SANITARY AND ENVIRONMENTAL ENGINEERING

Applicability of UV absorbance as an indicator of Atrazine presence into risk management of water supply watersheds

INGENIERÍA SANITARIA Y AMBIENTAL

Aplicabilidad de la absorbancia UV como indicador de la presencia de Atrazina en la gestión de riesgos en cuencas de abastecimiento de agua

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Abstract

The type of hazards and hazardous events in watersheds, depend on land uses around them. Atrazine is an organic pollutant widely applied as a pesticide and it is a potential chemical hazard present in water sources, which cause water pollution and negative effects on aquatic life and human health, due to its high solubility and persistence in soil. However, for developing countries, monitoring and quantification of atrazine can be complex and costly; thus, to contribute to establishing strategies for risk assessment in water supply watersheds, it was evaluated the potential use of an easy, rapid, and low-cost technique such as ultraviolet (UV) absorbance to identify the presence of atrazine. It was conformed distilled and surface water samples doped with Atrazine, and there were correlated with the UV typical

spectrum indicator of organic material presence (wavelength λ: 200 - 300 nm). The optimal λ range was 203 - 223 nm to identify this substance at levels possible to be found in surface sources, being UV_{223} more adequate than UV_{254}, which is more used to identify the presence of natural organic matter, which shows that UV_{223} is a complementary tool to chemical risk assessment for atrazine in drinking water supply systems.

Keywords: Atrazine, Land uses, Pesticide, Risk management, UV Absorbance.

Resumen

El tipo de peligros y eventos peligrosos en las cuencas de abastecimiento, dependen de los usos del suelo a su alrededor. La atrazina es un contaminante orgánico aplicado ampliamente como plaguicida y es un peligro químico potencial presente en las fuentes de agua, que causa contaminación del agua y efectos negativos en la vida acuática y la salud humana, debido a su alta solubilidad y persistencia en el suelo. Sin embargo, para los países en desarrollo, el seguimiento y la cuantificación de la atrazina pueden resultar complejos y costosos; por tanto, para contribuir a establecer estrategias de evaluación de riesgos en las cuencas de abastecimiento de agua, se evaluó el uso potencial de una técnica fácil, rápida y de bajo costo como la absorbancia ultravioleta (UV) para identificar la presencia de atrazina. Se conformaron muestras de agua destilada y superficial dopadas con atrazina, y se correlacionaron con el indicador de espectro típico UV para materia orgánica (longitud de onda - λ: 200 - 300 nm), siendo el rango óptimo 203 - 223 nm; UV_{223} fue más adecuado que UV_{254}, el cual se utiliza más para identificar la presencia de materia orgánica natural, lo que demuestra que UV_{223} es una herramienta complementaria, útil para la evaluación del riesgo químico por la presencia de atrazina en los sistemas de suministro de agua potable.

Palabras Clave: Absorbancia UV, Atrazina, Gestión de riesgos, Plaguicidas, Usos del suelo.

1. Introduction

Surface waterbodies are the main sources of water for human consumption and their complexity is associated with the land uses (e.g., agricultural, livestock, industrial, domestic) around watersheds and tributary sub-watersheds. These water sources are vulnerable to contamination by physicochemical, microbiological and/or radiological hazards, whose characteristics imply higher costs and complexity of the treatment processes required to make water suitable for human consumption [1,2].

In the framework of the Water Safety Plans (WSP), the water quality delivered to the end user depends on all steps of the Drinking Water Supply System (DWSS: watershed, treatment processes, distribution system and consumer), being essential to implement control measures as close as possible to the catchment area, which allows timely decision-making before treatment processes and promotes appropriate risk management in each step of the DWSS [3,4].

In Colombia, the Cauca and Magdalena rivers are the main water sources of water supply systems (10.6% of the national water supply), due to approximately 80% of the population and most of the socioeconomic activities are concentrated around these watersheds [5], where agriculture is one of the main land uses and pesticides (herbicides: 45%, insecticides: 32%, fungicides: 18% and others: 5%) are widely used to limit, inhibit and prevent the growth of animals, insects, plants, invasive herbs, bacteria and fungi [6].

Among herbicides, organochlorines (OCs) have been widely produced and used worldwide, and although their use has been limited and/or prohibited in many countries, mostly developed countries, they are still present in almost all environmental matrices due to their long half-lives; in addition, they are used in other countries due to their low cost and versatility [7,8]. Atrazine from the triazine group, is one of the most widely applied herbicides worldwide, with annual production between 70,000 and 90,000 tons per year, it is used for weed control in vegetable crops, cereals, fruit crops, citrus plantations,

pastures and particularly for energy biomass crops such as corn, sorghum and sugarcane [9,10].

