The impact of atmospheric wet deposition on roof runoff quality in an urbanized area

Hua-Peng Qin, Qiao-Ling Tang, Li-Yu Wang and Guangtao Fu

ABSTRACT

Understanding the sources of chemical components in roof runoff can help to prevent water quality problems in rooftop rainwater harvesting. To identify the contribution of wet deposition to the mass of components in roof runoff, the samples from air, rainwater, dust buildup and roof runoff were collected from an urban site in Shenzhen of China in 2011–2012. The results indicate that: (1) wet deposition has a dominant contribution to the mass of total organic carbon (TOC), NH_4^+, NO_3^-, Cl^- and organic acids in the roof runoff, while the mass of NH_4^+, acetic acid and formic acid in the roof runoff may be greatly reduced by the neutralization between the components with alkaline dust buildup on the rooftop; and (2) wet deposition partially contributes to the mass of Na^+, K^+, Mg^{2+}, Ca^{2+}, F^- and SO_4^{2-} in the roof runoff, while other factors like dust buildup on the rooftop and chemical reactions also have a non-negligible impact. Furthermore, TOC, NH_4^+, NO_3^- and organic acids in the wet deposition are mainly influenced by the atmospheric pollution due to fast increase in fossil fuel consumption (e.g. vehicle emissions). Therefore, the effects of wet deposition should be carefully considered for rooftop rainwater harvesting in urbanized areas.

Key words | air quality, rainwater harvesting, roof runoff, water quality, wet deposition

Hua-Peng Qin (corresponding author)
Qiao-Ling Tang
Li-Yu Wang
Key Laboratory for Urban Habitat Environmental Science and Technology,
School of Environment and Energy,
Peking University Shenzhen Graduate School,
Shenzhen 518055,
China
E-mail: *qinhp@pkusz.edu.cn*

Guangtao Fu
Centre for Water Systems,
College of Engineering, Mathematics and Physical Sciences,
University of Exeter,
Exeter EX4 4QF,
UK

INTRODUCTION

Rooftop rainwater harvesting has increasingly become an important supplementary means of water resources management in the areas where surface water and ground water are absent (Ragab *et al.* 2003). However, many chemical types of contaminants have been found in rooftop runoff including organic components (Abbasi & Abbasi 2011; Mendez *et al.* 2011), nutrients (Clark *et al.* 2008) and metals (Forster 1998; Lee *et al.* 2011). Several studies have reported that water quality of rooftop runoff exceeded the international or national guidelines set for portable or non-portable water (Abbasi & Abbasi 2011; Lee *et al.* 2011; Gikas & Tsihrintzis 2012; Hou & Zhang 2014). Thus, understanding the sources of chemical components in the rooftop runoff is essential for rainwater harvesting in order to control the water quality and develop appropriate measures to bring it within acceptable levels.

Roofs themselves can be a source of contamination through the leaching and disintegration of roofing materials. Leaching from metal roofing tends to raise the levels of zinc, copper, cadmium and sometimes lead in rooftop runoff (Clark *et al.* 2008; Wang & Li 2009; Rentz & Öhlander 2012; Wicke *et al.* 2014). Rainwater from asphalt fiberglass shingle roofs contains high levels of dissolved organic carbon (Mendez *et al.* 2011). In addition, nutrient releases in the runoff from roofing made of galvanized metal or wood products (Clark *et al.* 2008).

The atmospheric dry and wet deposition may have significant effects on the chemical composition in roof runoff (Burian *et al.* 2001; Polkowska *et al.* 2011). A study in an urban area of Shanghai indicated that the main contribution source to pollutant loads from roofs was atmospheric dry precipitation rather than the roofing materials (Wang & Li 2009). Rocher *et al.* (2004) measured the bulk atmospheric depositions (including dry and wet depositions) of hydrocarbons and metallic pollutants in central Paris (France). They found that atmospheric deposition acts as the main source

doi: 10.2166/nh.2015.209

of hydrocarbons and major elements (e.g. Ca, K, Mg, Na, P and S), while metallic and slate roofs act as sources of some heavy metals. Lamprea & Ruban (2011) reported that the morphology and composition of particles in the roof runoff are very similar to those observed in bulk atmospheric deposition. Huston *et al.* (2009) measured the bulk deposition at 16 sites in Brisbane and found that there was an increase in the deposition flux in traffic/industrial areas compared to outer suburbs.

Wet deposition has been investigated to reveal the mechanism of acid precipitation (Huang *et al.* 2010a; Tsai *et al.* 2011) or understand the local and regional dispersion of pollutants (Tian *et al.* 2011; Zhang *et al.* 2011). However, much less attention has been paid to the impacts of wet deposition on the roof runoff quality (Melidis *et al.* 2007; Polkowska *et al.* 2011). In addition, wet deposition has not been fully considered in the water quality management for rooftop rainwater harvesting. Before control measures are considered, it is necessary to characterize the input of wet deposition to the chemical components in roof runoff (Huston *et al.* 2009).

This paper focuses on analyzing the contributions of atmospheric wet deposition to the chemical components in the roof runoff at an urban site in Shenzhen, China, where the samples were systematically collected from atmospheric environment, rainwater, dust buildup on the rooftop and roof runoff in 2011–2012. The chemical components investigated in this study include: cations (NH_4^+, Ca^{2+}, Na^+, Mg^{2+} and K^+), inorganic anions (SO_4^{2-}, NO_3^-, PO_4^{3-}, Cl^-, F^-), total organic carbon (TOC), and organic acids (formic acid, acetic acid, methanesulfonic acid, glutaric acid malonic acid, succinic acid, adipic acid). These chemical components are chosen not only because they are widely found in the wet deposition in many urban areas (Huang *et al.* 2008), but also because they are relevant to the nutrient level, chemical oxygen demand or pH in the roof runoff, which has effects on the rainwater utilization. Heavy metals were not measured due to economic constraints. The objectives of this paper are (1) to characterize chemical components in both wet deposition and roof runoff and (2) to identify the contributions of wet deposition to the mass of different components in roof runoff.

METHODS

Study sites

This study was conducted on the roof of a four-storey building at the campus of Peking University Shenzhen Graduate School (PKUSZ) (Figure 1). The study site is located in the middle east of Shenzhen. There are no obvious pollution sources nearby. The experimental area is a 112 m^2 flat roof made of cement mortar. This roof was selected because the cement mortar roof is typical for the buildings in

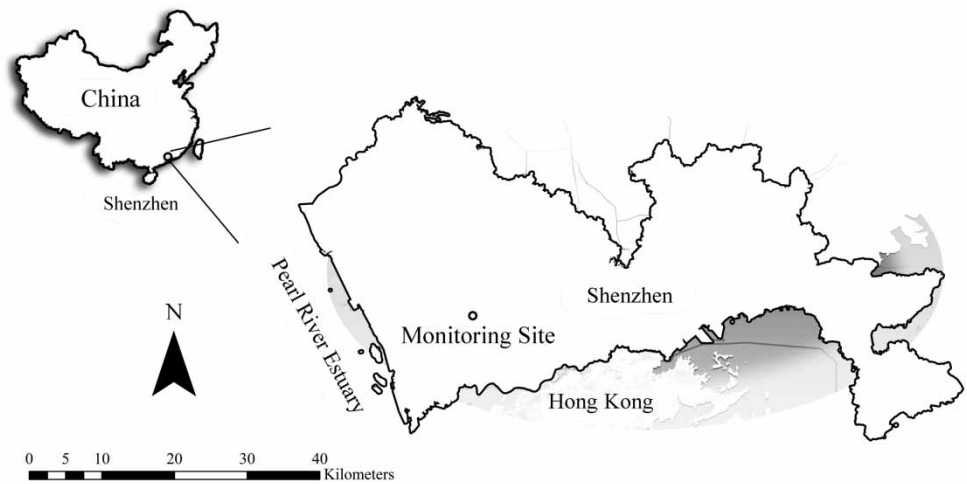

Figure 1 | The location of the sampling site.

