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Impact of urban land use on the physicochemical quality of surface runoff water in an urban watershed

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Abstract

The growing processes of urban expansion have led to changes in the biochemical and physical properties of the hydrological systems in watersheds, not only by altering the hydrological conditions of the territory, but also by introducing pollutants into water bodies. Thus, diffuse pollution from stormwater runoff is considered one of the main causes of water quality degradation in receiving waters in urban areas, especially in rainy regions such as the South American tropics, where urban development and management processes are generally poorly planned. This article presents the results of an evaluation of the relationship between land use and runoff water quality, taking into account different rainfall characteristics. Sampling was carried out in Medellín, Colombia, in areas with different land uses. Basic water quality parameters and some sources of urban pollution were studied. The results showed that parameters such as total suspended solids have a high variability, especially in the residential area, which makes it difficult to control the activities carried out there. The highest levels of pollution were found in the industrial area, where the presence of covers with very low or no permeability and the increase in anthropic activity cause a strong alteration in the quality of runoff water. These results open the door to question the impact of land use on the chemical composition of rainwater and promote a better understanding of surface runoff water pollution processes, thus providing a complete vision of the interactions in an urban ecosystem, establishing a key tool for water management in urban watersheds.

Keywords: heavy metals; land use; pollutant washing; rainfall characteristics; runoff; stormwater management; urban catchment; urban stormwater; water quality; water resources.

Impacto del uso del suelo urbano en la calidad fisicoquímica del agua de escorrentía superficial en una cuenca urbana

Resumen

Los crecientes procesos de expansión urbana han generado diversas alteraciones en las propiedades bioquímicas y físicas de los sistemas hidrológicos en las cuencas, puesto que además de modificar las condiciones hidrológicas del territorio, incorporan múltiples contaminantes a los cuerpos de agua. De esta manera, la contaminación difusa resultante de la escorrentía de aguas pluviales, es considerada como una de las principales causas de la degradación de la calidad del agua en las fuentes receptoras en zonas urbanas, lo cual es particularmente relevante en regiones lluviosas como el trópico suramericano donde los procesos de desarrollo y gestión urbana son poco planificados. Este artículo presenta los resultados de la evaluación de la relación entre el uso del suelo y la calidad de las aguas de escorrentía, considerando además diferentes características de la lluvia. Los muestreos se realizaron en la ciudad de Medellín, Colombia en zonas con diferente uso del suelo. Se estudiaron parámetros básicos de calidad del agua, además de algunas fuentes de contaminación urbana. Los resultados mostraron que parámetros como los sólidos suspendidos totales presentaron alta variabilidad, especialmente en la zona residencial, ocasionando así una complejidad en el control de las actividades que allí se desarrollan. Por otra parte, los mayores niveles de contaminación observados se encontraron en la zona industrial, donde la presencia de coberturas con muy baja o nula permeabilidad y el aumento de la actividad antrópica generan una fuerte alteración en la calidad de las aguas de escorrentía. Estos resultados abren la puerta a cuestionamientos en cuanto al impacto del uso del suelo en la composición química de las aguas pluviales y promueven una mejor comprensión de los procesos de contaminación del agua de escorrentía superficial y por ende una visión más completa de las interacciones que se presentan en un ecosistema urbano, estableciendo una herramienta clave para la gestión hídrica en las cuencas urbanas.

Palabras clave: *aguas pluviales urbanas; calidad del agua; características de la lluvia; cuenca urbana; escorrentía; gestión de aguas pluviales; lavado de contaminantes; metales pesados; recursos hídricos; uso del suelo.*

1. Introduction

In recent decades, urbanization processes have grown significantly around the globe, with the expectation that about 60% of the population will be living in cities by 2030, implying a greater urbanization of the territory (Braud et al., 2013). As the world's population continues to grow at a rapid pace, the expansion of urban areas is a major source of disruption to natural ecosystem dynamics, resource availability, and overall environmental quality (McGrane, 2016). One of the main impacts of urbanization is related to the degradation and alteration of soil surface properties, which has been greatly accelerated by the growth of urban areas (Trujillo et al., 2016), leading to changes in the biochemical and physical properties of hydrological systems in watersheds. In particular, changes in the physical and chemical properties of hydrological systems in urban and peri-urban areas have been linked to the impact of pollution sources associated with human activities on these systems (Jacobson, 2011). Specifically, impervious pathways and surfaces act as sinks for many elements, including heavy metals and nutrients (McGrane, 2016), thereby affecting the water quality of surface water sources.

