

Pollutant association with suspended solids in stormwater in Tijuana, Mexico

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Abstract Stormwater runoff from urban areas is a major source of many pollutants to water bodies. Suspended solids are one of the main pollutants because of their association with other pollutants. The objective of this study was to evaluate the relationship between suspended solids and other pollutants in stormwater runoff in the city of Tijuana. Seven sites were sampled during seven rain events during the 2009–2010 season and the different particle size fractions were separated by sieving and filtration. The results have shown that the samples have high concentration of total suspended solids, the values of which ranged from 725 to 4,411.6 mg/L. The samples were analyzed for chemical oxygen demand, total phosphorus, total nitrogen, and turbidity. The results show that most of the particles in suspended solids are in the particle fraction between 10 and 62 μm . A high association between the concentrations of suspended solids was found for chemical oxygen demand, phosphorus, and turbidity but not for total nitrogen.

Keywords Chemical oxygen demand · Nitrogen · Nutrients · Phosphate · Pollution · Urban runoff

Introduction

Stormwater pollution is a major problem in urban areas. The loadings and concentrations of water pollutants, such as suspended solids, nutrients, and heavy metals, are typically higher in urban stormwater runoff than in runoff from rural areas (Vaze and Chiew 2004). Stormwater has become a significant contributor of pollutants to water bodies. These pollutants can be inorganic (e.g. heavy metals and nitrates) and/or organic, such as polycyclic aromatic hydrocarbons and phenols from asphalt pavement degradation (Sansalone and Buchberger 1995). For example, stormwater runoff contributes 75–90 % of the pollution of the Anacostia River, one of the main tributaries in the Chesapeake Bay watershed (NRDC 2002). Factors such as land use and percentage of impervious area (parking lots and roads) can affect stormwater quality. Percentages of impervious areas as low as 10–15 % have been found to degrade the quality of streams (Bochis-Micus and Pitt 2005). Booth and Jackson (1997) analyzed data for streams in west Washington and concluded that developments that had approximately 10 % of impervious area produced degradation in the aquatic life of water bodies. Morse et al. (2003) found that a percent total impervious surface area of 6 % produces an abrupt change in stream insect community structure.

Total suspended solids alone are of the most important parameters measured in stormwater because their concentration and nature are frequently the basis for the selection and design of stormwater treatment facilities, such as retention ponds and wetlands. Moreover, suspended solids are linked to pollutants, such as phosphorus, organic compounds, and some heavy metals, since they tend to be adsorbed in particles (Morquecho and Pitt 2005; Vaze and Chiew 2004). Suspended solids play an important role in

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the transport of anthropogenic nutrients and heavy metals in streams (Horowitz et al. 2008). The concentration of sediment-bound contaminants varies with particle size, with large amounts attached to the finer particles (Taylor and Owens 2009; Brown et al. 2013). Hvitved-Jacobsen et al. (1994) found 60–80 % of phosphorus and lead, 50–60 % of nitrogen, and 30–40 % of zinc in road runoff to be associated with particulates.

Pitt et al. (1998) analyzed 550 samples from telecommunication manholes and vaults that were affected by stormwater. They found that chemical oxygen demand (COD) and zinc concentrations were mostly associated with the filterable fraction (14 and 30 %, respectively). Morquecho and Pitt (2005) studied runoff from roofs and paved areas. When suspended solids were removed, they found a reduction of 47 % in the COD, 23 % in total nitrogen (TN), 17 % in nitrate, and 92 % in total phosphorus (TP). For heavy metals, a reduction of 82 % for lead and 72 % for zinc was found. These last results show that lead and zinc concentrations are associated with suspended solids.

Vaze and Chiew (2004) found that the pollutant loads in different particle size ranges from different stormwater samples showed a large variability for TN and TP. According to these authors, all the particulates TP and TN in stormwater samples are attached to sediments between 11 and 150 μm . The percentage of the dissolved TN ranged between 20 and 50 % and TP between 20 and 30 %.

Mijangos-Montiel et al. (2010) found high concentrations of TSS in stormwater runoff from gas stations and sites with residential land use in Tijuana. TSS concentration ranged from 204 to 11,561 mg/L for gas stations and 121 to 6,717 mg/L for residential sites. They also found high concentrations of COD, ranging from 75 to 22,600 mg/L for gas stations and 60 to 2,135 mg/L for residential sites.