Shenzhen. The study site has a mild, subtropical maritime climate with a mean annual temperature of 22.4 °C and mean annual precipitation of 1,933 mm, 85–90% of which falls from April to September.

Sample collection

To identify the contribution of atmospheric wet deposition to the chemical components in roof runoff, a comprehensive measurement campaign was carried out from June 2011 to May 2012. The measurement included not only the components in the rainwater and the roof runoff during rainfall events, but also those in the dust buildup on the rooftop and the atmosphere.

Quantity and quality of rainfall

The rainfall amount was recorded at an interval of 10 min by an automated weather monitoring system (DAVIS weather station, Hayward, CA, USA) installed at PKUSZ. A plastic open tray was used to collect the rainwater. Before its use, the tray was washed with deionized water. The tray was placed on the roofs and a water quality sample was collected from the tray at the end of the rainfall event. Twenty-five rainfall events were monitored and the rainwater quality samples were collected (Table 1). The antecedent dry period (ADP), rainfall amount and rainfall duration ranged from 0.17 days to 12.25 days, 1.8 mm to76.8 mm and 0.33 h to 11.02 h, respectively.

Table 1 | Observed rainfall data

Date	ADP (day)	Rainfall amount (mm)	Rainfall duration (h)
11 June 2011	2	1.8	2
11 June 2011	0.42	76.7	6.2
12 June 2011	0.25	18.6	4.3
10 July 2011	7.8	4.8	2.17
11 July 2011	1	51.6	1.2
19 July 2011	0.5	4.6	2
28 July 2011	7	11.4	0.6
29 July 2011	0.58	4.1	0.5
9 August 2011	0.42	61.8	5.2
9 August 2011	0.33	56.4	0.8
17 August 2011	2.21	5.3	0.33
1 September 2011	12.25	1.8	0.5
2 September 2011	0.17	15	0.5
8 March 2012	0.63	3.6	5.93
5 April 2012	5.24	18.6	4.5
16 April 2012	2.89	1.3	2.08
16 April 2012	0.12	23.8	2.62
18 April 2012	0.91	2.7	0.83
19 April 2012	0.84	60.8	7.25
20 April 2012	0.66	52.3	11.02
25 April 2012	1.72	1.6	1.67
27 April 2012	1.72	76.8	8.5
4 May 2012	3.28	10.8	0.33
13 May 2012	2.12	2.8	0.17
13 May 2012	0.22	15.6	4

Quantity and quality of roof runoff

A 10-L PVC bucket was placed at the final point of the roof drain pipes for runoff collection. Before its use, the bucket was washed with deionized water. When a bucket was filled, the next bucket was applied in its place after 10 min intervals for rising water flow or 20–30 min intervals for receding flow. For each process, the start and end time for filling the runoff into the bucket was recorded, and then the average flow rate can be estimated by dividing the volume of the bucket by the time for filling the bucket; in addition, a water quality sample was collected from each bucket of the roof runoff. For each rainfall event, 1–8 samples were collected depending on the rainfall intensity and duration of the event. A total of 113 samples were collected from the roof runoff during the 25 rainfall events.

Air quality

The air quality in the study area was measured in the non-rain days. Nitrogen oxides (NO_x), sulfur dioxide (SO_2) and inhalable particles less than 10 microm in diameter (PM_{10}) were continuously measured by Model 42i-D NO_x Analyzer, Model 43i SO_2 Analyzer and TEOM 1405 (Thermo Scientific, West Palm Beach, FL, USA), respectively. The means for air quality within 30 min before each of the 25 rainfall events were selected for analysis in the study.

Dust buildup on the rooftop

The dust buildup on the rooftop comprises the dry deposition and the debris of the roofing material. The dust was sampled by a 1,200 W water filtration vacuum cleaner (ZW12-18EFT, Ogilvy, Korea) after a few days of dry weather. The cleaner inhales the dust into a water bucket, which is half-filled with deionized water, and the soluble fraction of dust can dissolve in the water, resulting in a filtering effect up to 99%. Sample collection was undertaken on 1×1 m roof surfaces plots. A plastic frame was used to demarcate the plot boundary during sample collection. Vacuuming was done three times in perpendicular directions in order to ensure that all the dust was collected. After the sampling, the mixed water solution was poured from the water bucket into a sampling bottle. Then, the water bucket was rinsed three times by deionized water, and the rinsed water was also poured into the sampling bottle. A total of 46 samples were collected in different plots of the roof at the time with ADP ranged from 0.17 to 12.25 days.

Sample analysis

The pH of samples was measured by the pH meter (PHS-3C, Shanghai Leici Instruments Co., Shanghai, China) immediately after collection. Then, samples were filtered through 0.45 μm pore size PTFE filters and stored at –20 °C in a refrigerator for further chemical analysis within 2 weeks. The TOC measurement was performed using a TOC analyzer (Multi N/C 3100, Analytik-jena, Jena, Germany). Ions were analyzed using an ion chromatography system (ICS-2500, Dionex, Sunnyvale, CA, USA) equipped with an electrochemical detector. The anions (SO_4^{2-}, NO_3^-, PO_4^{3-}, Cl^-, F^-, $HCOO^-$, CH_3COO^- and $C_2O_4^{2-}$) were determined using an AS-11 column and a gradient elution solution of N_aOH. The cations (NH_4^+, Ca^{2+}, Na^+, Mg^{2+} and K^+) were determined using a CS-12A column and an isocratic elution solution of methanesulfonic acid.

The test parameters for Multi N/C 3100 used in this study are furnace heating temperature of 800 °C, injection volume of about 20 mL, analysis time of about 15 min. The sampling and analysis procedures were conducted following the technical specifications required for acid deposition monitoring in China (State Environmental Protection Administration of China 2004). Field blank samples were collected monthly using deionized water (18.2 MΩ cm) (Millipore, Billerica, MA, USA) to flush the bucket and tubes of the sampler in the same way as for normal sampling. A pH difference of less than 0.05 and an electrical conductivity difference of less than 1 μS/cm between deionized water and the field blank solution were adopted as the standard to check the cleanliness of the sampler. Duplicate measurements of pH and electrical conductivity were carried out and a difference of less than 0.05 for pH and less than 1 μS/cm for electrical conductivity was acceptable. The relative standard deviations of the measured inorganic and organic ions and TOC were all less than 5% for reproducibility tests. The quality assurance was routinely carried out using Standard Reference Materials produced by National Research Center for Certified Reference Materials, China. Owing to the strict measures of sample collection, quality assurance and quality control during the experiment, we can assure the reliability and authenticity of data.