Multiple studies have identified specific sources or groups of pollutants that are present in urban runoff, which mostly reflect the land use of the area, the influence of factors such as rainfall characteristics, imperviousness, and population density which all contribute to increase the concentration of pollutants in water sources. In particular, such research highlights that rainfall intensity in the initial phase of a rainfall event is critical for the magnitude of the initial runoff (Maniquiz et al., 2022), in addition to the fact that rainfall duration and the preceding dry period determine the flushing of pollutant loads deposited on surfaces (Zhang et al., 2015).This, in turn, identifies vehicular traffic (Revitt et al., 2022) and atmospheric deposition as the main sources of urban stormwater pollution (Müller et al., 2019).

The most common pollutants in runoff from urban areas include total suspended solids (TSS), total phosphorus (TP), dissolved organic carbon (DOC), total nitrogen (TN), pH, and importantly heavy metals such as Cd, Cr, Cu, Ni, Pb and Zn (Müller et al., 2019) as well as to biological oxygen demand (BOD) or chemical oxygen demand (COD), indicators of organic matter. In studies that quantify runoff pollution, TSS was identified as the main variable of interest as it is easily measured and its directly related to the leaching of particles deposited on the surface. Similarly, the analysis of different forms of nitrogen (e.g., nitrate (, ammonia , total Kjeldahl nitrogen (TKN)) has been reported, and the extent of contamination has been found to be related to the extent of anthropogenic intervention in the watershed, flow and precipitation characteristics (Maniquiz et al., 2022). A large variability in urban runoff water quality has been observed, associated with the continuous emission of new chemical elements and the discharge of emerging pollutants that are potentially hazardous to communities and the environment, highlighting the need to improve the description of pollution sources (Müller et al., 2019). Even though there have been some advances in understanding this process, there is generally a knowledge gap in quantifying the impact of rainfall-runoff processes in urban areas (based on the dynamics of anthropic activities developed in the territory) on the quality and quantity of surface water sources, particularly in more humid areas in the tropics. This becomes one of the main problems facing the management of water resources in the territory, especially in tropical urban areas, which, together with topographic conditions, rainfall characteristics (Zhang et al., 2020) and the nature of urban development, contribute to a diversity of pollutants to rainwater and runoff.

Due to its geographical location, Colombia is one of the most water-rich countries in the world. However, the water quality of the main water sources that cross the country is in a significant state of degradation, as they receive sediments from the various erosion processes associated with deforestation and the degradation of watersheds and riverbeds, in addition to the discharge or dumping of contaminated water and solid waste from point and/or diffuse sources of pollution. In particular, the average annual rainfall in Colombia is 2,918 mm (while the global average annual rainfall is 900 mm) and the average annual runoff is 1,750 mm (IDEAM, 2018),

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which means that 60% of the rainfall is surface runoff. Most of the population and industry, agriculture and energetic matrix depends on runoff from rivers and other types of streams. However, the impact of land use in large urban areas on the generation of runoff and the potential contamination of these waters has not been studied in Colombia, representing a knowledge gap that affects the management of water resources and watersheds, with significant implications for communities and activities located downstream of large metropolitan areas. In this study, we analyze how the concentration of the main pollutants in rainwater varies between urban land use types, by sampling rainwater and runoff in different land uses, in addition to monitoring precipitation characteristics such as quality, intensity and frequency in the study area. Our results provide key elements for the design of strategies for adequate water resources management in urban areas in the country.

