

The contribution of wet deposition and particulate matter to total copper, lead and zinc in stormwater runoff

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Biography

Louise Murphy successfully defended her PhD in April 2015 with the department of Civil and Natural Resources Engineering at the University of Canterbury. Louise is currently working with Tonkin & Taylor Ltd as an environmental scientist; her work interests include contaminated land, stormwater quality and atmospheric pollution.

Abstract

Wet deposition is an important process in the removal of heavy metal particulates from the atmosphere. However, the contribution of wet deposition to the total heavy metal deposition flux can vary widely between different airsheds. Understanding the contribution of wet deposition to the total metal deposition flux is important for accurate knowledge of local atmospheric deposition processes, which will subsequently help in the selection of appropriate stormwater treatment and management options. This research monitored Cu, Zn and Pb loads in wet deposition samples and in bulk deposition samples from modular concrete paving slab systems. In conjunction, ambient particulate matter (PM) concentrations were monitored to determine their contribution to the wet deposition flux. All research was conducted in an industrial land-use area in Christchurch, New Zealand. Results showed that wet deposition efficiently removed PM from the atmosphere, but after 1–2.5 antecedent dry days, PM concentrations recovered. Subsequent antecedent dry days, i.e. > 1–2.5 d, did not influence PM concentrations. Pb loads in wet deposition were dependent on coarse PM (size range between 2.5 μm and 10 μm) concentrations. This suggested that there was a local source emitting coarse Pb particles into the atmosphere. Wet deposition was an important contributor of dissolved Zn to bulk deposition. However, dry deposition was the greatest source of total Cu, Zn, and Pb loads in bulk deposition. This is principally due to the low annual rainfall in Christchurch, which limits pollutant removal via wet deposition unlike dry deposition, which is continually occurring.

Introduction

Particulate matter (PM) is an atmospheric pollutant that is defined by its size rather than its chemical nature, structure, or origin.¹ PM is not a single pollutant, but rather a heterogeneous composite of particles varying in chemical composition, shape, size, solubility, residence time, toxicity, and origin.^{1,2} PM is typically subdivided into two categories: $\text{PM}_{2.5}$ and PM_{10} . $\text{PM}_{2.5}$ comprises of particles with a diameter smaller than 2.5 μm and are referred to as “fine” particles. PM_{10} refers to particles with a diameter smaller than 10 μm , which also encompasses the $\text{PM}_{2.5}$ fraction. Particles with a size range between 2.5 μm and 10 μm are called “coarse” particles

($\text{PM}_{10-2.5}$). In most urban environments, both coarse and fine particles are present together, but the proportion of fine to coarse particles varies between different urban airsheds depending on the local geography, meteorology, and the emission source(s).³ Fine particles, in comparison to coarse particles, have a longer atmospheric residence time and can be carried long distances, in some instances travelling 1,000–10,000 km from their source.¹

The majority of regulation and research initiatives involving PM are driven by its effects on human health,¹ unsurprisingly, as the WHO considers PM as a major risk factor for human health.³ In particular, fine particles are associated with the most adverse health effects from particulate air pollution because they can penetrate and lodge deeply in the lungs.³ However, PM can also be a substantial source of organic and inorganic pollutants. For example, fine particles are typically composed of SO_4^{2-} , NO_3^- , NH_4^+ , organic carbon, elemental carbon, and heavy metals; coarse particles are typically composed of bioaerosols, e.g. pollen, geological material, and sea salt spray.⁴ PM containing heavy metals are important to research because they can exist in varying chemical forms, i.e. water soluble, loosely particulate bound, or insoluble forms,⁵ and can be incorporated into stormwater pollution. In general, heavy metals are associated with fine particulates because fines have a greater surface area per unit mass and accumulate metals more efficiently.⁶ As fine particulates have a longer residence time in the atmosphere, concentrations are typically more homogeneously distributed in an airshed as they get farther from the emission source.