Due to its high solubility in water, massive use and persistence in the soil, Atrazine has a high risk of leaching, resulting in contamination of surface water and groundwater, which implies its possible presence in the DWSS [11]. Atrazine concentrations up to 1,000 μg/L have been found in waters adjacent to fields treated with this pesticide, and concentrations up to 80 μg/L have been found in drinking water; these are potential threats to human health due to their association with possible carcinogenic effects, endocrine disruption, and teratogenic effects [9]. According to the United States Environmental Protection Agency (USEPA) [12] and World Health Organization (WHO) [3], the permissible limit in drinking water is on the order of 3 and 100 μg/L respectively; however, these levels are often exceeded in countries where their application is not controlled, and their presence is not monitored [13,14].

Despite the potential effects of atrazine on the environment and human health, the analysis and quantification of this type of organic compounds in water is difficult, because most available laboratory techniques and specialized methodologies are complex such as high-performance liquid chromatography, mass spectrometry, and gas chromatography [15], which generally are not applicable *in situ* [16], are expensive and require qualified personnel and a high response time [17]. These factors demonstrate the need for alternative procedures [18].

Different pollutants have different chemical structure, and the absorbance occurs at different wavelengths [19]; the organic compounds absorb UV light (wavelength λ: 190 - 380 nm) proportionally to their concentration, which is a useful parameter for the qualitative estimation of organic substances, in addition to offering advantages such as versatility, low cost [18, 3] and the simplicity of measurement [20].

In general, disinfection by-products are better correlated at 272 nm [21], and the absorbance measured at 254 nm (UV_{254}) normally is associated with the presence of natural organic matter (NOM), such as humic and fulvic acids [22,23], and it is widely monitored as indicator in water and wastewater. According to Altmann et al. [24], UV_{254} is an indicator which has also been evaluate as real-time to monitoring and controlling the organic micropollutants removal in wastewater treatment, showing its applicability as control parameter; pollutants in stormwater are quantified at 225 – 230 nm [19], and Atrazine at 223 nm [15,25].

Thus, establish a correlation between variables of quick and easy measurement with the variables that measure substances of health interest, would allow lower costs, faster response times and the possibility of estimating the presence of these substances at the operational level [25]. This study evaluated the viability of using UV absorbance at different wavelengths (λ: 200 - 300 nm) as a quick indicator of the presence of pesticides, such as Atrazine, and as support of the risk management in watersheds.

2. Methodology

The Cauca River watershed was selected for its importance for the country, and due to is the supply source to 77% of the population of the Cali city (≈ 1900000 inhabitants), and it is highly impacted by agriculture [4]. Considering the variability of chemical water composition of surface sources associated with land uses and agrochemicals in watershed areas [2, 26-27], a map of study area was digitized in ARGGIS 9.3, locating the impacted areas by agricultural activities in the Cauca River watershed and identifying the predominant crops, according to Bueno et al. [1, 28].

To stablish correlations between Atrazine concentrations [29] and wavelengths, were doped

with Atrazine samples with distilled water (DW) and raw water (RW) from the Cauca River at the intake of the main Drinking Water Treatment Plant (DWTP) of the city of Cali. The Atrazine concentration ranges evaluated with DW samples were between 0.26 to 1478.00 µg/L and 0.26 to 1050 µg/L; and the ranges with RW were between 6.8 to 1523.7 µg/L, 6.8 to 920 µg/L and 6.8 to 260 µg/L, which were defined based on possible Atrazine levels found in surface water sources worldwide [14,30]. The doping process was performed using a commercial-grade Atrazine solution (Triasol®) of 20000 µg/L and 56% purity.

2.1. Evaluation of UV absorbance spectrum

The two water types (DW and RW), doped with the different Atrazine concentrations, were characterized in terms of the UV absorbance (λ range: 200 to 300 nm) (cm^{-1}: SM5910-B - HACH DR5000) using a quartz cell with 10×10 mm^2 [22]; which is according to authors such as Kim et al. [31] whose report UV absorption in this range for organic molecules, and emphasis was placed on the range of λ: 223 nm (approximation for the presence of Atrazine) [15, 25] and λ: 254 nm (historically used as an indicator of NOM) [15, 22].