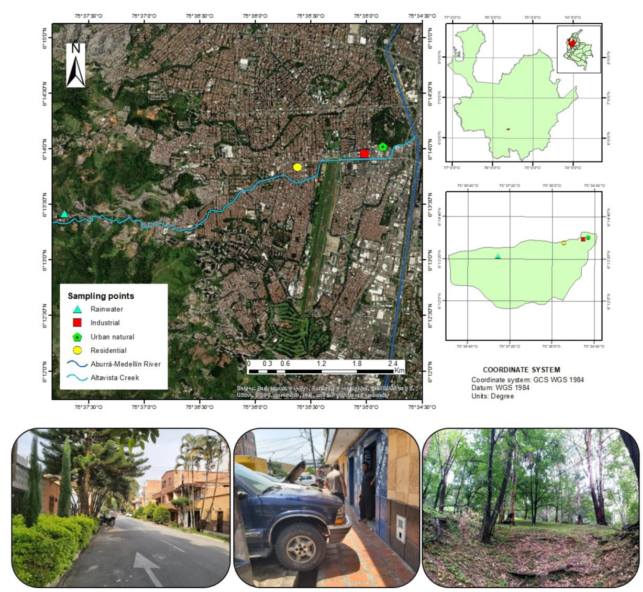
2. Methods

2.1. Study area

The study area, located in the central region of the Colombian Andes, corresponds to the sub-region of the metropolitan area of the Aburrá Valley, where the city of Medellín (the second largest city in the country) is located. Medellín is the capital city of the department of Antioquia (Figure 1a), concentrating 60% of its population and home to 69% of Antioquia’s productive units. These characteristics have augmented the demand for natural resources and the generation of multiple pollutants with significant consequences for water and soil resources. These urban dynamics aggravate the situation of the watershed where the city is located, as the various streams that feed the Aburrá - Medellín River have undergone serious changes, both in the natural environment of the channel and the watershed, associated with the settlement of people and the development of economic, residential, industrial and commercial activities, as well in hydrologic characteristics including water quantity and quality (Área Metropolitana del Valle de Aburrá, 2018a).

One of these sub-basins is the Altavista Creek (Figure 1b), located southwest portion of the municipality of Medellín, in the central zone of the Aburrá Valley sub-region. The length of the riverbed is 10.86 km, while the total area of the watershed is 24.15 km^2, of which 64% is rural and the remaining 36% urban. Specifically, the lower part of the watershed corresponds to the urban area of the basin, where there is a high population density, low slopes and the greatest urban activity (Alcaldía de Medellín & Corporación Autónoma Regional del Centro de Antioquia, 2007). Within this zone, the surface runoff sampling points for this work were in three areas representing the three main types of urban land use: (i) urban green (Figure 1e), (ii) residential (figure 1c) and (iii) industrial/commercial (figure 1d). Specifically, the locations where the runoff sampling instruments were installed correspond to the green areas of Cerro Nutibara, a natural urban area, a residential area with high vehicle traffic and, finally, an industrial area with a large number of auto mechanic shops where maintenance, restoration, and cleaning of vehicles are performed. In addition, rainwater was collected in the upper part of the watershed, particularly at the Altavista Public Library, in order to compare the runoff quality characteristics (Figure 1).

Figure 1. *Location of sampling points in the micro-watershed of Altavista stream, Medellín, Antioquia, Colombia. Where a corresponds to Antioquia department, b micro-watershed of Altavista stream, c residential zone, d industrial zone and e urban natural zone.*



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Six (6) sampling campaigns were developed between February and June 2021 and April 2022, analyzing different rainfall events covering the dry and wet seasons in the study area, monitoring rainfall characteristics such as intensity (I_Ll) and previous dry spell (TSP) corresponding to the cumulative number of days without rainfall before the specific event) for each of these events. Rainwater samples were taken before contact with the surface and containers were installed to collect run-off water in the urban drains before entering the sewerage system, as described by Estupiñán, 2009. These samples were collected at three points representative of each land use type. The meteorological stations used to obtain the rainfall characteristics were selected from the monitoring network of the Early Warning System of Medellín and the Aburrá Valley (SIATA), according to their proximity and radius of influence to the identified points of interest.

Each sample was analyzed for basic water quality parameters such as pH, electrical conductivity (EC), total suspended solids (TSS), chemical oxygen demand (COD), turbidity, and nutrients, especially phosphorus and nitrogen in the form of total phosphorus (TP), total Kjeldahl nitrogen (TKN), and nitrates ((Zgheib et al., 2012). For the assessment of urban sources, heavy metals such as zinc (Zn), copper (Cu), lead (Pb), cadmium (Cd), nickel (Ni), and chromium (Cr) were analyzed (Zgheib et al., 2008). The samples were analyzed at the Group for the Diagnosis and Control of Contamination (GDCON) of the University of Antioquia, following the methodologies established in the standard methods for each of the parameters. Specifically, pH and electrical conductivity were measured in situ using HACH HQ40D multiparametric instruments.

To analyze the spatial variation of runoff water quality according to the variables determined, as well as the relationship between these variables and the effect of both land use and rainfall characteristics, a correlation analysis was performed to identify, in addition to redundancy, the relationship or lack between the parameters measured. A Principal Component Analysis (PCA) was developed to reduce the dimensionality of the data while preserving as much variation in the data as possible, allowing the assessment of the contribution of each variable to be identified. Finally, a cluster analysis was performed to analyze the grouping tendencies between the different stations and campaigns according to the similarities between them. All statistical analyses were performed with the statistical package (car, moments, mvShapiroTest, corrplot, factoextra, ggplot2, MVN, normtest, pvclust, STAT, vegan, plotly, psy) in R.