Indicators

In the study, the bulk concentration of the ith chemical component in the rainwater was denoted as $C_{\text{rain},i}$. It was compared with the event mean concentration (EMC) of the ith chemical component in roof runoff during a rainfall event (EMC_i), which can be expressed as

$$\text{EMC}_i = \sum C_{t,i} Q_t \Delta t / \sum Q_t \Delta t \quad (1)$$

where $C_{t,i}$ and Q_t are concentration of the ith chemical component and runoff discharge, respectively, at time t; Δt is discrete time interval. EMC is regarded as a good measure to represent rainfall runoff quality (Kim et al. 2007).

The mass of the ith component in the wet deposition ($\text{WD}_{\text{rain},i}$) during a rainfall event can be expressed as

$$\text{WD}_{\text{rain},i} = C_{\text{rain},i} R_{\text{rain}} A \quad (2)$$

where R_{rain} is the rainfall amount during a rainfall event; A is the area of the roof. The $\text{WD}_{\text{rain},i}$ was compared with the

mass of the ith component in the roof runoff during a rainfall event ($M_{\text{runoff},i}$). $M_{\text{runoff},i}$ can be expressed as

$$M_{\text{runoff},i} = \sum C_{t,i} Q_t \Delta t \tag{3}$$

Another indicator used in this study is the ratio of mass of the ith component in the wet deposition to that in the roof runoff during a rainfall event, R_i, which can be expressed as

$$R_i = \text{WD}_{\text{rain},i} / M_{\text{runoff},i} \tag{4}$$

R_i can be used to denote the contribution of wet deposition to the component mass in roof runoff. Generally, the higher the ratio is, the more wet deposition contributes to the mass in roof runoff. If R_i is significantly higher than 0, WD_{rain} has a significant contribution to M_{runoff}. Furthermore, if R_i is significantly close to or higher than 1, WD_{rain} has a dominant contribution to M_{runoff}.

Method to explain the contributions of wet deposition

Generally, the components in the roof runoff are derived from wet deposition or dust buildup on the rooftop. However, the chemical reactions between the rainwater and dust buildup (e.g. neutralization reaction between acid and alkali) may change the component mass in the roof runoff. Assume that the proportions of the ith component in the wet deposition and the dust buildup on the rooftop are $P_{w,i}$ and $P_{b,i}$, respectively. The contributions of wet deposition to the component mass in the roof runoff may be possibly investigated by comparing $P_{w,i}$ with $P_{b,i}$ and considering the possible chemical reactions in the roof runoff. The following three cases may exist (Table 2)

1. $P_{w,i} \gg P_{b,i}$

R_i may be close to 1 if the chemical reactions have no or insignificant impacts on the roof runoff water quality; or R_i may be lower (or higher) than 1 if chemical reactions can significantly increase (decrease) the component mass in the roof runoff.

2. $P_{w,i} \approx P_{b,i}$

R_i may be lower than 1 if the chemical reactions have no or insignificant impacts on the roof runoff water quality or significantly increase the component mass in the roof runoff; or R_i may be close to 1 or even higher than 1 if chemical reactions can significantly decrease the component mass in the roof runoff.

3. $P_{w,i} \ll P_{b,i}$

R_i is usually lower than 1 no matter the chemical have impacts on the roof runoff water quality or not. However, R_i is possible to be close to or even higher than 1 if chemical reactions can significantly decrease the component mass in the roof runoff.

Table 2 | Impacts of dust buildup and chemical reaction on contribution of wet deposition

$P_{w,i}$ and $P_{b,i}$	Possible effects of chemical reactions on the component mass in roof runoff	Possible contribution
$P_{w,i} \gg P_{b,i}$	no or insignificant change	$R_i \approx 1$
	significant increase	$R_i < 1$
	significant decrease	$R_i > 1$
$P_{w,i} \approx P_{b,i}$	no or insignificant change	$R_i < 1$
	significant increase	$R_i < 1$
	significant decrease	$R_i \geqq 1$
$P_{w,i} \ll P_{b,i}$	no or insignificant change	$R_i < 1$
	significant increase	$R_i < 1$
	significant decrease	$R_i < 1$ or $R_i \geqq 1$

$P_{w,i}$ the proportion of the ith component in the wet deposition; $P_{b,i}$ the proportion of the ith component in the dust buildup on the rooftop; R_i the ratio of mass of the ith component in the wet deposition to that in the roof runoff.

Statistical analysis

The proportions of the components in the wet deposition and the dust buildup on the rooftop are highly variable, dependent upon different samples. Thus, the two-group independent sample t-test was used to detect whether the results of comparison of the component proportion between the wet deposition and the dust buildup are statistically significant or not.

R_i is also highly variable, dependent upon different rainfall events, and thus the one sample t-test was used to detect whether or not there is a statistically significant difference between R_i and 0 or between R_i and 1.

In addition, the Spearman's rank correlation coefficient was used to determine the relationship between the air quality and wet deposition. SPSS 11 was used to process the data.

RESULTS AND DISCUSSION

Rainwater and runoff quality

The volume-weighted mean concentrations (VWMs) of components in the rainwater were calculated based on the rainfall amount and rainwater quality data of 25 rainfall events during 2011–2012. TOC has a VWM of 3.98 mg/L, which is the highest among all the measured components; Ca^{2+} and NH_4^+ have VWMs of 0.86 mg/L and 0.47 mg/L, respectively, which are much higher than the other cations; NO_3^- and SO_4^{2-} have VWMs of 1.74 mg/L and 1.71 mg/L, respectively, which are much higher than the other inorganic anions; and formic acid and acetic acid have VWMs of 0.26 mg/L and 0.12 mg/L, respectively, which are higher than the other organic acids. Furthermore, the VWMs of PO_4^{3-}, glutaric acid, succinic acid, malonic acid, methanesulfonic acid in the samples are lower than 0.1 mg/L, and some of them are lower than detective limits. In addition, the VWM pH in the rainwater is 4.99, showing the acidity of rainfall in the study area. The concentrations of components in rainwater in the study area are lower than those in Guangzhou, Beijing, Shanghai, Nanjing, Ankara and Galicia; while they are similar to those in other cities listed in Table 3. Water quality of rainwater in rainfall events is shown in a box-whisker plot, which indicates that the concentrations of components in the rainwater are highly variable, dependent upon different rainfall events (Figure 2(a)).

