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Quality of Roof-Harvested Rainwater as a Function of Environmental and Air Pollution Factors in a Coastal Mediterranean City (Haifa, Israel)

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Abstract: The quality of roof-harvested rainwater in a Mediterranean climate, which is characterised by dry summers and erratic wet winters, was studied. The effects of environmental factors (rain depth, length of dry period between consecutive rain events, time since the beginning of the rainy season, roof type, wind speed, and wind direction) and air pollution parameters (O_3, SO_2, NO_2, NO, $PM_{2.5}$, and $PM_{2.5–10}$) on roof runoff quality were studied. Three roofs of three common types (concrete, steel sheets, and tiles) were constructed. Roof-generated runoff was collected over two rainy seasons (>50 rain events) and were analysed for presence of metals, chemical and physical constituents, and faecal coliforms (a total of 23 parameters). Rain depth and runoff volume from each roof were recorded for each rain event. Most parameters examined complied with the Israeli potable water regulations. A stepwise multivariate linear regression established a significant effect of roof type on runoff pollutant concentrations, especially for ones generated by the roof material itself (e.g., Ca from the concrete roof and Zn from roof tiles). A significant effect of various air pollutants on the quality of roof-runoff water was found, as explained by rain washing off pollutants that accumulated in the atmosphere during the antecedent dry period. Both O_3 and $PM_{2.5–10}$ affected 17 quality parameters each. Rain depth affected only four out of the 23 water quality variables. In contrast, the length of the dry period between consecutive rain events was an important factor, affecting 12 roof-runoff quality variables.

Keywords: rainwater harvesting; roof runoff quality; environmental factors; air pollution; Mediterranean climate

1. Introduction

In recent years, over-exploitation of natural water sources by anthropogenic activities has led to negative environmental effects, and, consequently, to a growing need for developing new sources of water. Pressure on natural water sources can be relieved by using alternative sources for uses that do not necessarily require potable water. One of these alternative sources is onsite rooftop rainwater, which may be used for toilet flushing, garden irrigation, laundry, car washing, etc. Harvested rainwater is used not only in areas where water supply is limited by climate or infrastructure, but recently also in well-developed, water-ample regions. It is driven by an increasing water demand and rising awareness of the negative environmental impacts of rainwater runoff, such as soil erosion and non-point source pollution [1–3]. Onsite rainwater harvesting also serves as a means for reducing urban flooding and for increasing water supply, with minimal costs for storage and use-dependent treatment.

Although rainwater is generally considered as non-polluted, or at least not significantly polluted, it may be acidic and/or contaminated by dirt, organic micropollutants, metals, pesticides, etc., which affect the quality of rainwater runoff [4]. Forster [5] suggested several factors that influence the quality of roof-harvested rainwater: roof material (chemical characteristics, roughness, surface coating, age, etc.); physical boundary conditions (size, slope, direction, and exposure); location (proximity to pollution sources); chemical properties and concentration of the considered substance (vapour pressure, water solubility, etc.); precipitation event characteristics (rainfall intensity and depth, wind characteristics, pollutant concentration in the rain); and, local meteorological factors (season, weather characteristics, length of antecedent dry period). Taffere et al. [6], in a study performed in Mekelle (Ethiopia), described other important factors that are related to air pollution. They indicated a clear effect of source-specific contaminants from traffic and industrial areas, while residential areas were found to be relatively free from immediate major pollutant sources.

The physicochemical quality of roof runoff, as reported by many studies, is quite similar to potable water quality guidelines, with the notable exception of pH values (pH of rainwater is 4.5–6.5, increasing slightly once on the roof [4,7]). However, wide variations in concentrations of ions, like lead, calcium, magnesium, sodium, potassium, chlorides, sulphates, and nitrates were observed [4,8–10]. These variations were reported to be a result of differences in roofing materials, orientation and slope of roofs, air quality in the region, and precipitation characteristics [7]. For example, Forester [5] compared rainwater runoff from similar roofs in different seasons and at six locations in Bayreuth, Germany. He observed large variations in ammonium concentrations that were measured during the same rain event in different locations (1.8–12.6 mg/L). The highest concentration was measured on a roof adjacent to an agricultural field. At the same location, large variations were also observed between seasons. Forester [5] further indicated that similar patterns were also observed for chlorides. Chang et al. [9], who studied rainwater runoff quality of four different roofing materials in east Texas, found that pH, EC (electrical conductivity), and Zn were significantly affected by the types of roofing material. In addition, they reported that Al, Mn, Cu, Pb, Zn, and pH concentrations in roof runoff exceeded the national quality standards in at least 5% of the rainfall events.

The microbial quality of roof-harvested rainwater often exceeds microbial quality standards, probably due to pollution originating from the excreta of animals (birds, rodents, etc.) that have access to roofs [3,4,11–13]. Evans et al. [12] indicated that local weather patterns, such as environmental conditions and wind speeds/directions, can significantly influence the microbial profile and loads in roof runoff. These authors also claimed that potential microbial risks that are associated with rainwater harvesting systems could be predicted by analysing weather patterns. Other studies pointed out that microbial quality of roof-harvested rainwater is strongly influenced by season, length of antecedent dry period, animal activities in close proximity to the roof, characteristics of rainwater storage tanks, and geographical location [4,13–15].