Domínguez-Chicas et al. (2004) measured the settling velocity of particles in stormwater samples from four sites in Ciudad Juárez, Mexico. They found that the amount of suspended solids and settling velocity of particles are related to urbanization. The amount of suspended solids is reduced and the settling velocity of particles is increased with urbanization. Hansen et al. (2007) found that sediment from urban runoff and wastewater discharge in Cencalli Lagoon in Villahermosa, Mexico was 5,300 m^3/year from an approximate area of 291 ha. They estimated that 80 % of the sediment originated from urban runoff and 20 % from untreated wastewater. The sediment yields from these discharges were calculated by analyzing the land use and population density of the basin.

Little research has been published on urban stormwater runoff quality in Mexico and even less in the Mexican side of the US–Mexico border cities where special urban

characteristics that affect the urban stormwater runoff quality exist. These special urban characteristics of Tijuana include: a high percentage of automobiles that circulate in Tijuana are used cars imported from the US; 78 % of the cars in Tijuana are more than 13 years old (INE 2000); and there is unplanned urban land use where a number of unpaved roads can still be found in areas that are considered completely urbanized. In these areas, soil can be transported to paved roads by car tires and then transported by runoff. Another urban feature of Tijuana is the number of vacant lots in the urban area and the steep cut slopes in the hills exposed to erosion, which can contribute suspended solids to stormwater in rain events. According to the municipal planning authority, 22 % of the area in Tijuana comprises vacant lots and approximately 36 % of the total vacant lots have slopes of more than 35 % (Implan 2002).

The aim of this study was to determine the relationship between some pollutants with different particle fractions of suspended solids in stormwater urban runoff in Tijuana, Mexico.