EMCs of each component in 25 rainfall events were calculated in terms of Equation (1). The VWMs of the components in the roof runoff were calculated based on the EMCs and runoff data of 25 rainfall events during 2011–2012. In the roof runoff, TOC has a VWM of 5.42 mg/L, which is the second highest among the measured components; Ca^{2+}, K^+ and Na^+ have VWMs of 10.01 mg/L, 1.64 mg/L and 1.24 mg/L, respectively, which are much higher than the other cations; NO_3^-, SO_4^{2-} and Cl^- have VWMs of 2.81 mg/L, 4.41 mg/L and 1.09 mg/L, respectively, which are much higher than the other inorganic anions; and formic acid and acetic acid have VWMs of 0.128 mg/L and 0.095 mg/L, respectively, which are higher than the other organic acids. In addition, the VWM pH in the roof runoff is 7.78, showing the alkalinity of roof runoff in the study area. VWM of NH_4^+ in the study is much lower than that in Beijing and a little lower than that in France and Greece; while VWM of NO_3^- in the study area is higher than that in the cities listed in Table 4. EMCs of the 25 rainfall events are shown in a box-whisker plot, which indicates that the EMCs are highly variable, dependent upon different rainfall events (Figure 2(b)).

Table 3 | The volume-weighted mean pH and component concentrations in rainwater in Shenzhen and other cities (mg/L)

Area	Time	pH	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	Reference
This study	2011	4.99	0.235	0.473	0.180	0.042	0.857	0.554	1.743	1.712	
Guangzhou	2006	4.56	1.265	1.271	1.283	0.204	2.072	3.077	3.311	7.838	Cao *et al.* (2009)
Shanghai	2005	4.49	1.152	1.453	0.581	0.355	4.08	2.067	3.088	9.581	Huang *et al.* (2008)
Beijing	2003	6.18	1.346	6.768	1.564	1.92	7.94	2.935	10.788	25.008	Hu *et al.* (2005)
Jinhua	2004	4.54	0.173	1.746	0.207	0.053	1.122	0.365	2.294	5.611	Zhang *et al.* (2007)
Nanjing	1992–2003	5.15	0.529	3.478	0.472	0.38	5.908	5.055	2.455	11.606	Tu *et al.* (2005)
Mexico	2001–2002	5.08	0.161	1.663	0.086	0.03	0.528	0.34	2.641	2.971	Báez *et al.* (2007)
Ankara	1994–1996	6.3	0.359	1.555	0.382	0.112	1.428	0.723	1.81	2.304	Topçu *et al.* (2002)
Singapore	1999–2000	4.2	0.754	0.344	0.281	0.078	0.322	1.212	1.383	4.008	Hu *et al.* (2003)
Tokyo	1990–2002	4.52	0.851	0.727	0.113	0.138	0.498	1.957	1.891	2.41	Okuda *et al.* (2005)
Seoul	1996–1998	4.7	0.242	1.195	0.137	0.083	0.698	0.645	1.854	3.403	Lee *et al.* (2000)
Galicia	1999	6.55	3.358	4.536	1.599	0.528	1.7	6.097	1.55	4.752	Vázquez *et al.* (2003)
Newark	2006–2007	4.6	0.251	0.439	0.051	0.04	0.12	0.379	0.893	1.829	Song & Gao (2009)

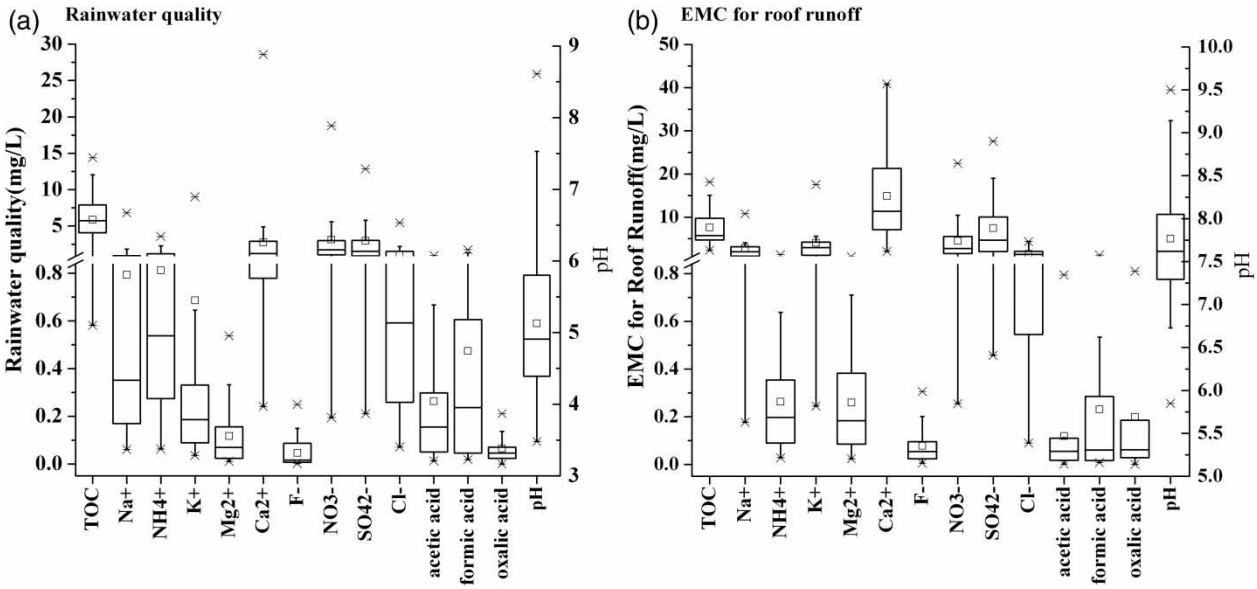

Figure 2 | Water quality of rainwater and roof runoff in rainfall events.

Table 4 | Mean pH and EMCs in roof runoff in Shenzhen and other cities (mg/L)

Area	Time	pH	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	PO_4^{3-}	Cl^-	NO_3^-	SO_4^{2-}	Reference
This study	2011	7.78	1.237	0.185	1.644	0.145	10.05	0.01	1.094	2.813	4.413	
Beijing	2000	6.82		3.47					2.78	1.98	55.24	Che *et al.* (2001)
Southwest France	2009	6.5	1.1	0.58	1.2	0.27	4.4	0.17	1.9	2.8	1.9	Vialle *et al.* (2011)
Xanthi	2002–2004	7.77		0.47	5.74	1.20	24.06			1.48	0.06	Melidis *et al.* (2007)

Compared to the rainwater quality, the concentrations of components in roof runoff have significant change (Figure 2), while different components have different change trends. The VWMs of TOC, Ca^{2+}, Na^+, K^+, Mg^{2+}, SO_4^{2-}, NO^{3-}, F^-, Cl^- and acetic acid in the roof runoff are higher than those in the rainwater. However, the VWMs of NH_4^+, acetic acid and formic acid in the roof runoff are lower than those in the rainwater. In addition, pH in the roof runoff is much higher than that in the rainwater.

Component proportions in wet deposition and dust buildup on the rooftop

Figure 3 shows the average proportion of each chemical component in all the samples collected from the wet deposition and the dust buildup on the rooftop. As seen in Figure 3(a), in the wet deposition, TOC accounts for the maximum proportion (30.6%) among all the measured components, followed by NO_3^- (16.3%) and SO_4^{2-} (15.5%); Ca^{2+} accounts for the maximum proportion (14.4%) among all the cationic components, followed by NH_4^+ (4.2%). As seen in Figure 3(b), in the dust buildup on the rooftop, Ca^{2+} accounts for the maximum proportion (40.1%) among all the measured components followed by TOC (25.0%), SO_4^{2-} (19.5%) and NO_3^- (4.4%). The five components, PO_4^{3-}, glutaric acid, succinic acid, malonic acid and methanesulfonic acid, are grouped as 'others' in Figure 3.