3. Results and discussion

3.1. Variation of parameters between land uses

The industrial land use registered the highest levels of heavy metals compared to the other land uses analyzed (Table 1). This is particularly related to vehicle washing activities and the wear of their paints during this process, which is an important source of Pb, Cd, Cr, and Zn (Müller et al., 2019). However, heavy metals showed a greater variation in residential land use, which is related to the variation of factors such as speed, traffic density, diversity of vehicles that can circulate in the sector, condition, and characteristics of the roads, which condition the concentrations of these pollutants in the material deposited on the surface (Torres, 2004). The next parameter with the greatest variation corresponds to total phosphorus, especially for the urban natural zone, with minimum and maximum values of 0.59 and 8.06 mg/L, respectively. Similarly, total Kjeldahl nitrogen shows the greatest variation in this land use. Both behaviors can be related to the nature of the ecosystems, the decomposition of organic matter, the presence of microorganisms in the soil, as well as horticultural practices in the area, such as the application of fertilizers. This is supported by previous studies, which have shown that green spaces in urban areas are critical points for nutrient inputs to runoff water (Hobbie et al., 2017). On the other hand, total suspended solids showed a greater variation in residential land use, with values ranging from 32 to 5138 mg/L, which is related to the presence of front yards and green spaces with little or no vegetation cover, which can add suspended solids to urban stormwater, especially during high-intensity precipitation events, causing soil erosion (Gromaire et al., 2001).

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Table 1. Statistical summary (average, coefficient of variation, minimum and maximum) of the 16 variables analyzed in the different sampling points selected for each of the land uses evaluated

PARAMETER	LAND USE	MINIMUM	MAXIMUM	ARITHMETIC MEAN	COEFFICIENT OF VARIATION
TSS	Industrial	955.00	4875.00	2562	69.94%
	Residential	32.00	5138.00	1556.33	126.35%
	Urban natural	309.00	3553.00	1351.67	87.04%
	Rainfall	10.00	22.00	12.00	40.82%
Turbidity	Industrial	83.80	296.00	213.63	38.90%
	Residential	36.30	210.00	120.72	60.96%
	Urban natural	45.00	583.00	274.00	63.70%
	Rainfall	1.00	12.80	5.57	81.15%
COD	Industrial	169.00	486.00	352.50	40.02%
	Residential	158.00	375.00	251.67	37.72%
	Urban natural	82.80	364.00	163.50	65.92%
	Rainfall	25.00	26.20	25.20	1.94%
TP	Industrial	1.33	8.01	3.93	61.65%
	Residential	0.80	9.40	2.88	113.85%
	Urban natural	0.59	8.06	2.37	120.14%
	Rainfall	0.02	0.08	0.04	66.85%
NTK	Industrial	8.15	40.30	18.59	70.10%
	Residential	6.11	15.90	10.97	32.14%
	Urban natural	6.86	72.70	27.51	86.84%
	Rainfall	5.00	5.00	5.00	0.00%
NO_{3-}	Industrial	0.20	1.22	0.58	61.90%
	Residential	0.20	0.76	0.43	43.43%
	Urban natural	0.35	1.41	0.80	62.22%
	Rainfall	0.55	4.89	1.56	106.59%
Zn	Industrial	0.28	1.28	0.96	36.63%
	Residential	0.88	3.36	2.00	57.07%
	Urban natural	1.10	3.60	2.12	48.92%
	Rainfall	0.10	0.10	0.10	0.00%
Cu	Industrial	0.10	0.36	0.21	52.27%
	Residential	0.10	0.28	0.13	55.54%
	Urban natural	0.10	0.10	0.10	0.00%
	Rainfall	0.10	0.10	0.10	0.00%
Pb	Industrial	0.04	0.28	0.14	65.47%
	Residential	0.02	0.19	0.06	100.00%
	Urban natural	0.01	0.07	0.03	84.98%
	Rainfall	0.01	0.01	0.01	0.00%

Table 1. Statistical summary (average, coefficient of variation, minimum and maximum) of the 16 variables analyzed in the different sampling points selected for each of the land uses evaluated