Roof material and its features may also have a significant impact on rainwater runoff quality. Studies investigating roof-harvested rainwater quality were conducted in Australia, Canada, Denmark, Germany, India, Japan, Spain, New Zealand, Thailand, and the United States [2,11,12,15,16]. Most of these locations are in temperate climate regions, where dry periods between consecutive rain events are relatively short. However, semi-arid/Mediterranean climates have been scarcely studied in this context. These climates are generally characterised by two distinct seasons: a long, completely dry, summer, and a short rainy winter with a limited number of rain events. These significant differences in weather conditions (rain intensity and depth, rain distribution, dry periods between consecutive rain events, etc.) may impact the quality of roof-harvested rainwater.

This research studied the quality of roof-harvested rainwater collected from three types of roofs in an urban Mediterranean environment in northern Israel. The study analyses the physicochemical and microbiological characteristics of the roof-harvested rainwater and its heavy metal concentrations. The study further estimates the association between harvested rainwater quality and weather characteristics, roof type, and selected air pollutants.

2. Materials and Methods

2.1. Study Site

Three experimental roofs were constructed at the Technion (Israel Institute of Technology) campus in Haifa, Israel (a coastal city in northern Israel; Figure 1). The climate in the area is Mediterranean, with the following characteristics: long and dry summer (May–September); 50 rainy days on average (range: 35–69 days/year) during winter (October–April); an average rainfall of 532 mm/year (S.D. ± 141 mm/year); an average dry weather period between rainy seasons of 151 days (range: 105–220 days); and, a length of dry period between consecutive rain events of 4.1 days (S.D. ±7.5 days; median: 1 day; 75 percentile: 7 days or less). Further details on the climatic conditions of the study site can be found in Muklada et al. [17].

Figure 1. Location of study site in Israel.

Three types of roofs, commonly used in Israel, were studied: concrete, tiles, and isolated steelsheets (Iskoorit™ Iskoor Metals LTD, Ramla, Israel; used for multi-storey buildings). Experimental roofs of each of these roofing materials (1 m^2 each) were constructed and placed on the roof of one of the Technion campus buildings (elevation 170 m above sea level), 1 m above the roof surface. The slopes of the experimental roofs were 1%, 30%, and 1% for concrete, tile, and steel-sheet, respectively. The slopes faced west, which is the prevalent direction of rain in this region. Each roof was fitted with a gutter leading to a 55 L collection tank (Figure 2). An automatic micro rain gauge (tipping bucket, Model 525; Texas Electronics Inc. Dallas, TX, USA) that recorded rainfall depth at 10 min intervals was placed adjacent to the system.

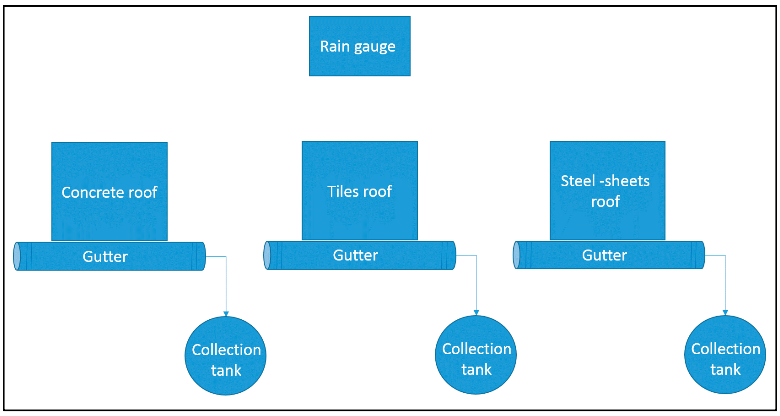

Figure 2. Schematic layout of the experimental system.

Measurements of the first rainy season (2007–2008) started at midseason, therefore, only 18 rain events were documented. During the second rainy season (2008–2009) 37 rain events occurred and all were documented and analysed. During the study period, rain depth ranged from 1 to 57 mm/event, and the length of the dry period between consecutive rain events ranged between 0 and 40 days (excluding the inter-seasonal dry period).

For each rain event and each roof, the following data were collected (Table 1): rain depth, volume of rain collected (in the collection tank), air pollution factors, physicochemical and microbial quality, and heavy metal concentrations in the harvested runoff.

Table 1. Potential explanatory variables for the examined roof-harvested rainwater quality parameters.

	Potential Explanatory Factors	Units
Environmental factors	Rain depth (RD)	mm/event
	Number of days from the beginning of the rainy season [1] (DN)	days
	Length of dry period between consecutive rain events (ADP)	days
	Roof type: concrete, tile and isolated steel sheets (RT)	-
Air pollution factors [2]	$PM_{2.5}$	$\mu g/m^3$
	$PM_{2.5–10}$	$\mu g/m^3$
	SO_2	ppb
	NO	ppb
	NO_2	ppb
	O_3	ppb
	WDD [3]	deg
	WDS	m/s

Notes: [1] The first rain event defined as the first day of the season, then, the number of days increase sequentially until the last rain event of the season. [2] All air pollution factors were measured the day before the rain event (d − 1). [3] 0^0 indicates Northern wind (blowing from North to South).