2.2. Statistical analysis

To determine the effect of the water type (DW and RW) and Atrazine concentration on terms of UV measured, were used an F test statistic associated with the experimental design and controlling the possible variability between the sample analyses by including blocks in the design and validating the assumptions of normality and homogeneity of variances, using the Anderson-Darling and Levene tests [32], respectively.

A Tukey-based multiple comparison tests were performed (significance level of 5%) to determine significant statistical differences between the factors (e.g., water type and Atrazine concentration). In cases where the assumption of normality was not validated, logarithmic transformations were made to the parameters. To evaluate the effects of the water type, Atrazine concentration and their possible interaction through the wavelength (absorbance), was used a linear mixed model, due to the correlation structure presented by the data when evaluating each water sample along the UV spectrum.

Additionally, correlation was determinate between the evaluated parameters, using Pearson correlation coefficient (assuming normality in both parameters to correlate) and Spearman correlation coefficient (assuming breach of the normality assumption in at least one of the parameters to be correlated), validating the assumption of normality through the Shapiro-Wilk test; the main correlation was observed with 5% of significance level. The statistical analysis was carried out according to R Development Core Team version 3.6.2 (2019)

3. Results and discussion

3.1. Map of land uses by agriculture in the study area

According to Instituto Colombiano Agropecuario [33], Atrazine is one of the most used pesticides in sugarcane, corn, and sorghum crops in Colombia, in addition to being one of the most used herbicides in the world and detected in watersheds affected by intensive agriculture [2, 34]. This represents a recognized hazard to human health when supply sources contaminated by this type of chemical substances are used [9].

Figure 1 shows the ArcGIS map in which the wide area dedicated to agriculture stands out, where the permanent crop of sugarcane represents about 50% of the area cultivated in the watershed and it is concentrated upstream of water intake of the city of Cali. Semi-permanent and miscellaneous crops are scattered throughout the study area and are mainly located in the high areas of the sub-watersheds. The measures of Atrazine in the raw water samples from the Cauca River were between 0.01 ± 0.00085 and 6.80 ± 0.01000 µg/L.
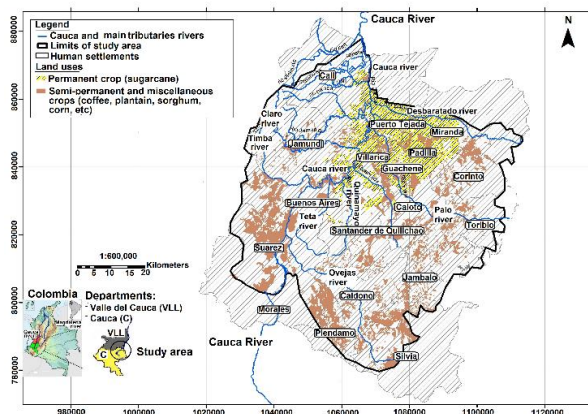
Figure 1. *Map of land uses by agriculture in the study area. Adapted from* [28]

It is important to highlight that the higher value is associated with the lowest precipitation in the year.

Although the environmental entity that annually monitors the environmental quality of the Cauca River, indicates that historically no concentrations of pesticides have been reported that exceed the regulatory limits, according to USEPA [12] and WHO [3], the predominant use of land in permanent crops and semi-permanent, in which Atrazine is used, as is the case in the study area [33], being one of the most used herbicides [28], mainly during the first 60 days after planting the crops, period during which the herbicide is usually applied [35].

Consequently, it is essential to have comprehensive approaches that consider land uses in the watersheds [27] as part of the risk assessment, thus allowing the institutions responsible of watershed management targeting the financial and human resources in relation to a particular water quality concern, focusing best management efforts, and maximizing benefits to water quality with minimal costs [26].