The removal process of PM metals from the atmosphere is via atmospheric deposition. Atmospheric deposition occurs in two ways: dry or wet deposition. Dry deposition (DD) is the direct settling of PM onto land or water surfaces via impaction, gravitational settling, turbulence, or Brownian motion depending on the size of the PM.⁷ Wet deposition (WD) occurs when PM leaches from the atmosphere with water droplets in the form of rain, snow, frost, fog, mist, and dew⁸ and it is considered the cleanser of the atmosphere.⁹ WD is one of the most important mechanisms through which airborne pollutants reach the land surface.¹⁰ WD has been reported to remove up to 70–80% of the pollutants, principally fine PM, from the

atmosphere.¹¹ However, this amount is dependent on the airshed studied, the chemical species, and the frequency of precipitation events.¹² Aside from being a major atmospheric pollutant removal pathway, WD is important because it leaches pollutants to a surface partly in solution, enhancing the possibility of biological interactions.¹³ The solubility of the pollutant is affected by rainfall pH, pollutant concentration, and the type of particle the pollutant is affiliated with in the atmosphere.¹⁴

WD becomes stormwater runoff after contact with the land surface.¹⁰ The runoff incorporates DD particles resulting in bulk deposition (BD) loads captured from an impermeable surface. Quantifying the relative contribution of WD and DD to BD loads is important for gaining knowledge on local atmospheric deposition processes, which will subsequently help in the selection of appropriate stormwater treatment and management options. In addition, ambient PM concentrations are also important to research as they can contain heavy metals, and thus, can contribute to WD and DD metal loads in stormwater. In particular, it is important to determine how ambient PM concentrations respond after a rain event as they will influence the amount of metal particulates available for deposition onto impermeable surfaces. Thus, this paper reports on research findings from monitoring the contribution of WD to the total Cu, Zn, and Pb deposition flux in an industrial area of Christchurch, New Zealand, a medium sized city with low intensity (95% events are < 10 mm/hr) and frequency (<81 wet annual days) of rainfall. PM concentrations were also assessed to elucidate relationships with WD metal loads and antecedent dry days.

Materials and methods

Study sites

Field investigations were conducted in a light industrial land-use area in Christchurch, New Zealand, from August 2013 to March 2014. The climate of Christchurch is associated with low rainfall and long antecedent dry periods, typically of a semi-arid environment. Christchurch is prone to smog events that commonly occur during cold calm nights when the atmosphere is stable and emissions from domestic heating are high.¹⁵ Smog events are a principal result of the strong near-surface temperature inversions during anticyclonic synoptic conditions.¹⁶ PM concentrations and WD were measured at an Environment Canterbury (ECan) air monitoring station that was within the vicinity of an old but operating gelatin factory, a shopping centre, and a shipping container terminal where air discharges were expected to be frequent. BD samples from concrete modular paving slab systems (here on referred to as boards) were collected 1.44 km away from the WD and PM samplers. The distance between the PM sampler and the board setup was due to the availability of secure and private land to host the experimental setup. BD was collected in the immediate vicinity of a shipping container terminal, liquid petroleum gas depot, retail premises, and warehouses.

Field sampling

The PM data were measured and analysed by ECan. PM₁₀ and PM_{2.5} were measured using a Tapered Element Oscil-

ating Microbalance (TEOM) with a Filter Dynamics Measurement System (FDMS). PM data from August 2013 to the end of November 2013 were audited by ECan; however, data afterwards were not officially audited, but results are unlikely to have changed by more than 1 – 2 µg/m³. WD samples were collected by a WD sampler (N-Con ADS Model 00-120-2). The WD sampler had an infrared transmitter and receiver that opened the sampler within 20 seconds of the onset of precipitation and closed it within a minute of the end of precipitation. BD samples were collected from four replicate impermeable concrete boards (as detailed in Murphy *et al.*^{17,18}). The concrete boards were designed to capture atmospheric pollutant build-up (DD) and atmospheric pollutant wash-off (WD). The concrete boards (1,000 mm x 1,000 mm) were elevated 500 mm from the ground and inclined at a 4° slope. A collection area (718 mm x 400 mm) was incorporated into the concrete board design to account for pollutant loss via splash and spray. Runoff from the collection area was conveyed to a 20 l high density polyethylene collection chamber via a stormwater collection funnel. Rainfall data were obtained from Christchurch City Council's weather station located 0.87 km away from the PM and WD samplers.