2.2. Analysis Methods

2.2.1. Physicochemical Parameters

Samples of harvested rainwater were analysed according to the Standard Methods [18] for the following parameters: EC by EC meter CD-4303 Lutron (Taipei, Taiwan); pH by pH meter PH-510, Eutech Instruments; total suspended solids (TSS; 2540D); volatile suspended solids (VSS; 2540E); chemical oxygen demand (COD; 5220C); turbidity by turbidity meter 2100p Hach (2130); alkalinity (2320B); absorbance at 254 nm by Genesis10 UV spectrophotometer Hermo Electronic Corp, USA; hardness (2340B); total nitrogen (TN) and total organic carbon (TOC) by Multi N/C 20000 Analyzer (Analytik Jena Analytical Instrumentation). For TOC/TN analyses, 100 mL samples were collected from the experimental site in glass stoppered Pyrex glass bottles, and were acidified to pH 2 by HCl 1 N and were stored at 4 °C until analysed.

2.2.2. Microbial Quality

The bacterial quality of the rainwater runoff was characterised by Faecal Coliforms (FC), which analysed by the membrane filtration method (method 9215D [18]). Samples were incubated according to the required conditions and were identified by specific confirmation test. FC were grown on mTEC agar (Acumedia) at 35 ± 0.5 °C for 2 h. Plates were then incubated at 44.5 ± 0.2 °C for 22–24 h. Confirmation test was performed using urea: each filter was transferred to a filter pad saturated with urea, and after 15 min yellow or yellow-brown colonies were counted as FC (method 9213D).

2.2.3. Heavy Metals

Heavy metals were analysed using ICP (Optima 3000 DV; detection threshold of 0.02 mg/L). Samples were filtered by a GF/A filter (1.6 μm), acidified by adding HNO_3 and stored at 4 °C until analysed. Examined metals (29 in total) included, among others, those that might be found in the air (originating in air pollution or natural sources), or in the roof components (listed in Table 2).

2.2.4. Air Quality

Air quality in the area was monitored as a part of a national monitoring network operated by the Israel Ministry of Environmental Protection. The monitoring station is located 940 m North-North-West (340°) of the experimental roofs. Air quality data was downloaded from an online database (http://www.svivaaqm.net/Default.he.IL.asp). Data was taken for the day preceding each rain event. The rationale for doing so was that air quality of the preceding day influences rainwater quality, since rain acts as an adsorber/absorber/cleanser of the atmosphere.

Air pollution data included daily averages of seven parameters (Table 1, above): SO_2 and NO_x (sum of NO and NO_2) were chosen since their presence in the atmosphere is related to industrial activity and combustion of fossil fuels. These compounds undergo oxidation in the atmosphere in combination with ozone, forming strong acids (sulphuric and nitric acids), which, when dissolved in rainwater, decrease its pH [19]. In addition, the station provided daily averages of wind direction (WDD) and speed (WDS), and daily average concentrations of particulate matter (PM). Airborne PM is a mixture of elemental and organic carbon, ammonium, nitrates, sulphates, mineral dust, trace elements, and water [20]. PM data included concentrations ($\mu g/m^3_{air}$) of two fractions: PM_{10} and $PM_{2.5}$, having aerodynamic diameters less than 10 and 2.5 μm, respectively. The difference between PM_{10} and $PM_{2.5}$ concentrations ($PM_{2.5-10}$) was calculated, yielding a fraction of particles having aerodynamic diameters between 2.5 and 10 μm.

2.3. Data Analysis

Multivariate linear regression (MLR) was performed using the above environmental and air pollution factors as possible explanatory variables, in order to study their effects on each of the roof-harvested rainwater quality parameters. Potential explanatory variables included four environmental factors and eight air pollution parameters (taken from the monitoring station a day before the rain event (day − 1); Table 1, above). For each quality parameter (the dependent variable), a MLR regression model was created using all twelve factors as potential explanatory variables. Factors having statistically significant effect on the examined quality parameter ($p < 0.05$) were left within the model, while all of the others were pruned.

3. Results and Discussion

3.1. Roof Runoff Quality

Quality parameters of the roof-harvested runoff, averaged over all roof types and all rain events, are depicted in Table 2. While concentrations of most parameters complied with Israel potable water quality regulations, three exceeded the maximum allowed concentrations. The observed range of turbidity was wide (0.7–143 NTU) and both the average and median values (26.0 and 12.7, respectively) were above the maximum (1 NTU, as defined by the regulations). FC do not appear in the regulations, however, they consist a sub-group of TC (total coliforms), which do appear in the regulations. Although quite low, FC concentrations were higher than the maximum allowed TC concentration, hence it is clear that the microbial quality of the harvested rainwater did not comply with the regulations. It should be noted that the turbidity and FC were measured in raw rainwater runoff and treatment, such as filtration and disinfection, may dramatically reduce their levels. Seventeen of the 23 heavy metals analysed were usually below detection limit, the concentrations of two (Ba and Zn) were always within the required limits, while only Cd (average concentration 0.018 mg/L) was 3.6 times higher than the maximum allowed concentration in the regulations. EC ranged from 0.19 to 660 μS/cm, with mean and median values of 91 and 77 μS/cm, respectively, indicating low salinity. It should be noted that 13 of the parameters in Table 2 do not appear in the regulations, but may still impact health and/or aesthetics.