3.2. Evaluation of the UV absorbance spectrum

Figure 2 and 3 present the UV absorbance spectrum (λ = 200 - 300 nm) for the non-doped and doped DW and RW, respectively, where significant effects are observed for the type of water (DW and RW).
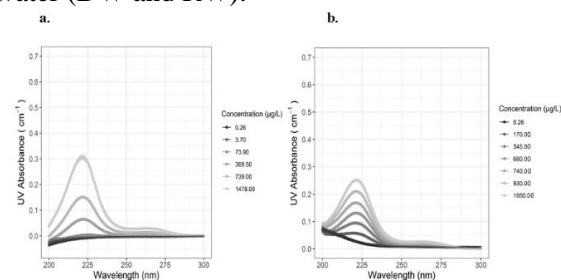
Figure 2. *UV absorbance spectrum for DW (a) Atrazine concentration between 0.26 to 1478 μg/L (b) Atrazine concentration between 0.26 to 1050 μg/L)*

The Tukey comparison tests indicate that there are no significant statistical differences between the curves for the non-doped (0.26 μg/L) and doped (3.70 and 73.90 μg/L) DW (Figure 2), which indicates that at low Atrazine concentrations, the capacity of use of UV absorbance to indicate the presence of organic compounds is limited; thus, in this range, neither wavelengths 223 nor 254 nm, can be used for low Atrazine concentrations.

a.

b.

c.
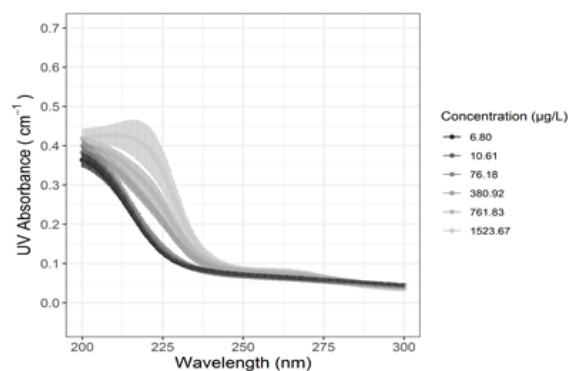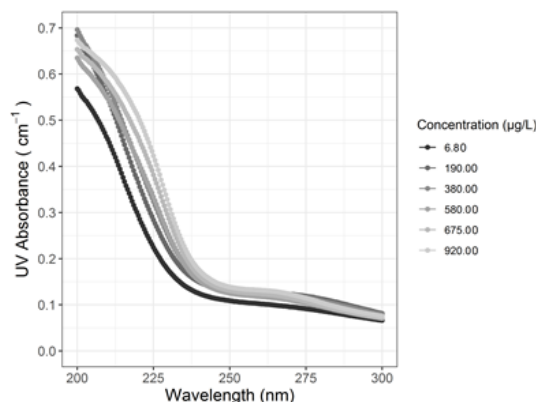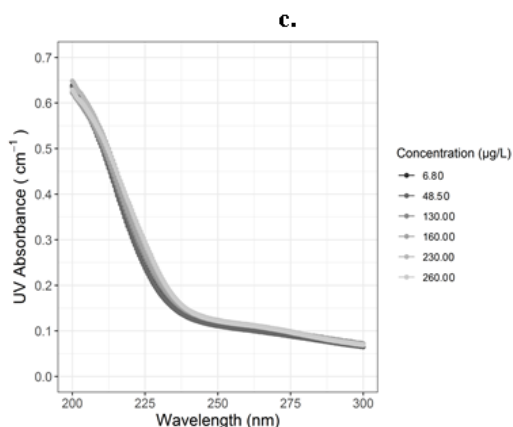
Figure 3. *UV absorbance spectra for RW (**a**) Atrazine concentration between 6.80 to 1523.67 µg/L. (**b**) Atrazine concentration between 6.80 to 920 µg/L. (**c**) Atrazine concentration between 6.80 to 260 µg/L)*

In case of the doped RW, has a larger standard deviation than does the doped DW (Figure 3), probably because the water matrix usually contains natural and no natural organic matter or iron that can be added to herbicides [18, 36], which can cause interference in the measurement of the data. Nevertheless, in UV measured, many of the bonds present in a complex molecule, or complex mixtures of molecules, are transparent to UV radiation, and structural complexity molecule or mixture does not necessarily result in increased spectral complexity, therefore, is possible determine the presence of general structural characteristics in a sample [36]. In these cases, the points of maximum absorbance were shifted towards wavelengths between 203 and 223 nm.

The non-doped RW curve (Figure 3) is a characteristic spectrum of the presence of nitrates in natural water because nitrate is the most stable form of nitrogen in water due to the oxidation of nitrite, ammonium, or organic nitrogen. The maximum absorbance of nitrate solutions occurs between 200 and 400 nm, depending on their concentration; even in the presence of other compounds, a convex shape in the region of 205 - 220 nm is related to its presence in water [25, 36].