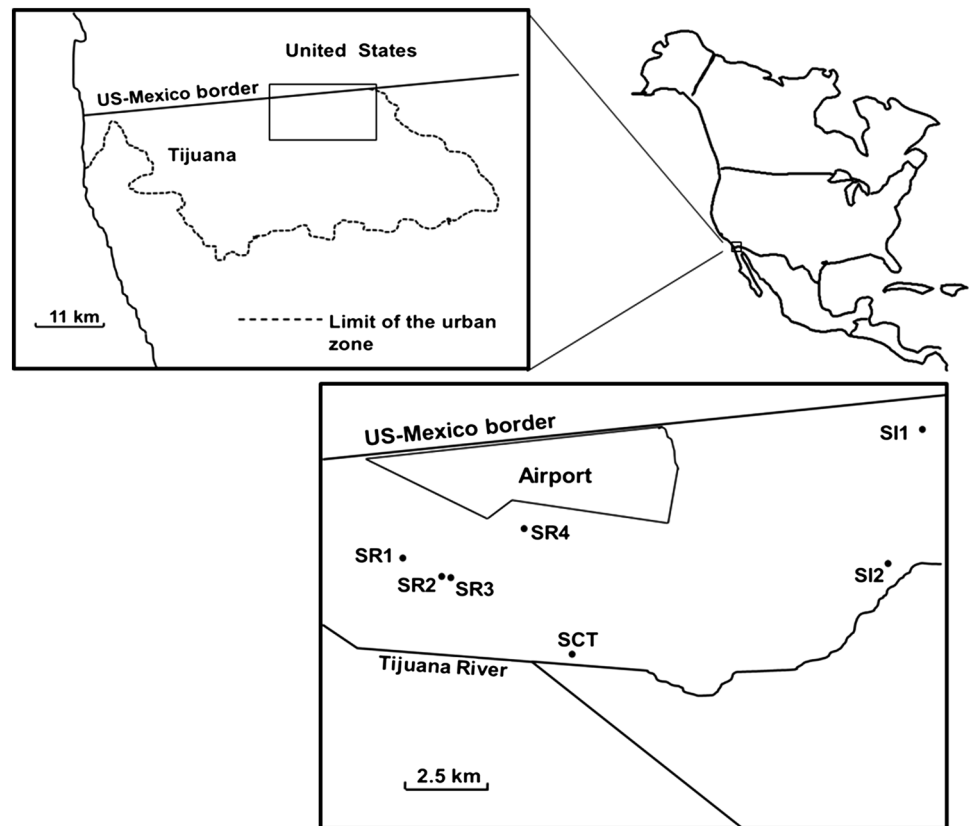
The study area

The city of Tijuana is located in the northwest corner of Mexico, on the US–Mexico border (Fig. 1). The region has a Mediterranean climate with distinct summer and winter seasons. The average annual rainfall is approximately 230 mm/year, with over 90 % occurring during the period from November to April (Implan 2002). The rainfall data of the rain events are shown in Table 1. The rainfall data were collected from Brown Field Airport located 5 km away from the sampling sites, and by analyzing historical data from another weather station located in the Tijuana area, the approximate rainfall variance across the sampled site area was between 1 and 2 mm.

Four sites have predominantly residential land use, two with industrial land use and one commercial and transport land use. Table 2 shows the sampling sites' characteristics.

Site SR1 has mainly residential land use with a number of street food vendors and businesses. Sites SR2 and SR3 drain an area with houses owned by low-income families. The approximate population density of these two sites is 63 inhabitants/ha and there are a number of auto repair shops. Site SR4 drains an area of approximately 13 ha with a higher population density (92 inhabitants/ha), populated by high-income families. Sites SI1 and SI2 are located in a zone of industrial land use. The predominant industry in the sampling sites is called “maquiladoras”, which are foreign facilities that produce mainly electronic, medical, and plastic products. Site SCT drains an area where three different bus stations are located and commercial land use is predominant.



Fig. 1 The study area showing the sampling sites**Table 1** Rainfall data of the rain events (modified from García-Flores et al. 2013)

Date (day-month-year)	Dry days previous to rainfall event (days)	Total rainfall (mm)	Average rainfall intensity (mm/h)	Maximum rainfall intensity (mm/h)
28-11-2009	39	10.4	1.6	4.0
12-12-2009	13	48.8	4.5	6.0
18-01-2010	27	14.5	3.8	9.0
05-02-2010	17	6.9	2.3	4.0
20-02-2010	14	8.9	2.2	3.0
27-02-2010	6	26.4	2.2	5.0
06-03-2010	6	2.5	1.0	1.0

Table 2 Sampling site characteristics (modified from García-Flores et al. 2013)

Site	Land use	Area (ha)	% pervious area	Average % slope
SR1	Residential and commercial	3.8	25	12.2
SR2	Mainly residential	8.0	12	4.0
SR3	Mainly residential	13.0	10	3.4
SR4	Residential	13.9	17	3.2
SCT	Commercial and transport	3.9	7	1.8
SI1	Industrial	3.5	9	0.7
SI2	Industrial	69.1	8	5.1

Materials and methods

The selected sampling sites were located in an area called Mesa de Otay. Seven sites were sampled in seven rain events during the 2009–2010 rainy season. In all of the sites, the samples were taken directly from roads and stormwater drains and inlets. Duplicate samples were taken in each site in the first 2 h of the rain events. Samples were transported in pre-cleaned, high-density polyethylene containers and were analyzed in the following 24 h.

The processing and analysis scheme for each stormwater was conducted as follows: the sample was first split. One split sample was set aside as the unsieved and unfiltered sample. The other was sieved through 300, 150, and 63 μm nylon sieves and then filtered using 10, 1.2, and 0.45 μm filters.

Each unfiltered/unsieved water sample was analyzed for total suspended solids (TSS), turbidity, total phosphorus as phosphate (TP), chemical oxygen demand (COD), and total nitrogen (TN) using standard methods. The sieved and filtered fractions were also analyzed using the same



parameters. Total phosphorus analysis was conducted using the method described in Mexican Standard NMX-AA-029-SCFI-2001 (SE 2001a); COD was measured using the reactor digestion method described in Mexican Standard NMX-AA-030-SCFI-2001 (SE 2001b); turbidity was measured using the method described in Mexican Standard NMX-AA-038-SCFI-2001 (SE 2001c); TSS was measured using the method described in Mexican Standard NMX-AA-034-SCFI-2001 (SE 2001d) and total nitrogen was measured by the persulfate digestion method (D'Elia et al. 1977). Quality control was provided by parallel analysis of spiked samples with certified standards. The percentage of spiked blank recoveries was as follows: 99 % for TP; 92 % for COD, 99 % for TN, and 97 % for TSS. The relative square deviation (RSD) was 0.6 % for TP, 1.52 % for COD, 0.4 % for TN, and 2.2 % for TSS. The detection limits in mg/L were as follows: 0.133 for TP, 1.83 for COD, 0.4 for TN, and 2.3 for TSS.