Observed pH levels of the collected rainwater were higher than the values measured in the same region during 1981–1990, that averaged 5.3 ± 1.1 [21]. The present study analysed roof-harvested rainwater runoff, while Mamane and Gottlieb [21] sampled rainwater directly, excluding the effects of roof material and residues on the roof. Hence, the pH values were lower in their study. Additionally, atmospheric emissions of sulphur dioxide by industry and transportation in the region significantly decreased during the last two decades, which may also explain the higher pH values.

Table 2. Quality of the Roof-harvested rainwater.

Parameter	Units	Avg.	Std	Median	Range	25%	75%	*N*	IPWQR
Rainwater depth	mm/event	15.1	14.9	9.9	57–0.2	3.9	20.9	158	NR
Antecedent dry weather period	d	4.97	7.52	1.0	0–40	0	6.75	156	NR
Turbidity	NTU	26.0	32.6	12.7	143–0.7	5.83	30.5	147	1.0
EC	μS/cm	91.1	85.3	77.1	660–0.19	51.04	106.1	147	
pH	mg/L	7.01	0.78	6.9	10.7–5.5	6.58	7.19	149	6.5–9.5
TSS	mg/L	29.2	47.0	13.4	279–0	2.9	33.4	153	
VSS	mg/L	20.0	39.2	5.4	244–0	0	20.4	153	
TOC	mg/L	4.75	3.14	4.19	14.4–0.7	2.28	6.89	130	
COD	mg/L	20.1	43.3	BDL	BDL-204	BDL	16.4	109	
OD_{254}	1/cm	0.01	0.01	0.006	0.06–0	0.002	0.014	151	
TN	mg/L	1.25	1.05	0.96	5.34–0.173	0.76	1.16	101	15.8 [1]
Alkalinity	mg/L [2]	75.2	87.7	48.0	0.21–428	18.46	91.9	114	
Hardness	mg/L [2]	28.1	17.1	24.9	98.7–3.7	14.7	36.18	128	
FC	cfu/100 mL	4.90	9.36	1.0	BDL-44.0	BDL	4	51	BDL(TC) [3]
Al	mg/L	0.021	0.02	0.015	0.13–0.002	0.009	0.026	131	0.2
Ba	mg/L	0.03	0.05	0.014	0.36–0.002	0.008	0.037	128	1.0
Ca	mg/L	9.80	8.06	7.9	55.9–1.014	4.3	12.6	130	
Cd	mg/L	0.018	0.024	0.012	00.0026–0.14	0.007	0.018	130	0.005
Fe	mg/L	0.014	0.01	0.013	0.002–0.07	0.007	0.02	131	1.0
K	mg/L	1.42	2.15	0.76	15.2–0.07	0.4	1.4	117	
Mg	mg/L	1.40	1.25	1.12	9.94–0.205	0.74	1.57	130	
Na	mg/L	6.53	5.79	4.5	29.3–1.33	2.8	7.5	122	
Si	mg/L	0.96	1.23	0.29	6.04–0.002	0.14	1.62	132	
Sr	mg/L	0.044	0.05	0.031	0.28–0.006	0.02	0.044	44	
Zn	mg/L	0.17	0.203	0.12	1.29–0.001	0.03	0.22	130	5.0

Notes: 25% and 75% columns are 25% and 75% percentiles. IPWQR—Israel potable water quality regulations (maximum allowed concentrations; [22]), Missing values—parameter not regulated, NR—not relevant, BDL—below detection limit. Ag, As, B, Be, Bi, Cr, Cu, Hg, Li, Mn, Mo, Ni, Sb, Se, Pb, Ti and V concentrations were mostly BDL, hence they do not appear in the Table. [1] NO_3 as N; [2] As $CaCO_3$; [3] Total coliforms (TC) should be BDL.

3.2. Factors Affecting Roof Harvested Rainwater Quality

As described in the methods section, the effects of all 12 potential explanatory factors on each quality parameter was interpreted by creating a MLR model. The explanatory factors that were found to have a statistically significant contribution to the regression model, and their regression coefficients, are shown in Table 3. For example, the MLR model describing alkalinity in the harvested runoff is:

$$Alkalinity = -248 - 0.69 \cdot DN - 5.55 \cdot ADP + roof\ type : \begin{cases} c: & 0 \\ t: & 0 \\ s: & -28.9 \end{cases} + 5.18 \cdot PM_{2.5} - 2.65 \cdot PM_{2.5-10}$$
$$+12.2 \cdot O_3 - 18.4 \cdot SO_2 + 6.02 \cdot NO_2 + 0.32 \cdot WDD - 24.8 \cdot WD$$

where: *DN* is the number of days since the beginning of the rainy season (d); *ADP*—the length of dry period since the previous rain event (d); *roof type*: *c*—concrete, *t*—tiles, *s*—steel sheets; quality parameters: $PM_{2.5}$ (μg/m^3); $PM_{2.5–10}$ (μg/m^3); O_3 (ppb); SO_2 (ppb); NO_2 (ppb); *WDD*—wind direction (deg); and, *WDS*—wind speed (m/s).

All of the explanatory factors having positive coefficients increase the alkalinity in the harvested rainwater, while those having negative coefficients decrease the alkalinity. For example, alkalinity of the runoff harvested from the steel-sheet roof (*s*) was lower than that of the other two roof types, as indicated by its negative coefficient (−28.9), when compared with 0 for concrete (*c*) and tile (*t*) roofs.

