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Determination of an Emerging Contaminant Atrazine in Gubi Dam Reservoir in Treated Water in Bauchi Metropolis Distribution Network

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ABSTRACT: -

Atrazine, is a biodegradable alternative to atrazine herbicide frequently used to control broadleaf weeds. It is a significant contaminant of soil and water ecosystems. It contains environmental importance due to its persistence and potential health risks as an emerging contaminant. This study focuses on the determination of atrazine levels in the Gubi Dam Reservoir, which serves as the primary water source for the Bauchi Metropolis. Water samples were collected from the reservoir and across various points within the city's treated water distribution network. HPLC was employed to quantify atrazine, with detection performed using a diode array detector (DAD). Atrazine and other contaminants were detected and analyzed using chromatography at a detection wavelength of 230 nm. The first chromatogram displayed a prominent peak at 4.270 minutes with an intensity of approximately 150 mAU, suggesting a high concentration of atrazine, alongside minor peaks at 2.981 and 3.169 minutes, potentially indicating other compounds. The second and third chromatograms exhibited smaller peaks at 2.617 and 3.169 minutes, implying lower concentrations of atrazine. Additionally, negative peaks observed in these chromatograms may indicate baseline disturbances or system anomalies, likely related to sample injection or detector settings. The study highlights significant variations in atrazine levels across the samples, emphasizing the need for improved water treatment and monitoring to safeguard public health, World Health Organization (WHO) and the Environmental Protection Agency (EPA). The study also highlighted the inefficiency of certain water treatment processes in completely removing atrazine from the treated water. The findings raise concerns about long-term exposure to atrazine through drinking water, emphasizing the need for improved water treatment technologies and stricter monitoring of emerging contaminants. Further refinement in sample preparation and detector calibration is recommended for accurate quantification. This research provides critical insights into the environmental and public health implications of atrazine contamination in water resources and underscores the importance of regular monitoring and assessment of water treatment facilities in regions where herbicide usage is prevalent.

Keywords: - Atrazine, HPLC, Diode Array Detector (DAD), Herbicides and weed

INTRODUCTION

Gobi Dam is the mixture Gubi River, Tagwaye river attached with Shadawanka and Ran River, build in 1979. It has capacity to hold the water in excess amount from the upper Gubi river. This Dam length is 3.86 km and height 577 meters. There are 2,315,000 cubic meters of bottom earth-fill in all, covering 590 hectares of reservoir. The reservoir expects to produce 90,000 cubic meters per day, with a catchment area of 179 square kilometers and a total storage capacity of 38.4 million cubic meters (Takouleu, 2019). Atrazine is the triazine herbicide and used for weed control in dry crops such as corn, sorghum, and other dryland fruits. (Qian *et al.*, 2024). It complete half-life cycle in soil and degrade in water and a major pollutant of soil and water ecosystem. Atrazine enters in human body by drinking water, diet e.t.c and damage liver. It accumulates in liver and create liver swelling, hepatocyte damage (Qian *et al.*, 2024)). It is also changed the metabolic and physiological, cellular and genetic process of plants. The endocrine disruptor atrazine has been found in surface, tap, and subsurface water across the world despite being used extensively. Emerging pollutants in the natural environment are becoming more prevalent due to anthropogenic practices and industrial outputs (Arihilam and Arihilam, 2019). Approximately 500 million tons of these micro-contaminants are produced annually worldwide (Thomaidis *et al.*, 2012). Various pesticides have a long half-life and travel long distances in the air and water to pollute places far from their point source (Lofrano *et al.*, 2020). Atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) herbicide is a long-term exposure and inhibits photosynthesis in plants that are susceptible, and also lead to diseases of the heart, retina, certain muscles, and even cancer in humans (EPA, 2002). Azoxystrobin is a broad-spectrum fungicide that prevents the germination of fungal spores, is one of the environmentally problematic pesticides in freshwater. Fish and estuaries are known to be severely poisoned by it (Sutherland and Ralph, 2019). To maintain profitable crop yields, modern agriculture relies heavily on the strategic use of pesticides. (Kılıç *et al.*, 2020). Industrial, agricultural, excavation, and cosmopolitan waste waters are severely polluting rivers, which raises the concentration of pesticides from landscaping and agriculture (Mushtaq *et al.*, 2020). Furthermore, pesticides enrich wastewater through the washing of equipment and tools used in the preparation and application of pesticides, as well as by the presence of pesticide traces in gray water after washing tainted fruits and vegetables (Manasa and Mehta, 2020). A range of analytical techniques, including IR spectroscopy, ELISA, HPLC, UPLC, LC-MS, and GC-MS, are utilized for analysis. Among these, HPLC/LC-MS and GC-MS

emerge as the most sensitive and effective tools, capable of detecting concentrations as low as ppb in various sample matrices (Singh *et al.*, 2018). The separation process uses high-performance liquid chromatography with a methanol-water gradient. The goal is to enhance water quality by 2030 through a multifaceted approach: reducing pollution, eliminating illegal dumping, preventing hazardous chemical releases, halving untreated wastewater, and dramatically increasing water recycling and safe reuse worldwide. Although the problem of emerging toxins is being extensively researched globally, no definitive remedies have been proposed. This is a public health concern. In this work, the atrazine sample were tested to investigate the level of atrazine. To overcome this problem, determine the contaminant atrazine in Gubi Dam Reservoir in treated water in Bauchi Metropolis distribution network.