Sample collection and analyses

Seventeen rain events were sampled from August 2013 (winter) to March 2014 (autumn) to analyse the relationship between WD loads and PM (Table 1). Eight WD samples were measured that could be directly compared to pollutant loads from BD (Table 1). WD and BD samples were collected and analysed for total and dissolved Cu, Pb, and Zn loads. All samples were stored below 4 °C after collection. Cu, Pb, and Zn concentrations were determined by ICP-MS (Agilent) following the APHA¹⁹ method 3125-B. Total metals were HNO₃ digested following the method described by Wicke *et al.*²⁰ The detection limit for Zn was 10 µg/l; the detection limit for Cu and Pb was 1 µg/l. Any data below the detection limit (principally dissolved Pb) were removed from the dataset. QA/QC protocols including blanks, duplicates (at least 10% of samples), spikes, standards, and instrument calibration were conducted.

Statistical analyses

Statistical analyses were conducted using the R 3.0.2 package.²¹ A multivariate analysis of variance (MANOVA) test was performed to ascertain whether statistical differences existed in the mean PM_{10-2.5} and PM_{2.5} concentrations with varying antecedent dry periods. Differences between antecedent dry periods were analysed by *post hoc* Gabriel analysis for its superior capabilities at handling unequal sample sizes.²² All dependent variables were transformed (natural log) to comply with the normal distribution criterion. Homogeneity of variance was confirmed using Levene's test.²² A Pearson's Correlation was used to determine statistical dependence between two variables.

Table 1. Summary of rain events captured during the sampling campaign [* = WD sampled; ** = WD and BD sampled]

Event no.	Date	Rain depth (mm)	Antecedent dry days (d)
1**	03/08/13	5.8	10
2**	25/09/13	2.0	2.7
3**	08/10/13	33	8
4**	13/10/13	8.4	2.5
5**	25/10/13	5.6	7
6**	31/10/13	2.0	5.5
7*	22/11/13	5.6	19.6
8**	25/11/13	13.0	3
9**	08/12/13	3.8	11
10*	17/12/13	5.2	6.8
11*	20/01/14	10.6	13.5
12*	26/01/14	3.6	5.4
13*	12/02/14	15.6	11.2
14*	23/02/14	9.6	9.4
15*	28/02/14	11.8	4.8
16*	03/03/14	138.4	2.1
17*	05/03/14	1.8	0

Results and discussion

Particulate matter with varying antecedent dry periods

A MANOVA statistical analysis was conducted to ascertain if there was a significant difference in fine and coarse particulate concentrations with varying antecedent dry periods. The antecedent dry periods were categorised into six groups: <1 d, 1 - <2.5 d, 2.5 - <4 d, 4 - <5.5 d, 5.5 - 7 d, >7 d. The mean concentrations of ambient fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) particles varied significantly with changing antecedent dry periods (Pillai's trace [$V = 0.166$, $F(10, 454) = 4.108$, p -value < 0.001]). For coarse particles, there was a significant difference in their concentrations when the antecedent dry period was

between 0-1 d. After one antecedent dry day, the concentrations of coarse particles did not alter significantly with increasing antecedent dry days (Table 2). Similarly, for fine particles, there was a significant difference in their concentrations when the antecedent dry period was between 0 - 2.5 d. After 2.5 antecedent dry days, the concentrations of fine particles did not alter significantly with increasing antecedent dry days (Table 2). Therefore, wash-off from a precipitation event had a significant effect on fine and coarse particle concentrations within the initial few days of the rain event occurring, but both fine and coarse particle concentrations were not influenced by longer antecedent dry periods (1 to 2.5 days). This differs to particulate build-up on urban impermeable surfaces, whereby, particulate build-up increases asymptotically with antecedent dry days, which ultimately plateaus after 6 days.²³ Therefore, particulate build-up on an impermeable surface is limited at the start of the antecedent dry period because wet deposition has removed the PM from the atmosphere.

The average concentrations of $PM_{10-2.5}$ and $PM_{2.5}$ ($\mu\text{g}/\text{m}^3$) within the light industrial land-use area with varying antecedent dry periods. Within each antecedent dry period, those sharing a common letter are not significantly different ($p > 0.05$) [n = number of cases analysed].