3.2.1. Physicochemical Parameters

Most of the examined physicochemical quality parameters were found to be affected by O_3 and PM ($PM_{2.5–10}$ and $PM_{2.5}$) concentrations during the day preceding the rain event (Table 3). The concentration of these two factors depend on aerosols emitted to the atmosphere by transportation and industrial sources (and sometimes by natural emissions). Positive correlation was observed between most examined physicochemical parameters and O_3. This is probably a result of reactions between O_3 and humic substances in the atmosphere, which form products, such as ammonium, organic acids, and hydroxylamines [23]. The effect of PM on some of the examined physicochemical quality parameters is straightforward, as it contains, among others, elemental and organic carbon, ammonium, nitrates, sulphates, mineral dust, trace elements, and water [20]. $PM_{2.5–10}$ usually contains airborne humic substances from soil erosion (organic substances), while $PM_{2.5}$ consists mainly of nitrate [23]. Therefore, $PM_{2.5}$ and $PM_{2.5–10}$ displayed opposite effects on TOC and TN. Hueglin et al. [20] indicated that nitrate is one of the main contributors to $PM_{2.5}$ mass concentration in rural, near-city, and urban background sites. Thus, an increase in $PM_{2.5}$ concentration should increase TN concentration in the collected runoff, thus supporting our findings. On the other hand, a negative effect of $PM_{2.5–10}$ on TN concentration was observed. A similar trend was observed for EC, while TOC displayed an opposite trend.

Negative correlation was revealed between most examined physicochemical quality parameters and WDS. As wind speed in the preceding day increased, concentrations decreased in the harvested rainwater. This is probably due to scouring and transport of dry matter accumulated on the roof surface during the antecedent dry period. A positive effect of WDS on EC was observed. Haifa is a coastal city (Figure 1, above), therefore, we assume that this positive correlation is due to the transport of salty aerosols from the Mediterranean Sea.

Roof type had a significant effect on most quality parameters in rainwater runoff (Table 3). Concrete and tile roofs had a negative effect on TN, TOC, and COD while the steel-sheet roof had a positive effect. The steel-sheet roof is smooth, while concrete and tile roofs have depressions and crevices, in which substances can more easily adhere, and thus, are not easily washed away. Therefore, the steel-sheet roof contributed more TN, TOC, and COD than the two other roofs. On the other hand, the concrete roof, as compared with the two other roof types, had a positive effect on hardness, EC, pH, and alkalinity.

SO_2 affected both alkalinity and hardness. A reaction between SO_2, O_3, and water produces H^+, which decreases the alkalinity [19]. However, Taffere et al. [6], described a positive correlation between Mg^{2+} and $SO_4{}^{2-}$ (created by SO_2 and water), resulting in an increased roof runoff hardness.

The length of the dry period between consecutive rain events had a significant effect on physicochemical quality parameters. Clearly, as the dry period lengthened, more atmospheric aerosols and dust accumulated on all roofs.

The R^2 of the examined physicochemical quality parameters spanned between 0.2 and 0.7 (Table 3). The R^2 of TSS, VSS, COD, TOC, EC, pH, turbidity, OD_{254}, and hardness were quite low ($R^2 < 0.5$), meaning that the MLR model only partly explains the variance in their concentrations. Other factors, not examined in this study, must also influence these parameters' concentration. The regression correlation coefficients of alkalinity and TN, on the other hand, were considerably higher ($R^2 > 0.6$).

3.2.2. Microbial Quality

FC concentration was found to be affected by 10 factors (Table 3), exhibiting very high R^2 (0.87). Positive correlation between FC and NO, O_3, and $PM_{2.5–10}$ was observed. $PM_{2.5–10}$ was found to be the most significant factor, explaining 32% of the FC variability. Rain depth, as expected, decreased FC concentration due to dilution. The results indicated a decrease in FC concentration during long breaks between consecutive rain events. This is in contrast to many other studies, reporting that longer dry-weather periods result in higher microorganism levels, due to the increased deposition of animal faeces on the roof surface (e.g., [24]). This discrepancy most likely stems from the limited number of FC measurements (51 samples, representing 17 rain events, in 25% of which FC was undetected) and the generally low FC concentrations, much lower than values reported in the literature (e.g., [14,25]). Furthermore, the location of the experimental system, on a high office building, with limited access to mammals and limited bird activity, may also contribute to the low FC concentration. This issue deserves further investigation.

3.2.3. Metals

Few factors had a significant effect on the examined heavy metals (Table 3). Positive correlations were found between most of the heavy metals in the roof-harvested rainwater and O_3, NO, NO_2, and SO_2. These four explanatory parameters are indicators of air pollution that are emitted by industry and combustion of fossil fuels, activities that concurrently emit metals to the air. Heavy metals concentrations were also positively correlated with the length of dry period between consecutive rain events. As explained above, a longer dry period means more dry deposition on the roofs. The type of roof also affected the concentrations of some heavy metals: the concrete roof increased concentrations of Si, Ca, and K, the tile roof increased Zn concentration, and the steel-sheet roof increased the concentration of Ba.