On the other hand, herbicides such as Diuron absorb UV light at 214 - 250 nm [25]. Studies such as Bueno et al. [28] show the presence of compounds such as iron (1880 - 2110 mg/L), manganese (0.340 - 0.460 mg/L), nitrates (2100 - 4290 mg/L), nitrites (0.016 - 0.067 mg/L), and Atrazine (<0.001 - <0.004 mg/L) in the RW of the Cauca River at sampling area.

The possible presence of these and other compounds make the matrix of the RW complex, which causes the observed displacement of the points of maximum absorbance [25]. For this reason, in each case it is important to know the characteristics of the watershed and perform a hazard identification and complementary quantification of potential pollutants present in the water.

Table 1 shows the analysis of variance for the adjusted linear mixed model, where it is evidence that absorbance changes significantly depending on wavelength, atrazine concentration and type of water.

Table 1. *Analysis of variance of the adjusted linear mixed model*

Factor	F Statistic	P-value
Type of water	137.3	<.0001 *
Atrazine concentration	1002.7	<.0001 *
Wavelength	2151.4	<.0001 *
Type of water × Atrazine concentration	771.0	<.0001 *
Type of water × Wavelength	887.9	<.0001 *
Atrazine concentration × Wavelength	3272.8	<.0001 *

* Significant effect at a 5% level

Tables 2 and 3 show the significant statistical differences between the Atrazine concentrations and absorbance (λ - nm) for DW and RW, respectively. It is observed the existence of significant statistical differences between the DW and the RW, both non-doped and doped with the different Atrazine concentrations. For the non-doped water, the absorbance spectra are different

between 200 - 266.5 nm; for Atrazine concentrations from 5 to 1000 μg/L, the differences are between 200 - 259.5 nm, and for the concentration of 2000 μg/L, the differences are between 200 - 223 nm.

On the other hand, in the doped water, between the absorbance curves for each type of water,

there are significant differences between 200 - 240 nm using DW. In the RW, these differences occur between 201.5 - 235.5 nm.

These results are similar values to those reported by Al-Degs et al. [15], who indicate that there are no significant statistical differences at 250 nm.

Table 2. *Wavelengths with significant statistical differences between the doses evaluated in the DW*

Comparison concentrations (μg/L)	Wavelength (nm)	Comparison concentrations (μg/L)	Wavelength (nm)
0 – 5	-	5 – 2000	200.0 – 240.0
0 – 100	-	100 – 500	219.0 – 224.0
0 – 500	216.0 – 227.0	100 – 1000	207.0 – 233.5
0 – 1000	206.0 – 234.0	100 – 2000	200.0 – 239.5
0 – 2000	200.0 – 240.0	500 – 1000	211.5 – 230.0
5 – 100	-	500 – 2000	200.0 – 238.5
5 – 500	216.0 – 227.0	1000 – 2000	204.0 – 234.5
5 – 1000	207.0 – 234.5	-	-

Table 3. *Wavelengths with significant statistical differences between the doses evaluated in the RW*

Comparison concentrations (μg/L)	Wavelength (nm)	Comparative concentrations (μg/L)	Wavelength (nm)
0 – 5	-	5 – 2000	203.5 – 235.5
0 – 100	-	100 – 500	216.0 – 227.0
0 – 500	213.0 – 228.5	100 – 1000	209.5 – 231.5
0 – 1000	206.5 – 232.0	100 – 2000	203.5 – 235.5
0 – 2000	201.5 – 235.5	500 – 1000	-
5 – 100	-	500 – 2000	206.5 – 232.5
5 – 500	215.0 – 228.0	1000 – 2000	211.5 – 229.5
5 – 1000	209.0 – 232.0	-	-

This confirms that 254 nm, which historically has been used as an indirect indicator of the presence of natural organic matter (NOM) [22, 37], does not adequately represent the presence of unnatural organic matter in water, such as Atrazine. On the contrary, 223 nm is including on the ranges that presents difference using doped DW and RW, indicating that this wavelength, present sensibility to Atrazine concentrations, similar to reported by Thomas and Burgess [25] and Al-Degs et al. [15].

With relation specifically to UV_{254} and UV_{223}, Tables 4 and 5 show the correlation between Atrazine concentration doped to DW and RW. It is ratified that UV_{254} presents a similar behavior with DW and RW, being the correlation with atrazine, relatively similar in both cases. This shows the low sensitivity of this variable as a possible indicator of this type of pollutants. In contrast, UV_{223} presented greater variability, which may be due to the heterogeneous water

matrix of the Cauca River, which generates interference in the UV absorbance values.