The two-group independent sample *t*-test was used to detect whether or not the population mean of the proportion of a component in the wet deposition (μ_1) and that in the dust buildup (μ_2) are different. The hypothesis was set: H_0: $\mu_1 = \mu_2$; H_1: $\mu_1 \neq \mu_2$, where H_0 and H_1 are null hypothesis and alternative hypothesis, respectively. According to the results of the independent sample *t*-test, the components can be classified into three groups (Table 5).

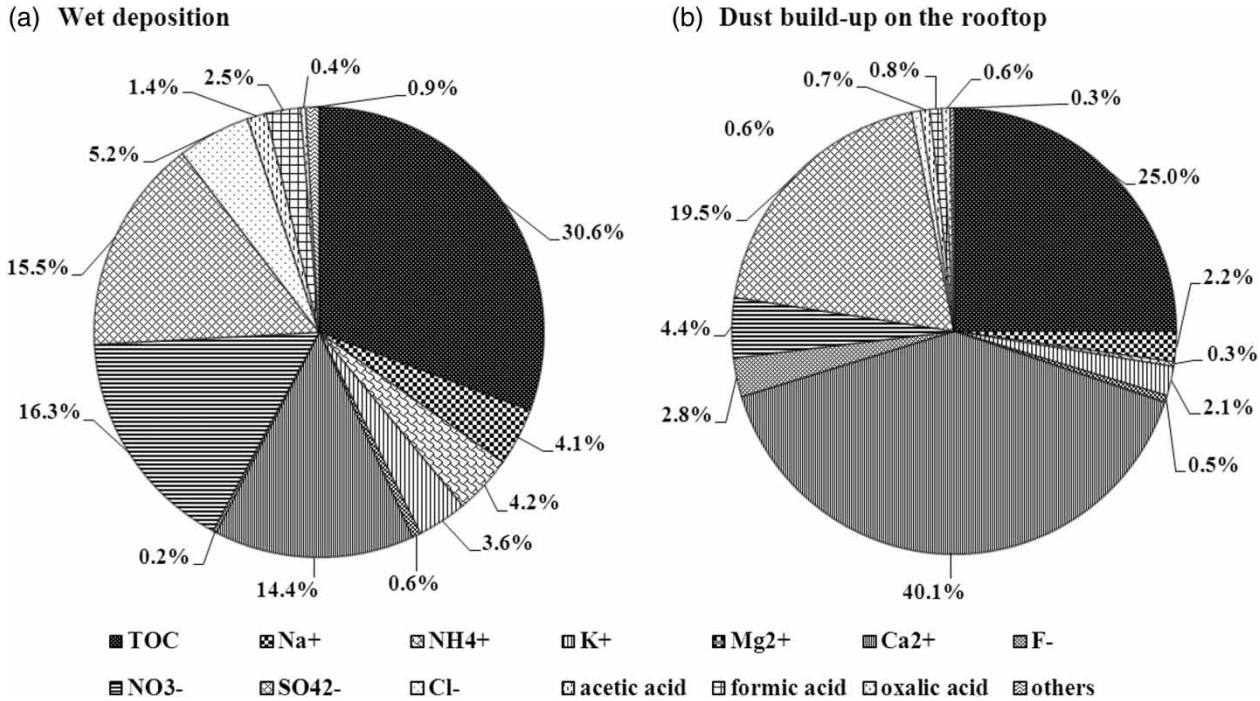

Figure 3 | Component proportions in wet deposition and dust buildup on the rooftop.

Table 5 | Comparison of components between wet deposition, dust buildup and roof runoff

	Two-group independent sample *t*-test for comparison between $P_{w,i}$ and $P_{b,i}$			One sample *t*-test for comparison between R_i and 1		
Component	***t*-value**	**Sig.**	**$P_{w,i}$ vs. $P_{b,i}$**	***t*-value**	**Sig.**	**R_i vs. 1**
TOC	3.204	0.003	$P_w \gg P_b$	–0.010	0.992	≈1
NO_3^-	6.945	0	$P_w \gg P_b$	–0.222	0.826	≈1
Cl^-	3.153	0.004	$P_w \gg P_b$	–0.502	0.621	≈1
oxalic acid	–1.732	0.094	$P_w \approx P_b$	1.028	0.327	≈1
NH_4^+	8.237	0	$P_w \gg P_b$	3.160	0.005	>1
acetic acid	4.405	0	$P_w \gg P_b$	3.453	0.004	>1
formic acid	3.261	0.005	$P_w \gg P_b$	2.569	0.022	>1
Ca^{2+}	–16.128	0	$P_w \ll P_b$	–59.643	0	<1
F^-	–3.901	0	$P_w \ll P_b$	–7.574	0	<1
K^+	–0.064	0.949	$P_w \approx P_b$	–19.791	0	<1
Mg^{2+}	1.832	0.076	$P_w \approx P_b$	–5.347	0	<1
SO_4^{2-}	–0.98	0.333	$P_w \approx P_b$	–5.481	0	<1
Na^+	2.426	0.023	$P_w \gg P_b$	–15.396	0	<1

$P_{w,i}$ the proportion of the ith component in the wet deposition; $P_{b,i}$ the proportion of the ith component in the dust buildup on the rooftop; R_i the ratio of mass of the ith component in the wet deposition to that in the roof runoff.

Group 1 includes K^+, Mg^{2+}, SO_4^{2-} and oxalic acid. In this group, the null hypothesis is accepted (p-value > 0.05), and the difference between μ_1 and μ_2 is insignificant. Therefore, the proportions of the components in the wet deposition are significantly close to those in the dust buildup on the rooftop, which can be denoted as $P_w \approx P_b$.

Group 2 includes TOC, NO_3^-, Cl^-, Na^+, NH_4^+, acetic acid and formic acid. In this group, the null hypothesis is rejected (p-value < 0.05), the difference between μ_1 and μ_2 is significant, and $\mu_1 > \mu_2$. Therefore, the proportions of the components in the wet deposition are significantly higher than those in the dust buildup on the rooftop, which can be denoted as $P_w > P_b$.

Group 3 includes Ca^{2+} and F^-. In this group, the null hypothesis is rejected (p-value < 0.05), the difference between μ_1 and μ_2 is significant, and $\mu_1 < \mu_2$. Therefore, the proportions of the components in the wet deposition are significantly lower than those in the dust buildup on the rooftop, which can be denoted as $P_w < P_b$.

Ratio of component mass in wet deposition to that in roof runoff

The mass of the ith component in the wet deposition ($WD_{rain,i}$) and the roof runoff ($M_{runoff,i}$) during a rainfall event were calculated in terms of Equations (2) and (3), respectively. The ratio of the ith component mass in the wet deposition to that in the roof runoff during a rainfall event (R_i) was calculated in terms of Equation (4). As shown in Figure 4, different components have different values of R_i. Acetic acid has the highest mean R_i (14.0) followed by formic acid (10.4), NH_4^+ (7.4) and oxalic acid (3.4). The mean R_i of TOC, F^-, NO_3^-, Cl^- are close to 1.0 (range from 0.75 to 0.99); while the mean R_i of Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} are much lower than 1.0 (range from 0.55 to 0.14).