Hierarchical clustering of the concentrations of heavy metals (Figure 3) reveals that Fe and Al belong to the same cluster. This may indicate that they originate from a natural source (Geological Survey of Israel, personal communication). Cd joins the cluster at a higher level and may also originate from natural sources in the region (ibid). Si and Ba form another cluster, both are affected by the type of roof material. Mg and K form a third cluster, both may have been transported to the roofs along with fine soil particles by winds during dry weather periods. Na was not designated to any of the above clusters. This may be due to the fact that its most probable source in Haifa is marine aerosols.

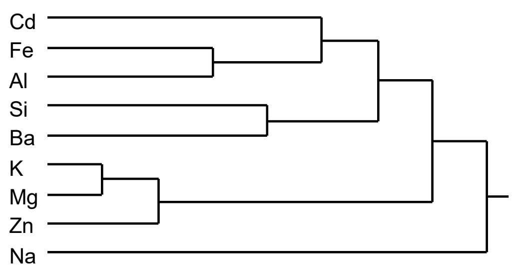

Figure 3. Hierarchical Clustering of metals in the roof-harvested runoff.

Table 3. Regression coefficients of factors affecting the quality parameters of the roof-harvested rainwater.

Parameter	Intercept	RD	DN	ADP	Roof Type **	$PM_{2.5}$ * ($\mu g/m^3$)	$PM_{2.5-10}$ * ($\mu g/m^3$)	O_3 * (ppb)	SO_2 * (ppb)	NO * (ppb)	NO_2 * (ppb)	WDD * (deg.)	WDS * (m/s)	NEV	R^2
FC	**76.5**	**−0.47**		**−1.52**	−1.31 t	−0.45	**0.49**	**1.13**	**7.58**		**−1.83**	**−0.29**	**−7.83**	10	0.87
Sr	**0.397**	−0.002	**−0.001**			**−0.005**	**0.003**	**0.003**	**0.144**	**0.066**	**−0.009**	**0.0023**	**−0.002**	10	0.86
Si	0.4599	**−0.009**		**0.0112**	**−1.108 s**	−0.0105	**0.0092**	**0.0186**	**0.2195**		**0.0387**			8	0.78
Alkalinity	**−248**		**−0.69**	**−5.55**	**−28.9 s**	**5.18**	**−2.65**	**12.2**	**−18.4**		**6.02**	**0.32**	**−24.8**	10	0.70
TN	−0.025	−0.009	**−0.01**	−0.036	**−0.22 c**	**0.099**	**−0.056**	**0.103**					−0.15	8	0.63
TOC	**16.6**		**0.248**		**−0.57 c**	**−0.095**	**0.07**	**−0.16**		**1.23**	**−0.55**	−0.009	−0.48	9	0.49
OD_{254}	**0.017**	**1.0e-4**		**3.0e-4**	**−0.002 c**		**0.00025**		**0.0020**		−5.0e-4	**−3.53e-5**	**−1.5e-3**	8	0.47
Na	**−0.848**	**−0.076**	0.0532	**0.065**				**0.2441**	**3.012**	**−2.471**	**0.1123**	**0.145**	**0.123**	9	0.47
Zn	**0.123**			**0.0068**	**0.164 s**				**0.039**	**−0.0194**			**−0.0067**	5	0.47
EC	**−130**			**−0.55**	**−6.9 s**	**0.70**	**−0.60**	**2.8**			**4.4**		**8.6**	7	0.44
Ca	**8.287**	**−0.085**		**0.367**	**−3.421 s**		**0.089**							4	0.44
Turb.	**−19.6**		**0.21**	**0.71**		**−0.32**	**0.83**							4	0.43
Hardness	9.54	−7.07		**17.7**	**−8.66 s**		**17.54**	7.67	**16.95**	−14.8				7	0.42
Al	0.0035	0.0002	**0.0004**	**0.0075**		**−0.0008**	**0.0007**		**0.0043**	**0.0098**	**−0.0009**			8	0.42
COD	**−129**			**1.87**	−7.49 c		−0.26	**2.57**		**−9.76**	**6.32**		9.62	7	0.38
pH	**4.88**		**0.0034**		**0.486 c**			**0.018**			**0.086**		**0.187**	5	0.34
Fe	0.0011				−0.0014 c			**0.0002**		0.0012			**0.0001**	4	0.30
K	−1.08				**0.4644 c**	**0.0158**		**0.068**	**0.11**	**−0.093**			**−0.052**	6	0.29
Mg	**−1.041**		**0.006**				**0.0117**	**0.0348**	**0.543**	**−0.432**				5	0.29
Ba	**0.065**				**−0.021 c**									1	0.28
Cd	**0.0462**						**0.0002**		**0.0042**		**−0.0026**			3	0.28
TSS	−20.9		0.055				**0.64**	**1.61**					**−8.74**	4	0.24
VSS	−3.48						**0.52**	**0.82**					**−5.48**	3	0.20

Notes: RD—rainwater depth, DN—day number (from the beginning of the season); ADP—antecedent dry period; WDD—wind direction; WDS—wind speed; NEV—number of significant exploratory variables * Measured a day before the rain event; ** Roof Type: c—concrete, s—steel-sheets, t—tiles.

3.3. Overall Effects of the Explanatory Factors

The most statistically significant factors were the ones that affected the highest number of roof-harvested runoff quality parameters (Figure 4). Five factors were found to be the most significant ones: two were related to air pollution ($PM_{2.5–10}$ and O_3), two to weather conditions (wind speed and length of dry period), and roof type. $PM_{2.5–10}$ and O_3 affected 17 quality parameters each, demonstrating their negative effects on roof-harvested runoff quality.