PARAMETER	LAND USE	MINIMUM	MAXIMUM	ARITHMETIC MEAN	COEFFICIENT OF VARIATION
Ni	Industrial	0.02	0.15	0.06	81.62%
	Residential	0.01	0.14	0.04	134.21%
	Urban natural	0.01	0.03	0.02	48.75%
	Rainfall	0.01	0.01	0.01	0.00%
Cr	Industrial	0.02	0.29	0.12	84.96%
	Residential	0.01	0.12	0.04	113.15%
	Urban natural	0.01	0.06	0.04	46.39%
	Rainfall	0.01	0.01	0.01	0.00%
Cd	Industrial	0.00	0.02	0.01	142.43%
	Residential	0.00	0.02	0.005	141.65%
	Urban natural	0.00	0.00	0.00	68.37%
	Rainfall	0.00	0.00	0.00	11.66%
pH	Industrial	6.64	7.72	7.24	5.57%
	Residential	6.29	7.70	6.787	7.15%
	Urban natural	6.48	7.48	6.98	5.02%
	Rainfall	5.78	8.77	7.48	13.94%
EC	Industrial	91.60	1118.00	356.100	106.58%
	Residential	75.20	1223.00	405.533	104.17%
	Urban natural	105.00	357.00	207.167	51.94%
	Rainfall	25.00	53.10	29.917	38.01%

3.2. Association between water quality parameters

As expected, multiple water quality parameters relate to others and, these associations configure the impact of each land use type on the overall quality of runoff water. Figure 2 shows the correlation matrix for the set of variables analyzed. Some variables such as nitrates and pH were not strongly correlated with the other variables, as the highest correlation coefficient values correspond to 0.32 and 0.24, respectively. Figure 2 also shows a negative relationship between pH and zinc (-0.24), as expected, because the bioavailability and toxicity of metals are determined by the chemical composition of the water, specifically factors such as pH, hardness, alkalinity, and dissolved organic matter (Price et al., 2021). Zinc solubility tends to increase in slightly acidic solutions (Choque, 2020).

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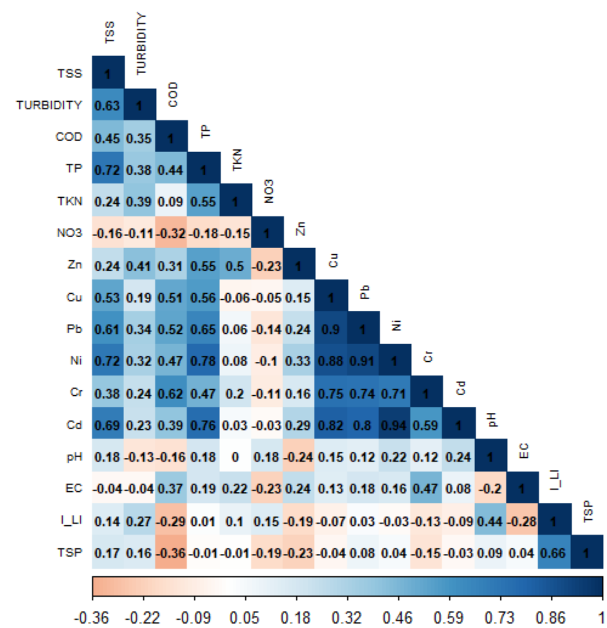
There is also a high correlation between total suspended solids and turbidity (0.63), which is related to the fact that the latter is an indirect measure of the suspended solids present in the water. A high correlation was also found between total phosphorus and total suspended solids (0.72), which is related to the fact that solids can form a medium for encapsulation or settlement of organisms in the aquatic environment (Du et al., 2022), while nutrients, especially nitrogen and phosphorus, are incorporated into organic molecules that perform vital functions in the cells of organisms.

Figure 2. Correlation matrix between different water quality parameters and analyzed precipitation characteristics.



In addition, a high correlation is observed between each of the metals evaluated, which is related to their source of generation, as the main sources of heavy metals in roads are associated with the gradual elimination of gasoline from vehicles, as well as the wear and tear of tires and brake pads (Revitt et al., 2022). Similarly, a high correlation of COD with parameters such as heavy metals is observed, which is related to the oxidation of these compounds in water. A positive correlation is also found between electrical conductivity and parameters such as nutrients and heavy metals, a case related to diluted ions in the water, which are the product of organic and inorganic contamination (Sierra, 2011). In addition, as for the preceding dry weather, it is observed that it presents a positive correlation with rainfall intensity, total suspended solids and turbidity, which is related to the fact that , as the TSP increases, the concentration of TSS and other pollutant compounds that are deposited on the land surface and are available to be transported to water bodies through surface runoff increases: results similar to those reported by Maniquiz et al., 2022, who found that the average concentration of the pollutants evaluated was higher during events with greater antecedent dry weather.