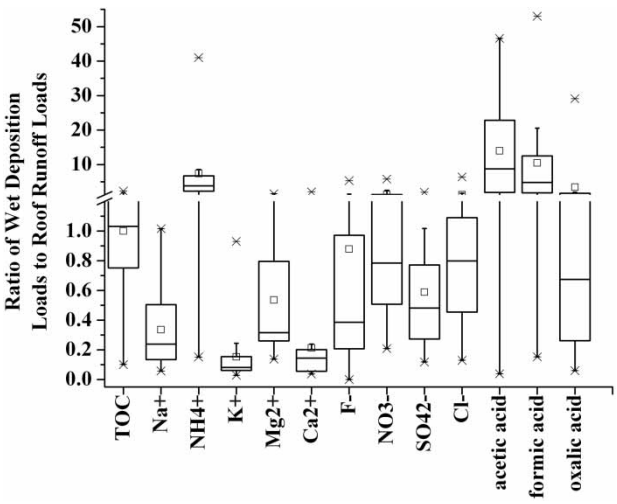

Figure 4 | Ratio of component mass in wet deposition to that in roof runoff.

R_i is highly variable, dependent upon different rainfall events, thus the one sample t-test was used to detect whether or not the population mean (μ_3) of R_i for each component and 0 is different. The hypothesis was set: H_0: $\mu_3 = 0$; H_1: $\mu_3 \neq 0$. The results indicate that the differences for all the components except for oxalic acid are significant (p-value < 0.05), the null hypothesis is rejected, the difference between μ_3 and 0 is significant, and the mean difference is positive. Therefore, the mass of the components in the wet deposition has a significant contribution to that in the roof runoff during a rainfall event.

Furthermore, the one sample t-test was used to detect whether or not the population mean (μ_3) of R_i for each component and 1 is different. The hypothesis was set, H_0: $\mu_3 = 1$; H_1: $\mu_3 \neq 1$. According to the results of the one sample t-test, the components can be classified into three groups (Table 5).

Group 1 (including TOC, NO_3^-, Cl^- and oxalic acid). In this group, the null hypothesis is accepted (p-value > 0.05), and the difference between the population mean (μ_3) for the component in the group and 1 is insignificant. The results implicate that the mass of the components in the wet deposition is close to that in the roof runoff during a rainfall event, which can be denoted as $R_i \approx 1$. However, different components may have different reasons for it.

The proportions of TOC, Cl^- and NO_3^- in the wet deposition are much higher than those in the dust buildup on the rooftop, and the chemical reactions in the roof runoff have no or insignificant impact on the mass of the components. This implies that wet deposition has a dominant contribution to the mass of the components in the roof runoff.

The proportion of oxalic acid in the wet deposition is close to that in the dust buildup. However, R_i of oxalic acid is close to 1. One possible reason is that the chemical reactions between oxalic acid and alkaline dust buildup on the rooftop (e.g. calcium carbonate and sodium carbonate) significantly decrease the oxalic acid in the roof runoff. The possible reactions may be expressed as follows:

$$CaCO_3 + HO_2C - CO_2H - - - > Ca(C_2O_4) + CO_2\uparrow + H_2O \quad (5)$$

$$Na_2CO_3 + HO_2C - CO_2H - - - > Na_2(C_2O_4) + CO_2\uparrow + H_2O \quad (6)$$

Group 2 (including NH_4^+, acetic acid and formic acid). In this group, the null hypothesis is rejected (p-value < 0.05), and $\mu_3 > 1$ is significant. The results imply that the mass of the components in the wet deposition is higher than that in the roof runoff during a rainfall event, which can be denoted as $R_i > 1$.

As seen in Table 5, the proportions of NH_4^+, acetic acid and formic acid in the wet deposition are much higher than those in the dust buildup on the rooftop. Since the runoff from the cement mortar roofing is alkaline, the reaction between NH_4^+ and OH^- may produce volatile ammonium hydroxide and possibly release NH_3 into the air. In addition, because of the existence of weak acid ions (e.g. acetate and carbonate), NH_4^+ and the ions may occur double hydrolysis reactions, which promote the transform from NH_4^+ to NH_3. For example, the double hydrolysis reaction of NH_4^+ and acetate occurs as follows:

$$NH_4^+ + CH_3COO^- \rightarrow NH_3 + CH_3COOH \quad (7)$$

The formic acid, acetic acid and oxalic acid may react with alkaline dust buildup on the rooftop (e.g. calcium carbonate and sodium carbonate), which causes a significant reduction of the organic acids in the roof runoff. The possible reactions may be expressed as follows:

$$CaCO_3 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + H_2O + CO_2 \quad (8)$$

$$CaCO_3 + 2CH_2O_2 \rightarrow Ca(HCOO)_2 + H_2O + CO_2 \quad (9)$$

Group 3 (including Na^+, K^+, Mg^{2+}, Ca^{2+}, F^-, SO_4^{2-}). In this group, the null hypothesis is rejected (p-value < 0.05), and $\mu_3 < 1$ is significant. The results imply that the mass of the components in the wet deposition is lower than that in the roof runoff during a rainfall event, which can be denoted as $R_i < 1$.

This is because the proportions of K^+, Mg^{2+}, Ca^{2+}, F^- and SO_4^{2-} in the wet deposition are lower than or close to those in the dust buildup on the rooftop. Furthermore, the acidic rainwater may corrode the cement mortar roof and facilitate the leaching of K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} into the roof runoff.

The proportion of Na^+ in the wet deposition is higher than that in the dust buildup. However, the cement mortar roofing usually contains Na_2CO_3, which is added to composite cement as activator. Owing to the influence of acid rain, some mass of Na^+ may leach from the roofing materials, which may significantly increase the mass of Na^+ in the roof runoff and cause the R_i of Na^+ to be lower than 1.

Therefore, in this group, wet deposition is part of the contribution to the mass of Na^+, K^+, Mg^{2+}, Ca^{2+}, F^- and SO_4^{2-} in the roof runoff, while other factors like dust buildup on the rooftop and chemical reactions also have non-negligible impact.

Components in wet deposition and atmosphere

The results above indicate that some components (such as TOC, NH_4^+, NO_3^-, acetic acid, formic acid and oxalic acid) in wet deposition have dominant contributions to the mass of the components in the roof runoff. Generally, the components in the wet deposition are affected by the air quality. Spearman rank correlation analysis was used to evaluate the strength of links between the wet deposition during the rainfall events and air quality within 30 min before the rainfall events. The results indicate that TOC, NH_4^+, NO_3^-, formic acid and oxalic acid in the wet deposition have moderate or strong positive correlation with PM_{10} in the atmospheric environment; both NO_3^- and NH_4^+ in the wet deposition have strong positive correlation with NO_x in the atmospheric environment (Table 6). This is because the components may occur either as gaseous or aerosol forms in the atmospheric environment, and wet deposition rather than dry deposition is the main route through which the components in the atmospheric environment reach the rooftop (Zhang *et al.* 2007).