Particulate matter and wet deposition

A summary of WD pollutant loads and $PM_{2.5}$, PM_{10} , and $PM_{10-2.5}$ concentrations the hour preceding the rain event are shown in Table 3. The relationship between PM concentrations prior to rainfall and heavy metal loads in WD was determined using a Pearson's correlation. PM concentrations before rainfall did not show a significant relationship with heavy metal loads in WD, except for Pb, which had a significant relationship with $PM_{10-2.5}$ concentrations. This suggests that coarse particle concentrations in the atmosphere influenced Pb loads captured in WD. This finding was different to other research, which stated that Pb loads in WD were mainly associated with the submicron size range.²⁴ However, Lee and Park²⁵ also found that Cu did not correlate with PM, while Pb was highly correlated (p -value < 0.05) with PM in air emissions from an urban-residential and industrial land-use area in Ulsan, Korea. The reason that Cu and Zn were not statistically related to PM was probably due to the height of the PM monitoring station; PM concentrations were

Table 2. The average concentrations of $PM_{10-2.5}$ and $PM_{2.5}$ ($\mu\text{g}/\text{m}^3$) within the light industrial land-use area with varying antecedent dry periods. Within each antecedent dry period, those sharing a common letter are not significantly different ($p > 0.05$) [n = number of cases analysed]

	<1 d	1 - <2.5 d	2.5 - <4 d	4 - <5.5 d	5.5 - <7 d	>7 d
$PM_{10-2.5}$	9.03 ± 0.68 ^a	13.34 ± 0.84 ^b	16.11 ± 1.16 ^b	17.09 ± 1.61 ^b	15.44 ± 1.51 ^b	16.28 ± 1.23 ^b
$PM_{2.5}$	5.23 ± 0.31 ^a	6.78 ± 0.48 ^{ab}	7.70 ± 0.54 ^b	7.72 ± 0.58 ^b	8.67 ± 0.91 ^b	7.81 ± 0.49 ^b
n	30	47	43	32	27	54

Table 3. The range (min - max) and mean values of PM measured at the light industrial land-use area one hour prior to the rain event ($\mu\text{g}/\text{m}^3$) and total metals ($\mu\text{g}/\text{m}^2$) in WD

	PM_{10}	$PM_{2.5}$	$PM_{10-2.5}$	$tCu_{(WD)}$	$tZn_{(WD)}$	$tPb_{(WD)}$
Range	6.2 – 93.2	0 – 13.0	2.7 – 78.1	1.5 – 509.2	17.4 – 888.6	n/d – 130.3
Mean ± SE	26.8 ± 5.6	6.2 ± 3.2	20.1 ± 5.0	56.5 ± 28.3	213.6 ± 56.7	20.2 ± 9.0

measured approximately 3 m above the ground, which only reflects PM concentrations at the lower tropospheric level. Cu and Zn particulate concentrations higher in the troposphere, e.g. where cloud formation occurs and rain-particle impaction occurs, were not wholly represented. It is likely that the correlation between PM and Pb was due to a local source of Pb contributing to WD loads, for example, from nearby old residential houses with Pb-based paint being demolished after the 2011 Canterbury earthquakes. A local source of particulate Pb would explain why there was PM Pb concentrations in the lower troposphere – particulate Pb did not have sufficient time to reach higher altitudes in the troposphere before being washed-out. On the other hand, if the source of Cu and Zn were farther away, the Cu and Zn particulates would have been able to reach higher altitudes.

Wet deposition

Determining the speciation phase of metals in WD is important because metals can occur in either the particulate or the dissolved phase. Metals in their dissolved forms are most concerning because of their increased mobility in the aquatic environment, and thus, availability for biological uptake.²⁶ The partitioning of trace metals to the dissolved or particulate phase depends on the quantity and solubility of trace metals in a rain event.²⁷ The percentage contribution of dissolved to total metals in WD ($n=17$) was $40.58\% \pm 7.38\%$ and $83.07\% \pm 4.72\%$ for Cu, and Zn, respectively. A ratio of dissolved to total Pb was not evaluated as dissolved Pb concentrations were frequently below the detection limit ($1 \mu\text{g/l}$). Particulate Pb dominated the total Pb flux because Pb had a low solubility in WD and was principally washed-out in particulate form. The ratio of dissolved to total Cu was relatively high, which suggested that Cu was easily soluble in WD. Zn was mainly associated with the dissolved phase (83.07%); therefore, Zn was highly soluble in WD. Similarly, Morselli *et al.*²⁸ found that Zn had the highest solubility in WD followed by Cu; Pb had a very low solubility in WD. Colin *et al.*²⁹ found that Zn concentrations in WD in France were mainly associated with the dissolved phase (approximately 96%). Freydier *et al.*³⁰ found that Zn had the highest dissolved to total distribution of all metals studied (which included Pb, but not Cu) in intertropical Africa. WD results from Otago, New Zealand, found Zn atmospheric loads were present in a dissolved or easily dissolved forms, and thus, stated that Zn originated from a non-crustal source because metals generated from anthropogenic sources tend to be loosely bound to airborne particles.³¹ The results in this research differed to Conko *et al.*,²⁷ who found that Cu was more soluble than Zn in precipitate in Virginia, United States; however, this could be due to the lower rainfall pH in Virginia (3.7 – 4.7)

