sodium, and so forth. It is used in a variety of products including glass, cleaning products, agrochemicals, insecticides, flame-proofing compounds, corrosion inhibitors, and antiseptics (Moss and Nagpal, 2003). Anthropogenic sources of boron in the environment might yield logical explanations of the high boron values found in some of the samples: sewage sludge and effluents may lead to high values in the cow-manure and henhouse drainage. Boron use in cleaning compounds and agrochemicals might explain high measured values in garage samples. Boron limit for irrigation reuse in Israel is $400 \mu\text{g L}^{-1}$ (Cikurel et al., 2003), and was determined considering sensitivity locally observed, since in arid climates boron toxicity is more of a problem than in temperate climates (Moss and Nagpal, 2003). This value is more rigorous than the maximum

Table 6. Measured total suspended solids (TSS), pH, buffer capacity, potentiometric alkalinity, and electric conductivity (EC).

Site	TSS	pH	Buffer capacity	Potentiometric alkalinity	EC
	mg L ⁻¹		mM	mg CaCO ₃ L ⁻¹	µSi cm ⁻¹
Yiron Spring	60	7.47	0.6	141	275
Sewage reservoir	738	8.31	1.0	450	110
Cow manure drainage	830	8.51	1.8	1760	722
Gush Halav stream	1402	8.58	0.8	190	919
Henhouse puddles	2030	8.62	2.0	1450	918
Garage drainage	120	7.07	2.5	850	
Recreational pond	580	8.98	0.4	110	926
Washing machine	652	10.49	3.0	900	2820
Fish ponds	405	8.97	0.3	186	374

recommended in Canada even for blackberry, which is considered a very sensitive crop. All our samples present boron values lower than any recommended guideline.

Drinking water supplies usually contain from less than 1 µg L⁻¹ to occasional maximum concentrations of 30 µg L⁻¹ vanadium. Almost all our samples are in the indicated range, and match average concentrations presented in comprehensive surveys of approximately 5 µg L⁻¹ (ICPS INCHEM, 1988). The main use of vanadium is in ferrous metallurgy, which might explain its relative abundance in the garage water.

Strontium in water usually arises from rock composition. No enforceable standards have been established, but a health advisory is set to 17 000 µg L⁻¹ (DNR, 1996). Davis and DeWiest (1970) report concentration in most ground waters generally range between 10 and 1000 µg L⁻¹. All values in our measurement are in this range. It is interesting to notice the relatively low value in the washing machine sample. This, combined with the relative low values of calcium (see Table 2), should be ascribed to softening components introduced to increase efficacy of laundry powders and detergents.

Nickel is a ubiquitous trace metal and occurs in soil, water, air, and in the biosphere. Levels in natural fresh water had been found between 2 and 10 µg L⁻¹. Effluents from waste water treatment plants have been reported to contain up to 200 µg L⁻¹ (ICPS INCHEM, 1991). Nickel alloys (as stainless steel) and nickel compounds are used in vehicles, processing machinery, tools, electrical equipment, household appliances, coinage, catalysts, pigments, and in batteries; thus, it reaches sewage water mainly from industrial uses. The use in batteries and machinery might explain the relatively high values found in the garage water. In the USA there was a MCL of 100 µg L⁻¹, which was remanded on 1995. Limitations and nickel guidelines in drinking water range from 10 µg L⁻¹ in Japan to 50 µg L⁻¹ in the UK and Denmark. For irrigation and livestock purposes, limits in Canada are 20 and 50 µg L⁻¹, respectively (Radojevic and Bashkin, 1999, p. 452). As can be seen, most our samples are below those limiting values. Only garage water should not be allowed for irrigation purposes, although it might be used for livestock drinking (as for nickel pollution concerns).