3.3. Water quality in relation to sources and precipitation events

To evaluate the influence of the measured parameters on the variance of the set of sampled stations, a PCA analysis was performed. As shown in Table 2, 64.7% of the variance is explained by the grouping of the variables in the first two components, in the case of the first axis were those variables directly related to the levels of dissolved and particulate pollution over the water bodies, while the second component was mainly related to the characteristics of rainfall.

Table 2. Variable weights in the first PCA components

PARAMETER	PC1 (47%)	PC2 (17.7%)
TSS	0.344	0.197
COD	0.273	-0.341
TP	0.372	0.062
TKN	0.090	0.062
Pb	0.384	-0.027
Ni	0.401	0.053
Cr	0.424	0.054
EC	0.402	0.029
I_LL	0.098	-0.257
TSP	-0.027	0.634

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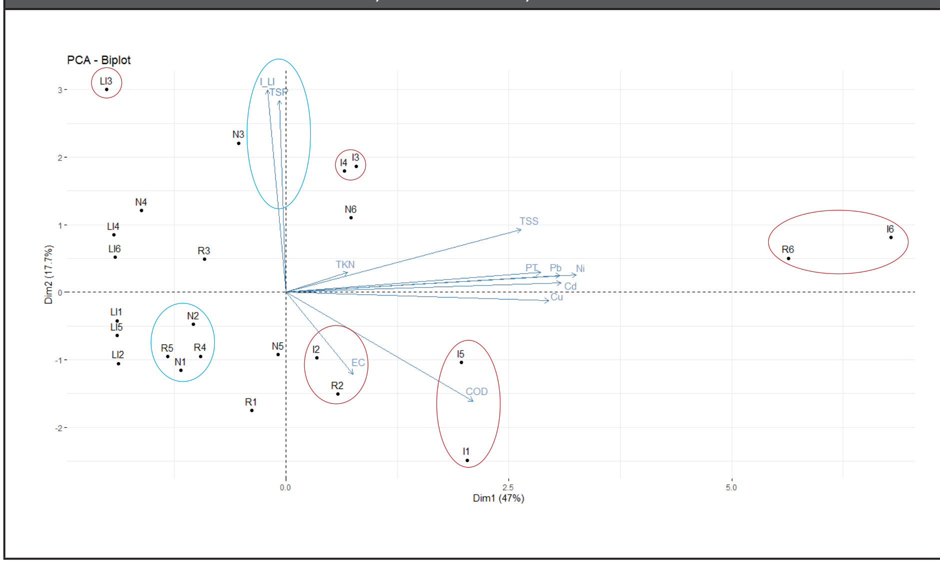
Figure 3 shows a grouping of the rainfall events, where the third rainfall event (LL3) was the one with the highest intensity and the longest preceding dry period, followed by the fourth rainfall event monitored. In the first case, the rainwater sample is characterized by the highest turbidity values (12.88 NTU) and pH (8.77 U. pH), which is related to the traffic flow on the roads near the Altavista Public Library facilities, as well as the anthropic activities that take place in the area (especially the Altavista Brick Factory), factors that significantly add particulate matter to the atmosphere, increasing the turbidity levels of the rainwater.

Figure 3. Biplot resulting from Principal Component Analysis used to determine water quality behavior related to precipitation sources and events. Ll: Rainwater; N: Urban natural; R: Residential; I: Industrial.



In addition, the basic pH can be related to the different mobility restrictions that were implemented between the first and fifth day of April 2021 to flatten the COVID-19 contagion figures, since with fewer vehicles circulating in the city, the CO2 concentration in the atmosphere is reduced, which, due to its interaction with water vapour, is converted into carbonic acid, causing a slight decrease in the pH of rainwater, a contrast that can also be observed during monitored events without specific road restriction conditions, where pH values are close to neutral. These results are related to those reported in the literature, where, when studying the effects of the mobility restrictions generated by the COVID-19 contingency, they found a significant decrease in the concentration of pollutants in the atmosphere, especially NOx, which is of particular interest due to the effects that nitrogen can have on ecosystems as an acidifying agent (Rogora et al., 2022).