than Christchurch (4.9 – 7.2)^{27,32} or from different source emissions of metals in each airshed. Kaya and Tuncel¹⁴ reported solubilities of $43\% \pm 29\%$, $49\% \pm 27\%$, $40\% \pm 35\%$ for Zn, Cu, and Pb, respectively, in rainwater from Ankara, Turkey.

Contribution of WD to BD loads

Total Cu, Pb, and Zn loads from WD and BD from concrete boards (as previously discussed) are summarised in Table 4. The results show that WD contributed approximately 10 - 13% of the total Cu, dissolved Cu, and total Pb (dissolved Pb was negligible) loads in BD. Therefore, DD was the major pathway for Cu and Pb removal from the atmosphere (Figs 1 and 2 respectively). Conversely, WD was an important contributor of total Zn (34%) and dissolved Zn (133%) to BD (Fig. 3). The value of Zn above 100% was attributed to Zn being highly soluble in precipitate at the pH range (4.7 – 7.2) found in Christchurch rainfall. Moreover, concentrations of dissolved Zn from WD were higher than dissolved Zn concentrations in runoff from a concrete surface. The decrease in dissolved Zn concentration in the runoff was probably due to calcium carbonates and calcium hydroxides adsorbing dissolved Zn.³³ Although dissolved Zn loads were dominated by WD, DD was the biggest contributor to total Zn loads. Overall, the results demonstrate that DD was the important controller of atmospheric pollutant loads in BD due to limited precipitation in Christchurch. Although DD is a slow process, it is continually occurring unlike WD; therefore, it is of greater importance to net pollutant deposition. Mitigating atmospheric pollutant loads in DD should be the focus of stormwater management through improved source control legislation or by choosing the best pavement material for attenuating DD loads, i.e. concrete.

Conclusions

Knowledge of the pathways dominating atmospheric deposition is important because it increases our understanding of atmospheric pollutant removal processes. As the processes affecting pollutant deposition can vary for different airsheds due to different meteorology and land-use activities, it is important to quantify the contribution of wet and dry deposition for each airshed individually. The results presented here demonstrate the importance of WD in removing fine and coarse PM from the atmosphere. Following a rain event, atmospheric PM concentrations begin to increase; after one to two antecedent dry days, PM concentrations stabilise, i.e. PM concentrations are not influenced by longer antecedent dry periods.

DD was the dominant pathway for atmospheric metal removal due to the low rainfall frequency in Christchurch.

Table 4. The range (min – max) and mean values of total metals ($\mu\text{g}/\text{m}^2$) in BD from August 2013 to December 2013 and the percentage ratio of pollutant in WD to BD (mean \pm SE) [n/d = not detected; n/a = not analysed due to insufficient data]

	dCu	tCu	dZn	tZn	dPb	tPb
Min	15.66	34.74	26.40	36.39	n/d	3.39
Max	202.87	254.26	223.08	693.71	0.91	78.50
Mean \pm SE	62.80 ± 20.04	108.28 ± 22.43	118.09 ± 26.40	334.16 ± 77.57	n/a	35.79 ± 8.81
Ratio (%) to WD	12.44 ± 6.36	10.39 ± 2.52	132.71 ± 11.20	34.22 ± 5.31	n/a	11.64 ± 3.41