Silicon is abundant in rocks and alumino-silicate minerals. Silicon concentration in water varies between 1 and 40 mg L⁻¹ (Radojevic and Bashkin, 1999, p. 365; Chapman and Kimstach, 1992). Most samples are indeed in this range. However, it is environmentally interesting to notice that water sources where considerable amounts of algae might be found (recreational pond and fishpond) are below the regular values. Pe-

tersen (1998) quotes several studies that relate decline of some diatom algae species due to the depletion of silicon, and the total exhaustion of silicon caused by eutrophication of Lake Erie, for example. Those results indicate an inverse correlation between some algae population and silicon concentration. The recreational pond water contains very large quantities of algae, as it arises from the over-saturation in dissolved oxygen (see Table 1). A less pronounced similar effect might be observed in the fishpond water. Both samples show low silicon amounts.

Additional Physical Parameters

Table 6 shows measured total suspended solids (TSS), pH, buffer capacity, potentiometric alkalinity, and electrical conductivity (EC). Results for alkalinity determined by methyl orange were very similar to those measured by potentiometric titration (differences less than 5%) and are not reported.

Solids are materials remaining in water after drying. Differentiation between suspended and dissolved solids is usually determined by filtration. Solids degrade quality of water for all purposes, by affecting osmoregulation of freshwater organisms, formation of sludge deposits, and increasing costs of mechanical and chemical treatment (Radojevic and Bashkin, 1999, p. 158). Solids in water may be from natural (soil and bedrock erosion) or anthropogenic sources (domestic wastes, road runoff, industrial processes, and so on). Total suspended solids is important in the analysis of waste water, and in the past was used as a measure of pollution. The degree of contamination is defined as *weak*, *medium*, or *heavy* for TSS values of 200, 500, or 700 mg L⁻¹, respectively (Radojevic and Bashkin, 1999, p. 159). According to those values, all samples except the spring and the garage should be considered medium or heavily contaminated. However, it should be emphasized that TSS is not intended to measure the concentration of any specific chemical, but rather give an empirical estimate of water quality that might mislead: the garage sample is "unpolluted" under this consideration, even though all other parameters show heavy pollution.

The pH of all samples is between 7 and 9, except for the washing machine, where a higher value is observed. At pH values measured for all samples except washing machine discharge, the alkalinity should be ascribed mainly to HCO₃⁻. Alkalinity is not considered to be a water pollutant and its main environmental significance is as an indicator for the susceptibility of the water to pH changes as a result of pollution. Alkalinity must be known to evaluate amount of chemicals needed for water treatment techniques (Manahan, 2000, p. 70).

Alkalinity values 20 to 200 mg L⁻¹ are typical for freshwater. The recreational pond, Gush Halav stream, fish ponds, and Yiron Spring values fall within that range, whereas all others present larger values. Untreated domestic waters usually present alkalinity between 50 and 2000 mg L⁻¹ (Radojevic and Bashkin, 1999, p. 181). Since alkalinity depends on several factors as carbonate mineral dissolution and precipitation, organic matter decomposition, and assimilation of nutrients (Stumm and Morgan, 1996), it is difficult to correlate it to a single parameter. Ammonia (strong base) and weak organic acids may also contribute to alkalinity (Manahan, 2000); thus, large values in our samples might be ascribed to the high organic pollution.

From a geochemical point of view Yiron Spring has alkalinity and calcium concentrations very close to calcite saturation (a saturation index of 0.99) all other samples are oversaturated with respect to calcite inducing eventual deposition of calcareous sinter, or so-called *tufa*. All samples are undersaturated in respect to gypsum, even if we consider all sulfur to exist as sulfate (Lindsay, 1979).

Electrical conductivity is a measure of the ability to convey electrical current, and it is related to the concentrations of ions. Usual values for fresh water ranges from 50 to 1000 $\mu\text{Si cm}^{-1}$, but may exceed those limits in polluted samples or waters receiving large volumes of land runoff (Chapman and Kimstach, 1992). Compounds that do not dissociate are poor conductors; hence, organic compounds and pollutants have generally a minor influence on the EC (Radojevic and Bashkin, 1999, p. 169). That effect is noticed in most samples with organic pollution (sewage, cow and hen manure drainage, recreational pond, and so forth). On the other hand, washing machine water with high content of salts and ionic surfactants added show an EC value higher than all other samples.