Results and discussion

The cumulative percentages of particle fractions in the samples are shown in Fig. 2. The results have shown that the highest particle fraction mass in the stormwater samples is between 10 and 62 μm . This particle fraction accounts for between 56 and 82 % of the TSS in the samples. The residential site SR1 has the lowest percentage of particle fractions between 10 and 62 μm (56 %) and the highest percentage of particle fractions

between 62 and 150 μm (20 %). This may be due to the high slope of the sampling site resulting in a higher flow velocity of the runoff that can carry bigger soil particles. Another characteristic of this site is the percentage of the basin area that is not paved (bare soil and unpaved streets). This produces higher levels of suspended solids because of the erosion produced by the urban drainage conditions of site SR1.

For the industrial sites (SI1 and SI2), as in all the sites sampled, the highest percentages of suspended solids were in the particle fraction between 10 and 62 μm . The highest percentage of particle fraction, between 1.2 and 10 μm , was in site SI1 (approximately 19 %); this value is more than three times higher than the average value found in the other sites (5.2 %). The industrial sites also have the highest percentages of impervious area (92 and 91 %, respectively). Sites SR1 and SR2 showed the highest percentage of particle fraction in the range from 0.45 to 1.2 μm (20 and 8 %, respectively), probably due to the high percentage of unpaved surface and the clayey soil.

Table 3 shows the concentration averages and standard deviations for the analyzed parameters. There is a high variability across all the parameters, especially those that are highly associated with solids (TSS, COD, TP, and turbidity). The high variability of stormwater quality is a well-known phenomenon caused by many factors such as: percentage of impervious area and its spatial distribution (roads, parking lots and roofs), type of pervious areas (Goonetilleke et al. 2005), basin soil (Uusitalo et al. 2000), rainfall quantity and quality (Zhang et al. 1999; Hathaway

Fig. 2 Particle size fractions in the stormwater samples

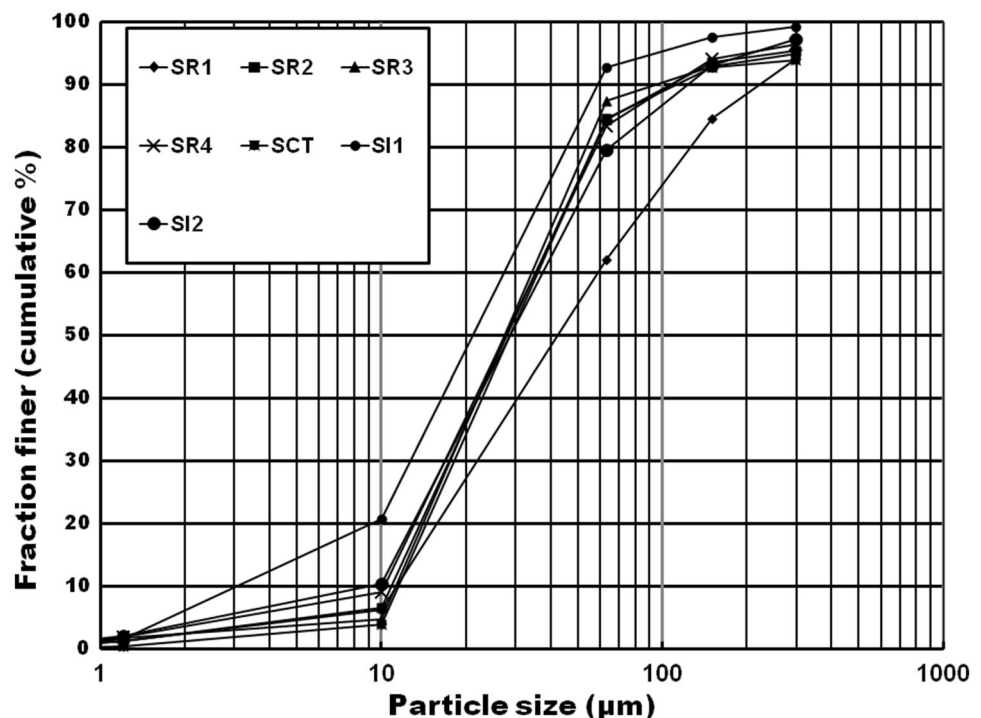


Table 3 Average concentration and standard deviation of measured parameters in unfiltered samples (all data in mg/L, except turbidity in NTU)