Table 4. *Correlations between Atrazine concentration and UV absorbance for doped DW*

Parameters	Atrazine concentration (µg/L)	UV$_{254}$ (cm^{-1})	UV$_{223}$ (cm^{-1})
Atrazine concentration (µg/L)	1.00	0.94*	0.97*
UV$_{254}$ (cm^{-1})	0.94*	1.00	0.98*
UV$_{223}$ (cm^{-1})	0.97*	0.98*	1.00

* Significant correlation at a 5% level

Other studies have found a high correlation degree between UV absorbance and other parameters associated with the presence of organic compounds such as Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) [31, 38].

Table 5. *Correlations between Atrazine concentration and UV absorbance for doped RW*

Parameters	Atrazine concentration (µg/L)	UV$_{254}$ (cm^{-1})	UV$_{223}$ (cm^{-1})
Atrazine concentration (µg/L)	1.00	0.98*	0.68
UV$_{254}$ (cm^{-1})	0.98*	1.00	0.80
UV$_{223}$ (cm^{-1})	0.68	0.80	1.00

*Significant correlation at a 5% level

According to authors as Weishaar et al. [36] and Gerrity et al. [17], the measurement of UV absorbance has taken a new significance for the drinking water industry, due to offer a promising tool due to minimal equipment, expertise, faster response times, and lower costs to supplement existing analytical methods based on liquid or gas chromatography and mass spectrometry, being an important complement to operate a drinking water treatment plant [20], due to allow a real time monitoring of processes performance.

Considering these results and those presented in the absorbance curves, it can be stated that the UV$_{223}$ is strongly related to the Atrazine concentration in the water, if compared to UV$_{254}$. In general, the measurement of this indicator can be important as a complementary risk control measure for DWSSs because it can be sensitive at concentrations above 70 µg/L, which is close to the reference value of the WHO [3] (100 µg/L) and can serve as an indicator of hazardous events in supply watersheds that are strongly affected by agricultural activities. It is worth mentioning that in these cases, diffuse pollution predominates [39], therefore, the measurement of UV absorbance can be useful for obtaining systematic information about this type of chemical hazard.

This parameter can be included in early warning stations, allowing along with other parameters such as turbidity and dissolved oxygen, to show the presence of potential chemical hazards at water supply watersheds [40], being advisable to measure the entire UV absorbance spectrum to detect not only natural organic matter - NOM (λ: 254 nm) or atrazine (λ: 223 nm), but the presence of different organic compounds potentially present in the water matrix and that may represent health risks.

4. Conclusions

The results confirmed that λ of 254 nm (UV$_{254}$), which is commonly used to indirectly indicate the presence of natural organic matter (NOM), is not suitable as an indirect indicator of other types of organic matter, such as Atrazine. For λ greater than 240 nm, no significant statistical differences were found between the concentrations and types of water; in contrast, UV$_{223}$ was most representative for identifying the presence of Atrazine regardless of the type of water. The representative λ ranges for the evaluated concentrations, were from 219.5 to 223.5 nm for DW and from 203 to 223 nm for RW. The difference between the regions of maximum absorbance for the two types of water may be due to the complexity of the raw water evaluated.

5. Acknowledgements and Funding Statement

6. References

(1) Pérez-Vidal A, Torres-Lozada P, Escobar-Rivera J. Hazard identification in watersheds based on water safety plan approach: case study of Cali-Colombia. Environ. Eng. Manag. J. 2016;15(4):861–72.

(2) Hansen S, Messer L, Mittelstet A. Mitigating the risk of atrazine exposure: identifying hot spots and hot times in surface waters across Nebraska, USA. J. Environ. Manage. 2019;250:109424. https://doi.org/10.1016/j.jenvman.2019.109424.

(3) World Health Organization (WHO). Guidelines for drinking-water quality, 4th edn, Geneva, Switzerland; 2018.

(4) Pérez-Vidal A, Escobar-Rivera J, Torres-Lozada P. Development and implementation of a water-safety plan for drinking-water supply system of Cali, Colombia. Int. J. Hyg. Environ. Health. 2020;224:113422. https://doi.org/10.1016/j.ijheh.2019.113422.

(5) Ojeda EO, Arias-Uribe R. Informe nacional sobre la gestión del agua en Colombia (National report on water management in Colombia). CEPAL, GWP; 2000.