It is interesting to note the differences between buffer capacity and alkalinity: *buffer capacity* indicates the amounts of acid needed to lower the pH in one unit, whereas *alkalinity* refers to the buffer capacity needed to lower the pH to 4. It is easy to convert the values in Table 6 to similar units by multiplying the buffer capacity with the molar weight of CaCO_3 (100 g mol^{-1}). For the pH values measured in our sample, all buffer capacity measurements are lower than the alkalinity, and this is obvious. However, we should test each case individually: for example, an addition of acid equivalent to 1.8 mM CaCO_3 (180 mg L^{-1}) will lower the pH of the henhouse puddles to about 7.8 to 7.9 (buffer capacity of 2 mM), the pH of the cow manure drainage will change in exactly one unit to about 7.5 (buffer capacity of 1.8 mM), but the pH of Gush Halav stream will be lowered to almost 4 (buffer capacity of 0.8 mM , with alkalinity of 190 mg L^{-1}). All three samples have almost the same initial pH, but the same amount of acid added per liter of water will lead to completely different final acidities.

CONCLUSIONS

We may summarize the properties of each water source and the influences of human activities as they arise from the Results section by comparing measurements with the new Israeli proposed standard for effluent treatment and discharge to streams, prepared by the Inbar Committee (Cikurel et al., 2003).

Yiron Spring. The water from the spring may be used as a baseline for the samples from their area. It has a high oxygen saturation level, low BOD, and no COD in April measurements. The SAR is low, and no danger for sodification of soils might be expected on irrigation. Nitrate concentrations are relatively high, due to intensive agriculture in the basin, but neither ammonium nor nitrite were measured. No phosphate was observed, even though a low concentration of phosphorus was measured. Concentrations of all metals measured were within normal levels. Conclusion: the spring is not polluted, and the waters from it might be used for any desired purpose after testing for microbial qualities.

Sewage Reservoir. Water from this source has a relatively high organic content, as it arises from its BOD and COD.

However, April measurements meet Israeli standards for irrigation. All other parameters meet new Israeli standard for reused water, except the TSS. Relatively high nitrite and ammonium concentrations were measured, and total phosphorus amounts are quite close to the limiting value for irrigation (5 mg L^{-1}) and well above the limiting value for discharge to streams (0.2 mg L^{-1}). No sodification danger is expected on irrigation. In conclusion, the sewage reservoir might be used for irrigation after filtration to reduce TSS.

Cow Manure Drainage. A very interesting sample as for the low oxygen saturation level and very high content of nutrients. The iron concentration is relatively high, and might be ascribed to the slightly reducing conditions due to oxygen level mentioned. Ammonium concentrations are well above limiting value for discharge to streams (1.5 mg L^{-1}). Considering that this leachate may reach surface streams, the amounts of phosphorus are hazardous, and are more than 50-fold the maximum allowed for discharge, and twice the maximum allowed for irrigation. Even Na concentrations are close to the limit allowed, and potassium concentrations are the higher measured in all our samples. In summary, discharge of those waters to streams should be controlled, considering mainly the concentration of nutrients, to avoid environmental hazards.

Gush Halav Stream. The raging flow of the water leads to high oxygen saturation levels, but the BOD indicates a high organic load, either from occasional sewage discharged or from leaching of pasturing animals manure. This is also reflected in the relatively high phosphates, potassium, and traces of ammonium. There are some interesting results that might need additional research—even though in the allowed range, barium and strontium concentration are the highest measured, and we could not find a coherent explanation for those values. In conclusion, considering most of the BOD is due to pasturing on the stream course, fences and controlled pasturing might be applied to lower levels of organic matter in the course of the water (Line et al., 2000).

Henhouse Puddles. In general, results are similar to those measured for the cow manure drainage, but even more extreme. Dissolved oxygen is slightly higher, and BOD reaches very large values. All nitrogen is ammonium based, and total phosphorus concentrations are 210-fold larger than the allowed for stream discharge. Potassium concentrations are also very high. Manganese and iron values are above limits allowed for irrigation (0.2 and 2.0 mg L^{-1}), and might indicate reducing conditions. In conclusion, henhouse puddles are severely polluted, with high concentrations of manganese, iron, and nutrients. It should be advised to remove chicken manure mounds immediately after emptying and cleaning the henhouses to avoid formation of highly polluted puddles during the winter, with eventual hazardous runoff toward the surrounding rivers.