Site	TSS	COD	TN	TP	Turbidity
SR1	4,412 ± 3,540	765 ± 382	15.7 ± 6.3	25.7 ± 20.9	2,061 ± 2,406
SR2	1,804 ± 349	421 ± 168	9.9 ± 3.5	17.1 ± 12.8	1,055 ± 398
SR3	1,358 ± 1,086	405 ± 120	8.4 ± 1.9	12.0 ± 6.1	1,497 ± 1,085
SR4	725 ± 765	324 ± 170	13.2 ± 6.1	7.9 ± 3.0	454 ± 320
SCT	3,803 ± 3,417	605 ± 176	14.1 ± 6.9	23.4 ± 10.7	1,975 ± 1,532
SI1	1,141 ± 545	218 ± 78	6.1 ± 3.4	7.5 ± 2.8	1,422 ± 1,093
SI2	2,935 ± 1,613	362 ± 228	7.3 ± 4.6	8.1 ± 3.6	789 ± 776

et al. 2012), and past and present basin activities (Mayer et al. 2002).

The average TSS in the sampling sites ranged from 725 to 4,412 mg/L, the highest TSS concentration observed being in site SR1 (Table 3). The average TSS concentrations are considerably higher than in other published studies (Baldy et al. 1998; He et al. 2010). The average TSS concentration in SR1 and SR4 is 65 and 10 times higher, respectively, than the National Stormwater Data Quality (NSDQ) (Pitt et al. 2004) for a mixed residential land-use site (68 mg/L). This high TSS concentration in site SR1 is probably due to the high slope and the unpaved streets located in the basin areas of the site that transport high quantities of sediment due to erosion. This site (SR1) also has the highest average concentration of total phosphorus, turbidity, and COD. The TSS concentration in site SR4 (725 mg/L) was the lowest. This residential site has characteristics that the other sites do not have. First, there is no main road in the basin area. Second, most of the permeable area in the basin consists of a park with grass cover and there are no unpaved streets. Finally, because of the higher socioeconomic level of the residents, the gardens are generally better maintained than in the other residential sites where the patios consisted mostly of bare ground.

The average TP concentrations found in the unfiltered stormwater samples range from 7.5 to 25.7 mg/L. The highest TP concentrations were found in sites SR1 and SCT (25.7 and 23.4 mg/L, respectively). The possible sources of the high TP concentrations in site SR1 may be street dirt and waste from a street market that is set up once a week in the drainage area of the site. For site SCT, the possible source is a small rodeo ring with a stable located just 50 m away from the sampling site. High TP concentrations were also found in sites SR2 and SR3 (17.1 and 12 mg/L, respectively); the sources may be the same as those mentioned for site SR1. In addition to the sources of TP mentioned above, TP can also originate from soil particles. The highest TP concentrations were found in the sites with a higher percentage of pervious area. Exceptions were sites SR4 and SCT. Site SR4 has a high percentage of pervious area, but phosphorus is not as high as in SR1, SR2 and SR3 because most of its pervious area is a park with no

erosion. Interestingly, even though site SCT has a low percentage of pervious area, its runoff presents a high TP concentration. This can be explained by the presence of a stable which acts as a main source point for TP and TN.

The highest average TN concentration was in site SR1 (15.7 mg/L), the most likely cause being organic debris and street dirt from the number of street food vendors located in the basin of this site. TN concentrations were also high in sites SCT and SR4 (14.1 and 13.2 mg/L, respectively). The source of TN in site SCT, as mentioned above, is the stable and the rodeo ring where the horses are kept during events. Organic debris may be the main source for site SR4 since this site drains runoff from a park. TN values found in the sampled sites were around three to sevenfold higher than the concentrations reported by Taylor et al. (2005) and the NSQD (Pitt et al. 2004).