Furthermore, TOC, NH_4^+, NO_3^- and organic acids in the atmosphere are mainly influenced by anthropogenic sources rather than natural and marine sources (Huang *et al.* 2010b). NO_3^- derives from the precursor of HNO_3 and aerosol $NO3^-$, both resulting from fossil fuel combustion (Zhang *et al.* 2007). NH_4^+ mainly comes from chemical emissions, vehicle emissions, biomass burning,

Table 6 | Correlative coefficients between concentrations of components in wet deposition and atmosphere

	TOC	NH_4^+	NO_3^-	SO_4^{2-}	Acetic acid	Formic acid	Oxalic acid
PM_{10}	0.600[a]	0.782[b]	0.891[b]	0.782[b]	0.515	0.891[b]	0.758[a]
NO_x	0.527	0.794[b]	0.842[b]	0.612	0.455	0.588	0.624
SO_2	0.636[a]	0.770[b]	0.806[b]	0.600[a]	0.576[a]	0.661[a]	0.624

[a]$0.01 < p < 0.05$.
[b]$p < 0.01$.

biological process and agricultural activities (Hu *et al.* 2005). Huang *et al.* (2006) investigated the water-soluble organic carbon (WSOC) in Shenzhen and found that biomass burning and in-cloud processing were the major contributors to the WSOC in fine aerosol particles. Organic acids in the wet deposition originate from both direct anthropogenic and natural emissions and secondary photochemical production from precursors (Chebbi & Carlier 1996).

Implications for roof runoff quality management

In this study, TOC, NH_4^+, NO_3^- and some organic acids in wet deposition have dominant contributions to the mass of the components in the roof runoff. Wet deposition is usually affected by the atmosphere pollution before the rainfall events. To ensure the water quality safety of rooftop rainwater harvesting, the initial or total roof runoff from the rainfall event after a period of heavy atmospheric pollution should be discarded. In addition, TOC, NH_4^+, NO_3^- and organic acids in the atmosphere are mainly influenced by fossil fuel consumption (e.g. vehicle emissions) in the study area. Therefore, the effects of wet deposition on the roof runoff quality can be reduced by implementing some atmospheric pollution control measures, e.g. improving vehicle fuel quality, promoting public transport system, promoting the use of clean energy in the power plants and industrial boilers and so on.

With rapid urbanization and industrialization, Shenzhen suffers from the atmospheric pollution problems due to fast increase in fossil fuel consumption (e.g. vehicle emissions). The water quality of roof runoff in Shenzhen is strongly affected by the atmospheric environment quality and the wet deposition. Therefore, the effects of atmospheric wet deposition should be carefully considered for the rooftop rainwater harvesting and storm water quality management, particularly in the urbanized areas suffering from atmospheric pollution due to fossil fuel consumption.

CONCLUSIONS

To identify the contributions of atmospheric wet deposition to the chemical components in roof runoff, the main components in rainwater and roof runoff were measured at an urban site in Shenzhen from 2011 to 2012. Atmospheric environment quality and the dust buildup on the rooftop were also measured to reveal the underlying reasons. The results obtained are summarized below.

The mass of the different components in the wet deposition may have different contributions to that in the roof runoff: (1) wet deposition has a dominant contribution to the mass of TOC, NO_3^-, Cl^- and oxalic acid in the roof runoff during a rainfall event, while other factors, e.g. dry deposition and debris of the roofing material, have an insignificant impact; (2) wet deposition has a dominant contribution to the mass of NH_4^+, acetic acid and formic acid in the roof runoff, while their mass may be greatly reduced due to consumption in the neutralization between the components with alkaline dust buildup on the rooftop; and (3) wet deposition partially contributes to the mass of Na^+, K^+, Mg^{2+}, Ca^{2+}, F^- and SO_4^{2-} in the roof runoff, while other factors like dust buildup on the rooftop and chemical reactions also have a non-negligible impact. The differences may be explained by comparing the component proportion in the wet deposition with that in the dust buildup on the rooftop and by considering the possible chemical reactions in the roof runoff. In addition, TOC, NH_4^+, NO_3^- and organic acids in the wet deposition have moderate or strong positive correlations with PM_{10} and

NO_x in the atmospheric environment. These components in the wet deposition are mainly influenced by the atmospheric pollution due to a fast increase in fossil fuel consumption (e.g. vehicle emissions) in the study area. Therefore, the effects of atmospheric wet deposition should be carefully considered for rooftop rainwater harvesting and storm water quality management, particularly in the urbanized areas suffering from atmospheric pollution due to fossil fuel consumption.

It should be noted that this study is limited to 1 year of measured data and the discussions in the case study are time- and site-specific. Further study is required on the impacts of wet deposition on water quality in roof runoff, particularly in various types of urbanized areas.

ACKNOWLEDGEMENTS

This research was supported by the National Natural Science Foundation of China (51079001), National Water Pollution Control and Management Technology Major Projects (No. 2013ZX07501005) and Shenzhen Science and Technology Development Fund Project (JCYJ20130329180732262).

REFERENCES

Abbasi, T. & Abbasi, S. A. 2011 Sources of pollution in rooftop rainwater harvesting systems and their control. *Crit. Rev. Environ. Sci. Technol.* **41** (23), 2097–2167.

Burian, S. J., Streit, G. E., McPherson, T. N., Brown, M. J. & Turin, H. J. 2001 Modeling the atmospheric deposition and stormwater washoff of nitrogen compounds. *Environ. Model. Softw.* **16**, 467–479.

Báez, A., Belmont, R., Garcia, R., Padilla, H. & Torres, M. C. 2007 Chemical composition of rainwater collected at a southwest site of Mexico City, Mexico. *Atmos. Res.* **86** (1), 61–75.

Cao, Y. Z., Wang, S. Y., Zhang, G., Luo, J. Y. & Lu, S. Y. 2009 Chemical characteristics of wet precipitation at an urban site of Guangzhou, South China. *Atmos. Res.* **94** (3), 462–469.

Che, W., Wang, H. Z., Ren, C., Liu, H. & Meng, G. H. 2001 Studies on roof runoff pollution and utilization in Beijing urban area. *China Water Wastewater* **17** (6), 57–61 (in Chinese).

Chebbi, A. & Carlier, P. 1996 Carboxylic acids in the troposphere, occurrence, sources and sinks: a review. *Atmos. Environ.* **30**, 4233–4249.

Clark, S. E., Steele, K. A., Spicher, J., Siu, C. Y. S., Lalor, M. M., Pitt, R. & Kirby, J. T. 2008 Roofing materials' contributions to storm-water runoff pollution. *J. Irrig. Drain E-ASCE* **134** (5), 638–645.

Forster, J. 1998 The influence of location and season on the concentrations of macroions and organic trace pollutants in roof runoff. *Water Sci. Technol.* **38** (10), 83–90.

Gikas, G. D. & Tsihrintzis, V. A. 2012 Assessment of water quality of first-flush roof runoff and harvested rainwater. *J. Hydrol.* **466–467**, 115–126.

Hou, L. Z. & Zhang, X. 2014 Comparing urban runoff quality of a felt roof and an asphalt road in Beijing. *Hydrol. Res.* **45** (2), 282–291.