In water samples from the industrial zone for events 3 and 4, the load of total suspended solids is greater in relation to the concentration of heavy metals, which is related to rainfall characteristics, as well as the dragging and transport of solids, since a greater accumulation of particles could have been generated during the preceding dry spell, in addition to falling with greater intensity probably generated a greater disintegration of the particles deposited on the surface. This behavior is related to previous studies (Mallin et al., 2009), where the values of turbidity, TSS, total phosphorus and other variables such as orthophosphates and biological oxygen demand (BOD_5) increased significantly with higher rainfall intensity. In particular, the second rain event analyzed in the industrial zone is similar to the samples taken in the residential zone, which is related to the fact that during the interval between the installation of the sampling containers and the rain event there was no development of any industrial activity, so that the pollutants deposited on the road are mainly related to the vehicular traffic in the area, while during the first and fifth monitored events, the industrial zone (as in Choe et al., 2002) is associated with the highest levels of heavy metals (1. 28 mg/L Zn, 0.32 mg/L Cu, 0.16 mg/L Pb, 0.29 mg/L Cr). Likewise, a high concentration of basic water quality parameters such as COD (483 mg/L) and EC (1118 µS/m) were identified, variables that are correlated because, as the concentration of dissolved ions increases due to the effect of contamination in the water, the amount of oxygen required to oxidize these compounds increases.

For the sixth rainfall event monitored, there were characteristics of prolonged dry weather, high rainfall intensities and, especially for the residential area, paint spills were found, which are reflected in the increase of the concentration of variables such as heavy metals, causing a contamination effect similar to that generated by the development of anthropic activity in the industrial zone. The samples taken in the urban and residential green areas have similar

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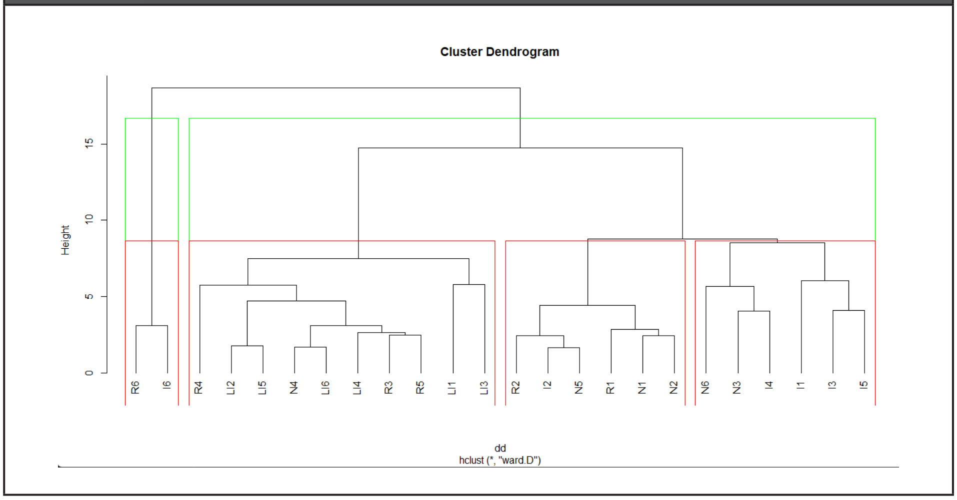
characteristics, probably related to the fact that the sampling points located in Cerro Nutibara (classified as an urban natural ecosystem) are adjacent to the access road of a busy road, which can contribute a series of contaminants due to vehicle traffic and the flow currents generated. In addition, the area is suitable with galvanized metal structures for the transit of people in the place, which (according Müller et al., 2022), when corroded they can release metals that concentrate on the surface of the sidewalks and roads. However, in other studies, the total concentration of pollutants in surface runoff is higher in the residential zone than in the industrial zone, and no significant variations in the physicochemical characteristics of stormwater are reported by land use in the residential zone and by type of industry in the industrial zone (Choe et al., 2002), contrary to what we found in this study, where a higher concentration of heavy metals was observed in the industrial zone, in addition to a high variation in the concentration of compounds, especially in the residential zone.

In conjunction with the PCA analysis, we developed a hierarchical cluster analysis. Four groups were identified among the different sampling sites according to each of the campaigns conducted (Figure 4). This analysis shows that the second cluster groups rainfall events with similar physicochemical characteristics, except for the case of the industrial (I6) and residential (R6) samples of the sixth sampling, which showed the highest concentrations of heavy metals, behavior related to the characteristics of the precipitation event generated in this sampling, since, similar to the results obtained by Mallin et al., 2009, the preceding dry weather and the high intensity of rainfall generated a greater accumulation and transport of pollutants deposited on the surface.

Figure 4. Cluster analysis for the grouping of the rainfall events evaluated in the different types of land use. Ll: Rainwater; N: Urban natural; R: Residential; I: Industrial.