(6) Badii M, Landeros J. Plaguicidas que afectan a la salud humana y la sustentabilidad (Pesticides that affect human health and sustainability). CULCyT. 2007;19(4):21-34.

(7) Zhou R, Zhu L, Yang K, Chen Y. Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. J. Hazard Mat. 2006;137(1):68–75. https://doi.org/10.1016/j.jhazmat.2006.02.005.

(8) Zhao Z, Jiang Y, Li Q, Cai Y, Yin H, Zhang L, Zhang J. Spatial correlation analysis of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in sediments between Taihu Lake and its tributary rivers. Ecotox. Environ. Safe. 2017;142:117–28. https://doi.org/10.1016/j.ecoenv.2017.03.039.

(9) Graymore M, Stagnitti F, Allinson G. Impacts of Atrazine in aquatic ecosystems. Environ. Int. 2001;26(7–8):483–95. https://doi.org/10.1016/S0160-4120(01)00031-9.

(10) Hou X, Huang X, Ai Z, Zhao J, Zhang L. Ascorbic acid induced Atrazine degradation. J. Hazard Mat. 2017;327:71–8. https://doi.org/10.1016/j.jhazmat.2016.12.048.

(11) Nasseri S, Baghapour M, Derakhshan Z, Faramarzian M. Degradation of Atrazine by microbial consortium in an anaerobic anaerobic submerged biological filter. J. water health. 2014;12(3):492–503. https://doi.org/10.2166/wh.2014.162.

(12) Environmental Protection Agency (EPA). 816-F-09-004, National Primary Drinking Water Regulations. United States. 2009.

(13) Shipitalo M, Owens B. Atrazine, deethylAtrazine, and deisopropylAtrazine

in surface runoff from conservation tilled watersheds. Environ. Sci. Technol. 2003;37(5):944–50. https://doi.org/10.1021/es020870b.

(14) Baldwin A et al. Organic contaminants in Great Lakes tributaries: Prevalence and potential aquatic toxicity. Sci. Total Environ. 2016;554–555: 42–52. https://doi.org/10.1016/j.scitotenv.2016.02 .137.

(15) Al-Degs Y, Al-Ghouti M, El-Sheikh A. Simultaneous determination of pesticides at trace levels in water using multiwalled carbon nanotubes as solid-phase extractant and multivariate calibration. J. Hazard Mat. 2009;169(1–3):128–35. https://doi.org/10.1016/j.jhazmat.2009.03. 065.

(16) Wu C, Hill H, Gamerdinger A. Electrospray Ionization-Ion Mobility Spectrometry as a Field Monitoring Method for the Detection of Atrazine in Natural Water. Field Anal. Chem. Technol. 1998;2(3):155–61. https://doi.org/10.1002/(SICI)1520-6521(1998)2:3%3C155::AID-FACT4%3E3.0.CO;2-U.

(17) Gerrity D et al. Development of surrogate correlation models to predict trace organic contaminant oxidation and microbial inactivation during ozonation. Water Res. 2012;46(19):6257-72. https://doi.org/10.1016/j.watres.2012.08.0 37.

(18) Amaral B, De Araujo J, Peralta-Zamora P, Nagata N. Simultaneous determination of Atrazine and metabolites (DIA and DEA) in natural water by multivariate electronic spectroscopy. Microchemical J. 2014;117:262–67. https://doi.org/10.1016/j.microc.2014.07.0 08.

(19) Ekanayake D et al. Interrelationship among the pollutants in stormwater in an urban catchment and first flush identification using UV spectroscopy. Chemosphere. 2019;233:245-51. https://doi.org/10.1016/j.chemosphere.201 9.05.285.

(20) Szerzyna S, Mołczan M, Wolska M, Adamski W, Wiśniewski J. Absorbance based water quality indicators as parameters for treatment process control with respect to organic substance removal. E3S Web of Conferences. 2017;17:00091. https://doi.org/10.1051/e3sconf/20171700 091.

(21) Beauchamp N et al. Relationships between DBP concentrations and differential UV absorbance in full-scale conditions. Water Res. 2018;131:110-121. https://doi.org/10.1016/j.watres.2017.12.0 31.

(22) American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF). Standard Methods for Water and Wastewater Examination, Washington D.C., United States. 2012.

(23) Lobanga K, Haarhoff J, Van Staden S. Treatability of South African surface waters by enhanced coagulation. Water SA. 2014;40(3):529-34. https://doi.org/10.4314/wsa.v40i3.17.