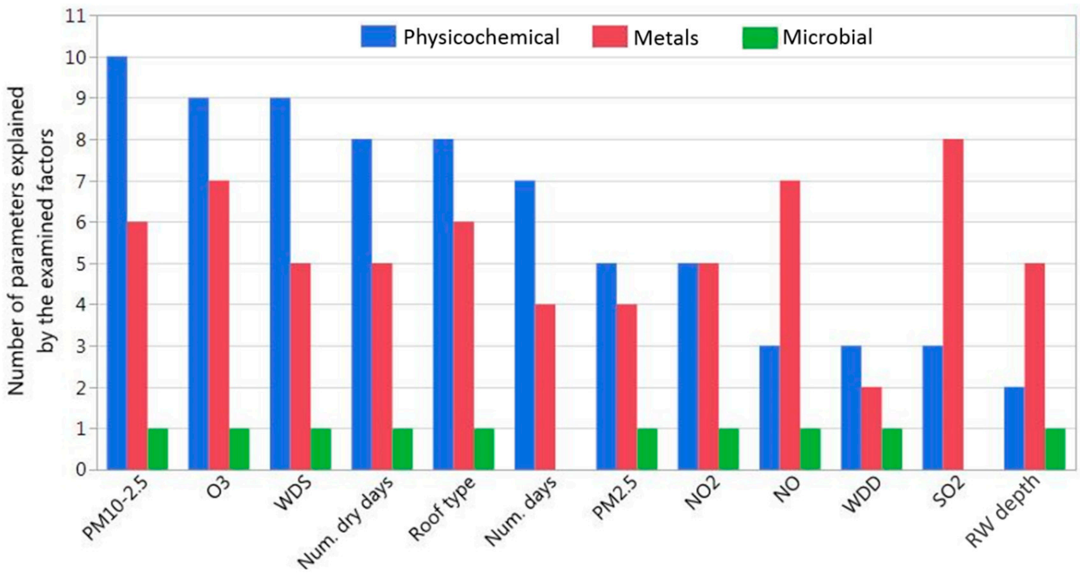

Figure 4. Number of quality parameters explained by each examined factor.

Wind speed and length of dry period affected 15 and 14 parameters, respectively. These factors are very important, as they represent local meteorological conditions. Roof type affected 15 quality parameters, meaning that each of them was affected by one roof type more than the other two. Airborne SO_2, while affecting less quality parameters (11), had the largest effect on the concentrations of heavy metals.

4. Summary and Conclusions

The quality of roof-harvested rainwater in a Mediterranean climate (northern Israel), characterised by dry summers and erratic wet winters, was studied on three experimental roofs (concrete, tiles, and steel-sheets). Twenty three quality parameters were analysed, including physicochemical ones, metals, heavy metals, and faecal coliforms (as indicators of microbial quality). Thirteen of the analysed parameters are not mentioned in local potable water quality regulations, although some may have health and/or aesthetic effects. Concentrations of most parameters that do appear in the regulations were below their maximum allowable limit. Turbidity and faecal coliforms levels in the harvested water were above maximum allowed values. Concentrations of most metals and heavy metals were very low, and Cd was the only one that did not comply with the regulations. This means that harvested water should be used only for non-potable uses.

The effects of 12 environmental and air pollution factors on each of the 23 quality parameters were assessed by multivariate linear regression, to quantify their impact. Five of the 12 factors were found to affect most quality parameters. O_3 and $PM_{2.5–10}$, measured during the day preceding the rain event, affected most of the physicochemical parameters and heavy metal concentrations, as well as microbiological quality (17 parameters each). Wind speed and length of preceding dry period were shown to have an effect on 15 and 14 quality parameters, respectively. Roof type significantly affected 15 harvested rainwater quality parameters, due to its structural characteristics and composition.

Regression correlation coefficients of the MLR models were quite high for some of the quality parameters, indicating that the explanatory factors explained most of their variability. On the other hand, regression correlation coefficients for other quality parameters were quite low, indicating that other factors (not examined in this study) may affect their concentrations. This deserves further investigation.

The study demonstrated that the quality of roof-harvested rainwater is affected by environmental conditions and air pollution. Many of the affecting parameters are specific to the region studied and to the roof materials that are used. Hence, further studies of this type are expected to enhance the knowledge needed for designing onsite rainwater harvesting systems in various locations.