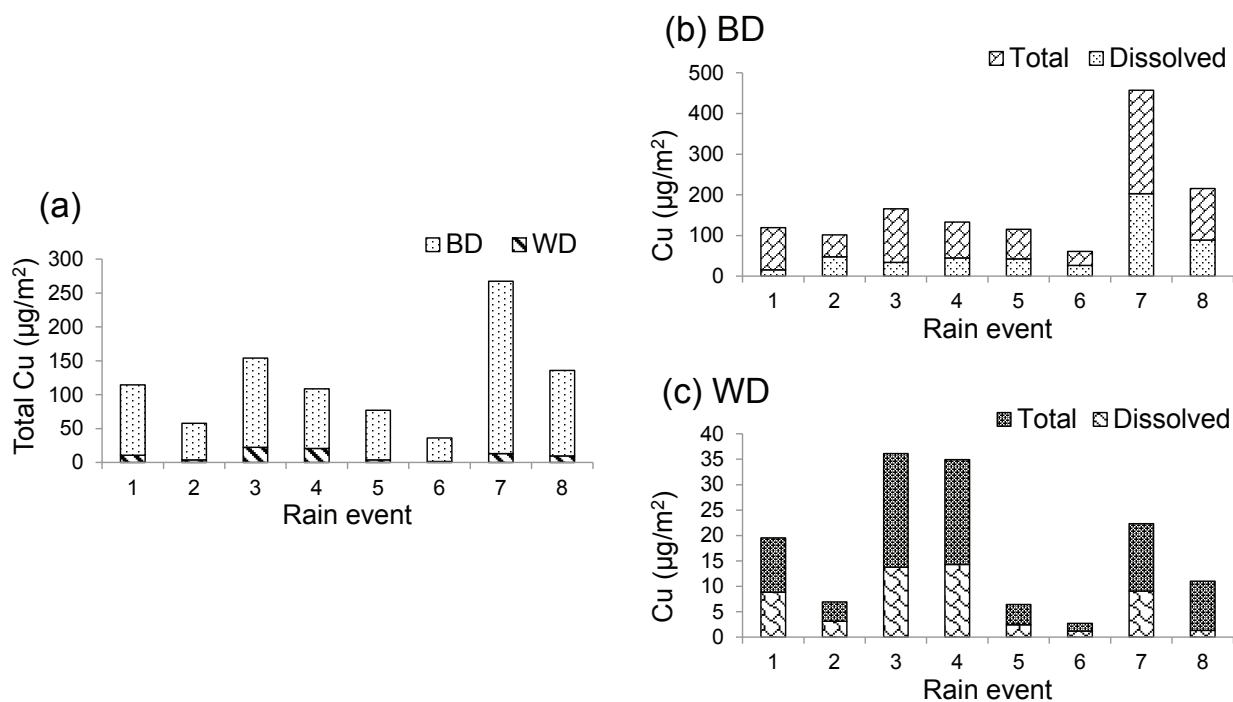


Fig. 1. (a) total Cu concentration in BD and WD; (b) the contribution of total and dissolved Cu in BD; and (c) the contribution of total and dissolved Cu in WD.

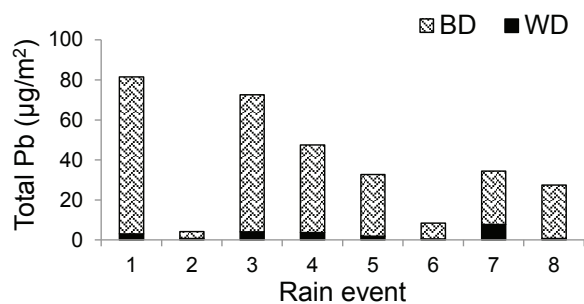


Fig. 2. Total Pb in BD and WD (dissolved Pb is not represented as it was frequently below detection limits)