Garage Drainage. Almost zero DO, leading to reducing conditions, confirmed by very high iron and manganese concentrations, way above the standards for irrigation. The BOD is high in both December and April, and the COD is very high during April measurements. Garage drainage was the only sample with limiting polluted concentrations of nickel and cobalt ($50 \mu\text{g L}^{-1}$ for both metals) and relatively high vanadium concentrations. All the results indicate high interactions with dyes, paints, oils, greases, and other industrial

products. Very high phosphorus values and great difference between total phosphorus and phosphates indicate large amounts of condensed organic phosphates arising from cleaning substances and detergents, but may be also a result of pesticides leachate from sprayers washing. In conclusion, the waters from the garage platform should be gathered in a septic tank and safely treated before releasing it to the environment. The main goal should be reducing phosphorus and BOD, while monitoring and controlling heavy metals to avoid dangerous pollution.

Recreational Pond. The large amount of algae and high photosynthetic activity can be easily confirmed by measuring changes in DO during the day; measurements performed during August 2004 show DO = 5.5 mg L⁻¹ at dawn, whereas at noon DO increases to 9.4 mg L⁻¹. Values measured in December and April during the morning show oversaturated levels. The COD values during April are very high, and the large COD/BOD ratio might be ascribed to nonbiologically degradable organic matter. Nitrogen is mostly nitrite and ammonium, with no measurable nitrate. Phosphate concentrations were well above eutrophic limits, allowing development of large algae populations. The high amount of algae lowers almost to zero the concentrations of silicon. The alkalinity and buffer capacity makes the pond relatively susceptible to pH changes if large volumes of acid come in contact with the pond. In conclusion, the pond is eutrophic. During summer algae bloom, the waters are covered with a sticky green layer, and aesthetic problems lead to direct implications to visitors' amount in the premises. Such a condition might be corrected by lowering the inputs of nutrients, either by avoiding contact of animal excrements with the water, or by reducing the amounts of visitors. A small wetland system based on circulation of pumped water through pools of suitable vegetation may bring partial solution to the problem by consuming nutrients, increasing DO during night hours, and reducing BOD. The recreational pond's management board is considering applying such a system by next year.

Washing Machine. Very high BOD might arise from enzymes and other biodegradable organic compounds in the detergents. Other effects ascribed to the washing powders are high phosphates, low calcium, magnesium, and strontium that might be ascribed to softening chemicals (high sulfur and phosphorus values), high sodium, EC, buffer capacity, and pH. All those results lead to high SAR and danger of sodification if those waters are used for irrigation. In conclusion, washing machine rinsing water still contain high amounts of organic compounds and traces of detergents, which makes the water unsuitable for release into the environment without additional treatment.

Fish Ponds. Water from fishing ponds have relatively low values of nutrients, when compared with other agriculture-related sources, indicating that the impact from fish agriculture to nitrogen, phosphorus, and potassium concentrations is considerably lower than mammals and bird contributions. Low silicon concentrations and a relatively large DO measured at daylight indicate large amounts of algae. Most pollutants appear in low values, indicating relatively clean water. However, phosphorus values are higher than those allowed for discharge to streams. In conclusion phosphorus values might be the main problem for the release of outflow from fish ponds to the

river. In general, such problems were treated in the Hulah Valley area in northern Israel, by partial restoration of the wetlands. The general purpose is to minimize the amounts of phosphate that flow downstream, toward the Lake of Galilee, to avoid eutrophication hazards in this important water source (Gophen et al., 2003).

This article presents a set of measurements performed on water sources from the same area, to induce students to think about the influences of anthropogenic activities on the water in the environment. We are convinced that this kind of work enlightens broad aspects of the complexity of the system, and helps to understand better how to cope with environmental problems.

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