(24) Altmann J, Massa L, Sperlich A, Gnirss R, Jekel M. UV_{254} absorbance as real-time monitoring and control parameter for micropollutant removal in advanced wastewater treatment with powdered activated carbon. Water Res. 2016;94:240-5. https://doi.org/10.1016/j.watres.2016.03.0 01.

(25) Thomas O, Burgess C. UV-visible Spectrophotometry of Water and Wastewater. 1st ed. Amsterdam, Netherlands. 2007.

(26) Mehaffey M, Nash S, Wade T, Ebert D, Jones K, Rager A. Linking land cover and water quality in New York city's water supply watersheds. Environ. Monit. Assess. 2005;107(1-3):29–44. https://doi.org/10.1007/s10661-005-2018-5.

(27) De Girolamo A, Porto A. Land use scenario development as a tool for watershed management within the Rio Mannu Basin. Land Use Pol. 2012;29(3):691– 701. https://doi.org/10.1016/j.landusepol.2011.11.005.

(28) Bueno K, Pérez A, Torres P. Identificación de peligros químicos en cuencas de abastecimiento de agua como instrumento para la evaluación del riesgo (Identification of chemical hazards in supply watersheds as an instrument for risk evaluation). Revista Ingenierías. 2014;13(24):59–75.

(29) Environmental Protection Agency (EPA). Method 523: Determination of Triazine Pesticides and their Degradates in Drinking Water by Gas Chromatography/Mass Spectrometry. 2009.

(30) Fairbairn D, Karpuzcu M, Arnold W, Barber B, Kaufenberg E, et. al. Sediment-water distribution of contaminants of emerging concern in a mixed-use watershed. Sci. Total Environ. 2015;505:896–904. https://doi.org/10.1016/j.scitotenv.2014.10.046.

(31) Kim C, Eom J, Jung S, Ji T. Detection of organic compounds in water by an optical absorbance method. Sensors (Switzerland). 2016;16(1):61. https://dx.doi.org/10.3390%2Fs16010061.

(32) Montgomery D. Design and analysis of experiments. John Wiley & Sons, (ed.). 8th ed. Arizona, United States. 2012.

(33) Instituto Colombiano Agropecuario (ICA). Registros nacionales (National records). 2020 [cited 2019 Sep 15]. Available from: http://www.ica.gov.co/getdoc/d3612ebf-a5a6-4702-8d4b-8427c1cdaeb1/registros-nacionales-pqua-15-04-09.aspx.

(34) Dalton R, Pick F, Boutin C, Saleem A. Atrazine contamination at the watershed scale and environmental factors affecting sampling rates of the polar organic chemical integrative sampler (POCIS). Environ. Pollut. 2014;189:134-42. https://doi.org/10.1016/j.envpol.2014.02.028.

(35) Tarazona GA. Manejo fitosanitario del cultivo de la caña panelera. Instituto Colombiano Agropecuario (ICA). Bogotá; 2011 [cited 2021 mar 4]. Available from: https://www.ica.gov.co/getattachment/6a54658e-1723-488d-a7ab-2f4baad793cb/Manejo-fitosanitario-del-cultivo-de-la-cana-panele.aspx.

(36) Weishaar J, Aiken G, Bergamaschi B, Fram M, Fujii R, Mopper K. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 2003; 37(20):4702–8. https://doi.org/10.1021/es030360x.

(37) Swietlik J, Sikorska E. Characterization of Natural Organic Matter Fractions by High Pressure Size-Exclusion Chromatography, Specific UV Absorbance and Total Luminescence Spectroscopy. Pol. J. Environ Stud. 2006;15(1):145–53.

(38) Ghernaout D, Ghernaout B, Kellil A. Natural organic matter removal and enhanced coagulation as a link between coagulation and electrocoagulation.

Desalination Water Treat. 2009; 2(1–3):203–22.
https://doi.org/10.5004/dwt.2009.116.

(39) Heathwaite A, Quinn P, Hewett C. Modelling and managing critical source areas of diffuse pollution from agricultural land using flow connectivity simulation. J. Hydrology. 2005;304(1–4):446–61. https://doi.org/10.1016/j.jhydrol.2004.07.0

43.

(40) Subantu P. Development of methods for the separation and characterization of natural organic matter in dam water [Master thesis]. Sudáfrica: Durban University of Technology. 2014. Available at:
http://openscholar.dut.ac.za/handle/10321/1182.