Hu, G. P., Balasubramanian, R. & Wu, C. D. 2003 Chemical characterization of rainwater at Singapore. *Chemosphere* **51** (8), 747–755.

Hu, M., Zhang, J. & Wu, Z. J. 2005 Chemical compositions of precipitation and scavenging of particles in Beijing. *Sci. China B Chem.* **48** (3), 265–272.

Huang, X. F., Yu, J. Z., He, L. Y. & Yuan, Z. 2006 Water-soluble organic carbon and oxalate in aerosols at a coastal urban site in China: size distribution characteristics, sources, and formation mechanisms. *J. Geophys. Res.* **111**, D22212.

Huang, K., Zhuang, G. S., Xu, C., Wang, Y. & Tang, A. H. 2008 The chemistry of the severe acidic precipitation in Shanghai, China. *Atmos. Res.* **89** (1–2), 149–160.

Huang, D. Y., Xu, Y. G., Zhou, B., Zhang, H. H. & Lan, J. B. 2010a Wet deposition of nitrogen and sulfur in Guangzhou, a subtropical area in South China. *Environ. Monit. Assess.* **171**, 429–439.

Huang, X. F., Li, X. A., He, L. Y., Feng, N., Hu, M., Niu, Y. W. & Zeng, L. W. 2010b 5-year study of rainwater chemistry in a coastal mega-city in South China. *Atmos. Res.* **97**, 185–193.

Huston, R., Chan, Y. C., Gardner, T., Shaw, G. & Chapman, H. 2009 Characterisation of atmospheric deposition as a source of contaminants in urban rainwater tanks. *Water Res.* **43**, 1630–1640.

Kim, L. H., Ko, S. O., Jeong, S. & Yoon, J. 2007 Characteristics of washed-off pollutants and dynamic EMCs in parking lots and bridges during a storm. *Sci. Total Environ.* **376** (1–3), 178–184.

Lamprea, K. & Ruban, V. 2011 Characterization of atmospheric deposition and runoff water in a small suburban catchment. *Environ. Technol.* **32** (10), 1141–1149.

Lee, B. K., Hong, S. H. & Lee, D. S. 2000 Chemical composition of precipitation and wet deposition of major ions on the Korean peninsula. *Atmos. Environ.* **34** (4), 563–575.

Lee, J. Y., Kim, H. J. & Han, M. Y. 2011 Quality assessment of rooftop runoff and harvested rainwater from a building catchment. *Water Sci. Technol.* **63** (11), 2725–2731.

Melidis, P., Akratos, C. S., Tsihrintzis, V. A. & Trikilidou, E. 2007 Characterization of rain and roof drainage water quality in Xanthi, Greece. *Environ. Monit. Assess.* **127**, 15–27.

Mendez, C. B., Klenzendorf, J. B., Afshar, B. R., Simmons, M. T., Barrett, M. E., Kinney, K. A. & Kirisits, M. J. 2011 The effect of roofing material on the quality of harvested rainwater. *Water Res.* **45**, 2049–2059.

Okuda, T., Iwase, T., Ueda, H., Suda, Y., Tanaka, S., Dokiya, Y., Fushimi, K. & Hosoe, M. 2005 Long-term trend of chemical

constituents in precipitation in Tokyo metropolitan area, Japan, from 1990 to 2002. *Sci. Total Environ*. **339** (1–3), 127–141.

Polkowska, Ż., Górecki, T. & Namiesnik, J. 2011 Determination of atmospheric pollutants in wet deposition. *Environ. Rev*. **19**, 185–213.

Ragab, R., Bromley, J., Rosier, P., Cooper, J. D. & Gash, J. H. C. 2003 Experimental study of water fluxes in a residential area: 1. Rainfall, roof runoff and evaporation: the effect of slope and aspect. *Hydrol. Process*. **17**, 2409–2422.

Rentz, R. & Öhlander, B. 2012 Urban impact on water bodies in the Luleå area, northern Sweden, and the role of redox processes. *Hydrol. Res*. **43** (6), 917–932.

Rocher, V., Azimi, S., Gasperi, J., Beuvin, L., Muller, M., Moilleron, R. & Chebbo, G. 2004 Hydrocarbons and metals in atmospheric deposition and roof runoff in central Paris. *Water Air Soil Poll*. **159**, 67–86.

Song, F. & Gao, Y. 2009 Chemical characteristics of precipitation at metropolitan Newark in the US East Coast. *Atmos. Environ*. **43** (32), 4903–4913.

State Environmental Protection Administration of China 2004 *Technical Specifications for Acid Deposition Monitoring*. State Environmental Protection Administration of China, Beijing (in Chinese).

Tian, Y. H., Yang, L. Z., Yin, B. & Zhu, Z. L. 2011 Wet deposition N and its runoff flow during wheat seasons in the Tai Lake Region, China. *Agric. Ecosyst. Environ*. **141**, 224–229.

Topcu, S., Incecik, S. & Atimtay, A. T. 2002 Chemical composition of rainwater at EMEP station in Ankara, Turkey. *Atmos. Res*. **65** (1–2), 77–92.

Tsai, Y. I., Hsieh, L. Y., Kuo, S. C., Chen, C. L. & Wu, P. L. 2011 Seasonal and rainfall-type variations in inorganic ions and dicarboxylic acids and acidity of wet deposition samples collected from subtropical East Asia. *Atmos. Environ*. **45**, 3535–3547.

Tu, J., Wang, H. S., Zhang, Z. F., Jin, X. & Li, W. Q. 2005 Trends in chemical composition of precipitation in Nanjing, China, during 1992–2003. *Atmos. Res*. **73** (3–4), 283–298.

Vázquez, A., Costoya, M., Pena, R. M., Garcia, S. & Herrero, C. 2003 A rainwater quality monitoring network: a preliminary study of the composition of rainwater in Galicia (NW Spain). *Chemosphere* **51** (5), 375–386.

Vialle, C., Sablayrolles, C., Lovera, M., Jacob, S., Huau, M. C. & Montrejaud-Vignoles, M. 2011 Monitoring of water quality from roof runoff: interpretation using multivariate analysis. *Water Res*. **45** (12), 3765–3775.

Wang, B. & Li, T. 2009 Buildup characteristics of roof pollutants in the Shanghai urban area, China. *J. Zhejiang Univ. Sci. A* **10** (9), 1374–1382.

Wicke, D., Cochrane, T. A., O'Sullivan, A. D., Cave, S. & Derksen, M. 2014 Effect of age and rainfall pH on contaminant yields from metal roofs. *Water Sci. Technol*. **69** (10), 2166–2173.

Zhang, M. Y., Wang, S. J., Wu, F. C., Yuan, X. H. & Zhang, Y. 2007 Chemical compositions of wet precipitation and anthropogenic influences at a developing urban site in southeastern China. *Atmos. Res*. **84**, 311–322.

Zhang, H. P., Zhu, Y. P., Li, F. P. & Chen, C. 2011 Nutrients in the wet deposition of Shanghai and ecological impacts. *Phys. Chem. Earth* **36**, 407–410.

First received 17 November 2014; accepted in revised form 19 January 2015. Available online 5 March 2015