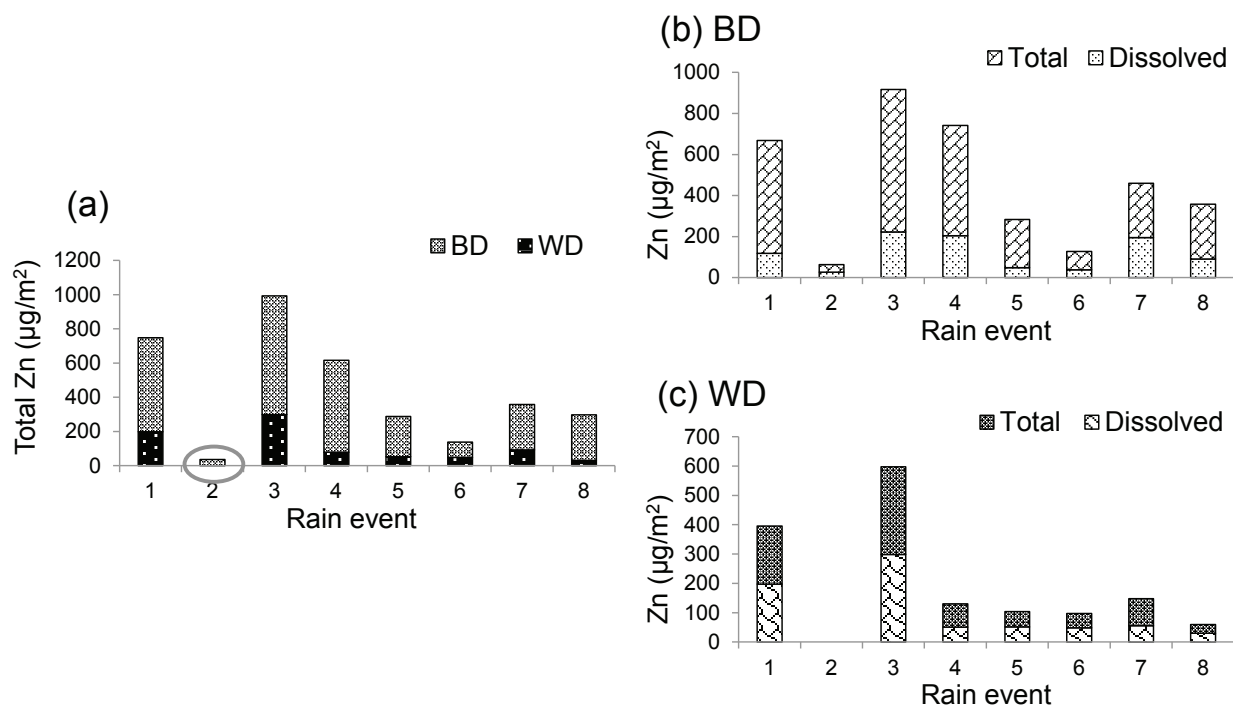


Fig. 3. (a) total Zn in BD and WD; (b) the contribution of total and dissolved Zn in BD; (c) the contribution of total and dissolved Zn in WD (Zn loads in WD from rain event 2 (circled) is not represented as it was below detection limit)

Therefore, from a stormwater manager's perspective, to manage atmospheric deposition as a source of stormwater pollution, emphasis should be placed on removing pollutant loads from DD. Frequent street vacuuming practices during dry days is an option; however, frequent street cleaning is costly and would not be suitable as a long-term pollution mitigation strategy. Implementing effective measures to mitigate atmospheric heavy metal deposition will be challenging unless effective legislation is enforced to mitigate heavy metal emissions to the atmosphere. Implementing controls on atmospheric heavy metal emissions in Christchurch, however, may not be effective (although, they should still occur) as pollutants can be transported from other regions beyond the legislative control, i.e. transboundary pollution (see Murphy *et al.*¹⁷). Therefore, current focus should be on treating the stormwater runoff as close to the source as possible. A high proportion of total Cu and total Zn are in the dissolved form; therefore, when treating stormwater pollution, emphasis should be placed more on treating the dissolved forms of Cu and Zn rather than the particulate forms.

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References

- Grantz, D. A.; Garner, J. H. B.; Johnson, D. W. *Enviro. Int.* **2003**, *29*(2-3), 213-239.
- Tecer, L. H.; Süren, P.; Alagha, O.; Karaca, F.; Tuncel, G. *J. Air & Waste Manage. Assoc.* **2008**, *58*(4), 543-52.
- WHO *Air quality guidelines - global update. 2005. Particulate matter, ozone, nitrogen dioxide and sulfur dioxide*; World Health Organization Regional Office for Europe: Copenhagen, 2006.
- Salomon, V. *Air quality status report PM_{2.5}; R14/53*; Environment Canterbury: Christchurch, New Zealand, 2014.
- Awan, M.; Ahmed, S. H.; Aslam, M. R.; Qazi, I.; Baig, M. A. *Arab. J. Sci. Eng.* **2013**, *38*(7), 1655-1661.
- Li, H.; Qian, X.; Wang, Q. *Env. Sci. Tech.* **2013**, *47*(23), 13210-13211.
- (a) Shrivastav, R. *Resonance* **2001**, *6*(4), 62-68; (b) Azimi, S.; Ludwig, A.; Thévenot, D. R.; Colin, J.-L., *Sci. Total Env.* **2003**, *308* (1-3), 247-256.
- Göbel, P.; Dierkes, C.; Coldewey, W. G. *J. Contam. Hydrol.* **2007**, *91*(1-2), 26-42.