For the second grouping, it is possible to identify that it groups the 6 rainfall events characterized, however, it is divided into 2 subgroups. The first one gathers most rain events, except the events one (Ll1) and three (Ll3), which were characterized by similar conditions in terms of nutrient and heavy metal concentrations. Similarly, the highest concentrations of both turbidity and nitrates were observed during these events, a concentration that, in addition to being related to the natural nitrogen cycle in the soil (Zeng et al., 2023), may increase with the development of anthropogenic activities such as coal and fuel burning by introducing nitrogen oxide into the atmosphere. Specifically, in the case of rainfall event 4 monitored (LL4); the lowest pH value reported (5.7 U. pH) was presented, which is possibly related to the burning of solid waste in rural areas and the occurrence of fires in different parts of the city, since, according to the news reported, during the month of May (fourth month of sampling), the highest number of fires of the first half of the year 2021 was recorded.

The samples corresponding to the residential, rainwater and urban natural sites (R4, LL4 and N4) of the fourth rainfall event and to the residential sites of the third (R3) and fifth (R5) monitoring show close levels of the parameters associated with nutrients, as well as values below the detection limit for some heavy metals such as copper and cadmium, which in the case of nutrients for residential

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and urban natural uses are related to the contribution of organic matter, fertilizers and animal waste (Gromaire et al., 2001), while in the case of the rainwater sample, these nutrient levels are associated with atmospheric deposition (Pandey & Raghubanshi, 2022).

The third cluster groups the samples from the residential (R1, R2), natural urban (N1 and N2) and industrial (I2) points of the second rainfall event evaluated, in addition to the sampling in the natural zone (N5) of the fifth sampling; where the last three (3) events are grouped in a more specific level, since in them there were high concentrations of TSS, similar concentrations of turbidity, nutrients, heavy metals, EC and neutral pH. It is important to mention that within this category point I2 is found, because during the period prior to sampling there was no development of industrial activity, thus presenting an affinity with the trends presented in the residential and/or natural urban areas.

In the fourth cluster, events one, three and five, analyzed in the industrial zone, are the most distant from the conditions presented by the rainwater, characterized by the highest concentration of heavy metals. The highest TSS values are for events three and six in the urban green zone and four in the industrial zone. In the first case, the impact of the development of industrial activities (especially vehicle maintenance) on the incorporation of heavy metals in the runoff can be clearly observed. In general, runoff water in less disturbed areas (i.e., parks and residential areas) has different physico-chemical characteristics and, in turn, different from rainwater samples, so that the alteration caused by the development of any type of anthropic activity is evident and, as expected, the most disturbed group is the industrial group.

4. Conclusions

In this work, which is a pioneer in the evaluation of the variation of runoff quality characteristics as a function of rainfall characteristics for different sectors in a tropical urban area, a high variability of total suspended solids was observed in all the monitoring carried out for the different uses, especially in the residential area. This is related to the pruning of lawns and front gardens, washing of vehicles and sidewalks, separation of waste by recyclers on the edges of roads, thus causing complexity in the control of activities that take place in residential areas, especially those that affect the concentration of this parameter.

A chemical alteration of the runoff water has been demonstrated independently of the use evaluated in relation to the rainfall. However, our results confirm that the sampling points have a tendency to group according to the pollution levels measured in these areas, which varies slightly between the different samplings carried out, so that it is not possible to use the data obtained to predict such alteration with a reliable degree of certainty, especially in a residential area, given the wide range of anthropic activities carried out in this particular area. Therefore, the impact generated in the industrial area, where the same activities are constantly taking place, is more stable in terms of chemical change. Through an adequate characterization of the pollutants carried by runoff water, it is possible to improve and increase the management, use and exploitation of this water, in order to reduce its negative impact on surface waters and the pressure generated by the high consumption of water, which in the Aburrá Valley sub-region comes from external basins, creating water dependency.

A larger number of studies on the characteristics of runoff in urban areas is needed, since knowledge of the accumulation and washing of pollutants, the mobilization of compounds by rainwater and, therefore, the water quality in surface systems affected by mixed pollution is limited, which in turn conditions the standards and policies established in the territory in terms of water management, since the formulation of effective strategies requires a broad collection and analysis of specific data from the area of interest, in order to establish specific ranges in the concentration of the main pollutants reported in the physicochemical quality of runoff water, given that the current regulations in Colombia require analysis and reporting for only some of them, leading to a limited vision of the functionality of the systems. Likewise, the generation of specific information of the territory will allow the understanding of the variety of compounds, their sources and the complex interactions

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between them, facilitating the development of models that under different scenarios will allow identifying, for example, the effects of climate change on the quality of runoff water, represented in the alteration of dry and rainy seasons, in order to generate adequate adaptation strategies that promote the conservation of ecosystems.

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