The range of COD was from 218 to 765 mg/L, the highest concentration being in site SR1. This may be produced by the high content of TSS in the samples as well as the oil and grease generated by crankcase oil leakages and the street food vendors situated in the drainage area of the site. The average COD values for the other residential sites are between 324 and 421 mg/L, which are approximately 5–8 times higher than the average value reported by the NSQD (Pitt et al. 2004). The high COD values may be the result of crankcase oil leakage from poorly maintained vehicles onto street and parking lot surfaces (Mijangos-Montiel et al. 2010). García-Flores et al. (2013) found high concentrations of polycyclic aromatic hydrocarbons in the sampled sites: 4,866 µg/L for site SR4 and 3,483 µg/L for site SCT. García-Flores et al. (2009) found high concentrations of oil and grease in stormwater samples for the same residential sites (an average of 20 mg/L), for the industrial sites (14 mg/L) and for site SCT (19 mg/L). These values are five and threefold higher, respectively, than the median values reported for stormwater from residential and industrial land-use sites by the NSDQ (Pitt et al. 2004).

Since turbidity is an indication of the number of particulates in a sample, one would expect higher turbidity values in samples with higher TSS concentration. This was observed for the sampled sites. The highest value of



Table 4 Percentage of the measured parameters associated with particulate matter

Site	COD			TN			TP			Turbidity		
	%AP	%FF	SD	%AP	%FF	SD	%AP	%FF	SD	%AP	%FF	SD
SR1	79	21	14	59	41	13	93	7	3	99.9	0.1	0.002
SR2	76	24	9	66	34	18	93	7	6	99.8	0.2	0.001
SR3	76	24	7	67	33	19	91	9	3	99.9	0.1	0.001
SR4	75	25	11	49	51	20	82	18	5	99.5	0.5	0.003
SCT	82	18	9	60	40	21	92	8	2	99.9	0.1	0.002
SI1	78	22	13	81	19	25	92	8	4	99.9	0.1	0.016
SI2	81	19	18	68	32	18	88	12	6	99.7	0.3	0.004

%AP percentage associated with particulate, %FF percentage filterable fraction, SD standard deviation

turbidity was measured in site SR1 (2,061 NTU) and the lowest value in SR4 (454 NTU). The turbidity value for site SR1 is around 34-fold higher than the values reported by Morquecho (2005).

Table 4 shows the percentage of measured parameters associated with particles in the stormwater samples. The percentage of particle-associated COD varies from 75 to 82 %, the highest percentage being in site SCT and the lowest in SR4. The samples from the other sites (SR1, SR2, SR3, SI1, and SI2) show slight variation in the percentage of particle-associated COD (76–81 %). The percentage of particle-associated COD concentrations in this study was higher than the values reported by other studies (Pitt et al. 1998; Morquecho 2005). These authors reported particle-associated COD concentrations from 14 to 63 %. This difference in the percentage may be the result of the pollutants adsorbed in the particle surfaces. Crankcase oil stains are commonly seen on streets and parking lot surfaces in Tijuana, where sediment has been deposited. These particles are transported by stormwater and a small amount of the hydrocarbons will be desorbed in water. García-Flores et al. (2009) found that total hydrocarbon concentrations in deposited road sediments were between 1,870 and 7,069 mg/kg.

The percentage values of particle-associated TP were between 82 and 93 %, showing a high association with TSS. The lowest percentage of particle-associated TP was

observed in site SR4 where pervious surfaces are mostly gardens and a grassy park. The percentage of particle-associated TP was higher than 90 % in most of the samples. These values show, not surprisingly, that most of the phosphorus in the stormwater samples was bound to particles that may originate from eroded soil particles. The percentage of particle-associated TP was also higher than other reported studies. Waschbusch et al. (1999) found 42–79 % of the particle-associated TP in two urban residential basins. The major TP contributor to stormwater in these basins was the runoff from lawns. Runoff from lawns accounted for 55 % of the total TP load from these basins. Morquecho (2005) found a range of 44–64 % of particle-associated TP in stormwater from roofs and paved areas.

The percentage of TN associated with TSS in the stormwater samples was lower than those observed in COD and TP. The percentage values were from 49 to 81 %, the majority of the samples being between 59 and 68 %. These values are similar to those reported by Vaze and Chiew (2004) which ranged between 50 and 80 % of the total TN associated to particulate. Taylor et al. (2005) reported a lower percentage value for particulate organic nitrogen (24 %) in stormwater.