- Hendry, C. D.; Brezonik, P. L. *Env. Sci. Tech.* **1980**, *14*(7), 843-849.
- Polkowska, Z.; Górecki, T.; Namieśnik, J. *Env. Rev.* **2011**, *19*(1), 185-213.
- (a) Lindberg, S.; Harriss, R. *Water, Air, Soil Pollution* **1981**, *16*(1), 13-31; (b) Radke, L. F.; Hobbs, P. V.; Eltgroth, M. W. *J. Appl. Meteorol.* **1980**, *19* (6), 715-722.
- Poissant, L.; Schmit, J.-P.; Béron, P. *Atmos. Env.* **1994**, *28*(2), 339-346.
- Lindberg, S. E. *Atmos. Env. (1967)* **1982**, *16*(7), 1701-1709.
- Kaya, G.; Tuncel, G. *Atmos. Env.* **1997**, *31*(23), 3985-3998.
- Kossmann, M.; Sturman, A. *Int. J. Climatol.* **2004**, *24*(1), 93-108.
- Sturman, A.; Titov, M.; Zavar-Reza, P. *Sci. Total Env.* **2011**, *409*(4), 810-821.
- Murphy, L. U.; O'Sullivan, A.; Cochrane, T. A. *Water, Air, Soil Pollution* **2014**, *225*(7), 1-13.
- Murphy, L. U.; Cochrane, T. A.; O'Sullivan, A. *Sci. Total Env.* **2015**, *508*, 206-213.
- APHA, *Standard methods for the examination of water and wastewater*. 21th ed.; American Public Health Association: Washington D.C., 2005.
- Wicke, D.; Cochrane, T. A.; O'Sullivan, A. D. *J. Environ. Monit.* **2012**, *14*(1), 209-216.
- R Core Team R: *A language and environment for statistical computing*, <http://www.R-project.org/>: Vienna, Austria, 2014 (accessed 10/01/16).
- Field, A., *Discovering statistics using IBM SPSS Statistics* 4th ed.; SAGE Publications Ltd: London, 2013.
- (a) Gunawardena, J.; Egodawatta, P.; Ayoko, G. A.; Goonetilleke, A., Atmospheric deposition as a source of stormwater pollution in Gold Coast, Australia. In *Proceedings of the 34th IAHR World Congress, 33rd Hydrology and Water Resources Symposium and 10th Conference on Hydraulics in Water Engineering*, Engineers Australia: Brisbane, Australia, 2011; pp 1849-1856; (b) Wicke, D.; Cochrane, T. A.; O'Sullivan, A. *J. Env. Manage.* **2012**, *113*, 347-354.
- Beilke, S.; Elshout, A. J.; Commission of the European Communities, *Acid deposition: proceedings of the CEC workshop organized as part of the concerted action "physico-chemical behaviour of atmospheric pollutants", held in Berlin, 9 September 1982*. Reidel: 1983.
- Lee, B.-K.; Park, G.-H. *J. Hazard. Mat.* **2010**, *184*(1-3), 406-416.
- Vollertsen, J.; Lange, K. H.; Pedersen, J.; Hallager, P. *Water Sci. Tech.* **2009**, *60*(4), 1071-1079.
- Conko, K. M.; Rice, K. C.; Kennedy, M. M., *Atmos. Env.* **2004**, *38*(24), 4025-4033.
- Morselli, L.; Olivieri, P.; Brusori, B.; Passarini, F. *Env. Poll.* **2003**, *124*(3), 457-469.
- Colin, J. L.; Jaffrezou, J. L.; Gros, J. M. *Atmos. Env. A. Gen. Topics* **1990**, *24*(3), 537-544.
- Freydier, R.; Dupre, B.; Lacaux, J. P., *Atmos. Env.* **1998**, *32*(4), 749-765.
- Halstead, M. J. R.; Cunninghame, R. G.; Hunter, K. A., *Atmos. Env.* **2000**, *34*(4), 665-676.
- Wicke, D.; Cochrane, T. A.; O' Sullivan, A. D.; Cave, S.; Derksen, M. *Water Sci. Tech.* **2014**, *69*(10), 2166-2173.
- Haselbach, L.; Poor, C.; Tilson, J. *Construction Build. Mat.* **2014**, *53*, 652-657.