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References

1. Aladenola, O.O.; Adeboye, O.B. Assessing the potential for rainwater harvesting. *Water Resour. Manag.* **2010**, *24*, 2129–2137. [CrossRef]
2. Jones, M.P.; Hunt, F.W. Performance of rainwater harvesting systems in the southeastern United States. *Resour. Conserv. Recycl.* **2010**, *54*, 623–629. [CrossRef]
3. Campisano, A.; Butler, D.; Ward, S.; Burns, M.J.; Friedler, E.; DeBusk, K.; Fisher-Jeffes, L.N.; Ghisi, E.; Rahman, A.; Furumai, H.; et al. Urban rainwater harvesting systems: Research, implementation and future perspectives. *Water Res.* **2017**, *115*, 195–209. [CrossRef] [PubMed]
4. Meera, V.; Ahammed, M.M. Water quality of rooftop rainwater harvesting systems: A review. *J. Water Supply Res. Technol. AQUA* **2006**, *55*, 257–268.
5. Forster, J. The influence of location and season on the concentrations of macro-ions and organic trace pollutants in roof runoff. *Water Sci. Technol.* **1998**, *38*, 83–90.
6. Taffere, G.R.; Beyene, A.; Vuai, S.A.; Gasana, J.; Seleshi, Y. Characterization of atmospheric bulk deposition: Implications on the quality of rainwater harvesting Systems in the Semi-Arid City of Mekelle, northern Ethiopia. *Environ. Process.* **2016**, *3*, 247–261. [CrossRef]
7. Neibaur, E.E.; Anderson, E.P. An examination of factors affecting sustainability of domestic rainwater harvesting systems in a rural, semi-arid region of Mexico. *Water Sci. Technol. Water Supply* **2016**, *16*, 1388–1397. [CrossRef]
8. Forster, J. Patterns of roof runoff contamination and their potential implications on practice and regulations of treatment and local infiltration. *Water Sci. Technol.* **1996**, *33*, 39–48.
9. Chang, M.; McBroom, M.W.; Beasley, R.S. Roofing as a source of nonpoint water pollution. *J. Environ. Manag.* **2004**, *73*, 307–315. [CrossRef] [PubMed]
10. Magyar, M.I.; Ladson, A.R.; Diaper, C.; Mithchell, V.G. Influence of roofing materials and lead flashing on rainwater tank contamination by metals. *Aust. J. Water Resour.* **2014**, *18*, 71–84. [CrossRef]
11. Uba, B.N.; Aghogho, O. Rainwater quality from different roof catchments in the Port Harcourt District, Rivers State, Nigeria. *J. Water Supply Res. Technol. AQUA* **2000**, *49*, 281–288.
12. Evans, C.A.; Coombes, P.J.; Dunstan, R.H. Wind, rain and bacteria: The effect of weather on the microbial composition of roof-harvested rainwater. *Water Res.* **2006**, *40*, 37–44. [CrossRef] [PubMed]
13. Ahmed, W.; Gardner, T.; Toze, S. Microbiological quality of roof-harvested rainwater and health risks: A review. *J. Environ. Qual.* **2011**, *40*, 13–21. [CrossRef] [PubMed]
14. Lye, J.D. Rooftop runoff as a source of contamination: A review. *Sci. Total Environ.* **2009**, *407*, 5429–5434. [CrossRef] [PubMed]
15. Despins, C.; Farahbakhsh, K.; Leidl, C. Assessment of rainwater quality from rainwater harvesting systems in Ontario, Canada. *J. Water Supply Res. Technol. AQUA* **2009**, *58*, 117–134. [CrossRef]
16. Farreny, R.; Morales-Pinzon, T.; Guisasola, A.; Taya, C.; Rieradevall, J.; Gabarrell, X. Roof selection for rainwater harvesting: Quantity and quality assessments in Spain. *Water Res.* **2011**, *45*, 3245–3254. [CrossRef] [PubMed]

17. Muklada, H.; Gilboa, Y.; Friedler, E. Stochastic modelling of the hydraulic performance of an onsite rainwater harvesting system in Mediterranean climate. *Water Sci. Technol. Water Supply* **2016**, *16*, 1614–1623. [CrossRef]
18. American Public Health Association; American Water Works Association; Water Environment Federation. *Standard Methods for the Examination of Water and Wastewater*; APHA: Washington, DC, USA; AWWA: Denver, CO, USA; WEF: Alexandria, VA, USA, 2005.
19. Ramlall, C.; Varghese, B.; Ramdhani, S.; Pammenter, N.W.; Bhatt, A.; Berjak, P. Effects of simulated acid rain on germination, seedling growth and oxidative metabolism of recalcitrant-seeded Trichilia dregeana grown in its natural seed bank. *Physiol. Plant.* **2015**, *153*, 149–160. [CrossRef] [PubMed]
20. Mamane, Y.; Gottlieb, J. Ten years of precipitation chemistry in Haifa, Israel. *Water Air Soil Pollut.* **1995**, *82*, 549–558. [CrossRef]
21. Kieber, R.J.; Long, M.S.; Willey, J.D. Factors influencing nitrogen speciation in coastal rainwater. *J. Atmos. Chem.* **2005**, *52*, 81–99. [CrossRef]
22. Israel Ministry of Health. *Potable Water Quality Regulations*; IMH: Jerusalem, Israel, 2012; p. 35. (In Hebrew)
23. Hueglin, C.; Gehrig, R.; Baltensperger, U.; Gysel, M.; Monn, C.; Vonmont, H. Chemical characterisation of PM2.5, PM10 and coarse particles at urban, near-city and rural sites in Switzerland. *Atmos. Environ.* **2005**, *39*, 637–651. [CrossRef]
24. Yaziz, M.I.; Gunting, H.; Sapari, N.; Ghazali, A.W. Variations in rainwater quality from roof catchments. *Water Res.* **1989**, *23*, 761–765. [CrossRef]
25. Sanchez, A.S.; Cohim, E.; Kalid, R.A. A review on physicochemical and microbiological contamination of roof-harvested rainwater in urban areas. *Sustain. Water Qual. Ecol.* **2015**, *6*, 119–137. [CrossRef]