As expected, the percentage values of turbidity are highly associated with particles and the values are almost 100 %. The results show that COD and TP concentrations are highly associated with suspended solids in the samples.

Table 5 Percentage of measured parameters associated with particle sizes higher than 10 and 0.45 μm

Site	COD		TN		TP		Turbidity	
	10	0.45	10	0.45	10	0.45	10	0.45
SR1	78 \pm 20	84 \pm 14	53 \pm 11	59 \pm 17	89 \pm 3	93 \pm 3	86 \pm 8	99.9 \pm 0.2
SR2	76 \pm 14	82 \pm 9	49 \pm 21	66 \pm 15	92 \pm 7	93 \pm 6	96 \pm 9	99.8 \pm 0.1
SR3	68 \pm 16	78 \pm 7	31 \pm 22	67 \pm 20	87 \pm 4	91 \pm 3	96 \pm 2	99.9 \pm 0.1
SR4	56 \pm 12	84 \pm 11	51 \pm 13	60 \pm 23	75 \pm 5	82 \pm 4	93 \pm 5	99.5 \pm 0.2
SCT	55 \pm 11	85 \pm 9	26 \pm 21	42 \pm 5	89 \pm 2	92 \pm 2	96 \pm 11	99.9 \pm 0.4
SI1	80 \pm 29	86 \pm 13	26 \pm 17	56 \pm 22	87 \pm 5	92 \pm 2	82 \pm 20	99.9 \pm 1.6
SI2	82 \pm 21	94 \pm 17	56 \pm 25	58 \pm 25	80 \pm 15	88 \pm 9	96 \pm 7	99.7 \pm 0.4



However, no clear association was observed between suspended solids and TN.

Table 5 shows the percentage of the measured parameters associated with particle fraction higher than 10 and 0.45 μm in the stormwater samples. Because most of the particle mass in the samples was in the fraction between 62 and 10 μm , a high percentage of measured parameters was associated with this range of particle fraction. COD percentages of the particle fraction bigger than 10 μm vary from 55 to 82 % of the total COD. The particle fraction between 0.45 and 10 μm in sites SR4 and SCT was only 5 % of the TSS (Fig. 2), but contributed with 28 and 30 % of the total COD. In the rest of the sites, this particle fraction (0.45–10 μm) contributes between 6 and 12 % (Table 5).

The percentages of TN concentration associated with the particle fraction higher than 10 μm were between 26 and 56 %. The percentages of soluble and particulate TN do not follow a trend, unlike COD and TP. For example, 30 and 36 % of the measured TN in sites SI1 and SR3 are associated with the particle fraction between 0.45 and 10 μm . Total nitrogen associated with soluble forms of nitrogen in the samples was between 42 and 67 %. Total phosphorus measured in the samples was mainly in the particle fraction bigger than 10 μm , the values ranging from 75 to 92 %. The percentage values of particle-associated TP in the range from 0.45 to 10 μm were between 1 and 8 %.

The results suggest that to effectively remove particulate COD, TP, turbidity, and TN, treatment facilities may have to remove particulate down to 10 μm . Even so, the facilities may only remove slightly more than half of the TN for sites SR1, SR2, SR4, and SI2 and around a third of the TN for sites SR3, SCT, and SI1 since a large amount of TN is in solution. Due to the biological availability of dissolved nitrogen, its concentration can be reduced by using systems that combine nitrification and subsequent denitrification. Stormwater wetland or biofiltration systems can be appropriate for this role (Taylor et al. 2005).

Conclusion

The results show that TSS is highly associated with TP, turbidity, and COD. Between 82 and 93 % of the TP and 75 and 82 % of the COD are associated with particles suspended in stormwater. TN concentrations in stormwater samples are not totally linked to particulate since 19–51 % of the TN were dissolved. It is important to know these pollutant:TSS ratios because the selection of a stormwater treatment method must take into account that the removal of this TSS fraction would also eliminate a large proportion of particle-associated pollutants. The results suggest that to effectively remove turbidity, COD, and TP, stormwater

treatment facilities must be able to remove particulate down to 10 μm . Moreover, this facility must be able to combine nitrification and denitrification in order to eliminate nitrogen, since a high percentage of nitrogen is in dissolved form.

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