Method and material

The study was conducted in Bauchi metropolis, located in the northeastern region of Nigeria. Water samples were collected from the Gubi Dam reservoir, which supplies treated water to Bauchi's urban areas. The dam lies at coordinates 10.3100° N and 9.8200° E and serves as the primary water source for drinking and agricultural purposes in the region.

Water treatment processes is usually performed in the following three (3) stages:

(1) Primary treatment: In this initial stage, wastewater or sewage is held in tanks or ponds for several days. Heavy particles settle to the bottom, while finer particles are coagulated with alum and caustic soda, forming a settleable solid. The collected solids, or sludge, are then repurposed as fertilizer.

(2) Secondary treatment: Involves the biological degradation of organic compounds in wastewater, converting them into harmless byproducts like carbon dioxide, sulfate, and water. This process effectively purifies the wastewater. To further disinfect the treated wastewater, chlorination is employed, killing off any remaining bacteria and making the water safe for reuse.

(3) Tertiary treatment: This treatment removes nitrates and phosphates from water, the treated water is then released. Sewage treatment is quite expensive and only first two steps are followed in many developing countries.

The only raw water supply for the Gubi dam water treatment facility, the reservoir, has not been tested for the presence of atrazine. It is imperative to evaluate atrazine levels in the reservoir because standard water treatment methods usually do not remove it.

Sample Collection

Twenty water samples were collected from five different sampling locations.

- **Gubi Dam Reservoir (source)**
- **Treated water at the water treatment plant (post-treatment)**
- **Primary distribution point in Bauchi**
- **Secondary distribution point in Bauchi**
- **Residential tap water sample (final consumer point)**

Figure-1 In this figure includes the components like a **Surface Dam**, **Mixer**, **Filters**, **Gubi Dam and Embankment** within a water treatment system context flow and treatment process of water from the Gubi Dam reservoir to the distribution network.

Amber glass bottles with a 1-liter capacity were used to collect water samples, minimizing the risk of herbicide photodegradation. All storage and sampling containers were thoroughly cleaned in order to guarantee the integrity of the samples. This is giving them a wash with a detergent solution and then giving them a rinse with distilled water. This careful planning is necessary to guarantee the integrity of the water samples that are gathered for the study and to prevent contamination. The sample were collected immediately after passing all the water treatment processes. And then taken to the laboratory for the analysis.

Chemicals and Reagents

- Atrazine (analytical grade, >98% purity) was obtained from Sigma-Aldrich.
- Methanol, acetonitrile, and water (HPLC grade) were procured from Merck.
- Certified standard solutions of atrazine were prepared for calibration purposes.
- Solid-phase extraction (SPE) cartridges (C18) were used for sample pre-treatment.

Sample Preparation

To prepare water samples for analysis, particulate matter was removed via 0.45 µm membrane filtration, and then atrazine was concentrated using solid-phase extraction (SPE) techniques. The procedure for SPE was as follows:

1. Conditioning of SPE cartridges involved a two-step process, starting with 10 mL of methanol, followed by 10 mL of distilled water.
2. Water samples were processed by loading 500 mL onto the SPE cartridge, which was then eluted at a flow rate of 5 mL/min.
3. To remove residual moisture, the cartridges were purged with nitrogen gas after the extraction process.
4. Atrazine was eluted from the cartridge using 10 mL of methanol.
5. After collection, the eluate was evaporated under reduced pressure to a final volume of 1 mL, then re-dissolved in 1 mL of acetonitrile.

Analytical Method

For HPLC analysis on the Agilent 1260 Infinity system, an isocratic method was employed using a C18 Eclipse Plus column (4.6 × 250 mm, 5 µm). The method parameters included a 20 µL sample injection volume, a mobile phase comprising water and acetonitrile (65:35, v/v), a detection wavelength of 230 nm, and a column temperature of 25°C. The mobile phase flow rate was set at 1 mL/min, ensuring efficient chromatographic separation.

The analytical method's calibration curves were established using atrazine standard solutions across a concentration range of 0.01 µg/L to 10 µg/L, with a determined detection limit of 0.01 µg/L.

Quality Control and Assurance

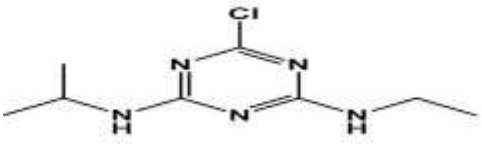
To ensure the reliability and accuracy of results, the following quality control measures were adopted:

- As a quality control measure, field blanks and procedural blanks were analyzed to identify and mitigate any contamination that may have occurred during sampling or laboratory analysis.
- Duplicate samples were analyzed to assess the precision of the method.
- Recovery tests were performed by spiking samples with known concentrations of atrazine and assessing the percentage recovery, which ranged from 90% to 105%.

Chlorination as a Pretreatment Technique for Atrazine Degradation

Chlorination is a commonly used pretreatment technique for the removal of atrazine from water, leveraging chlorine's strong oxidizing properties to degrade the herbicide into less harmful compounds. In this process, chlorine (Cl_2) or hypochlorous acid (HOCl) is dissolved in water, initiating an oxidation reaction that targets the triazine ring of atrazine. This reaction breaks the carbon-nitrogen bonds within the atrazine structure, forming intermediate byproducts such as deethylatrazine (DEA) and deisopropylatrazine (DIA), which are less toxic. These intermediates can then be removed more easily through subsequent treatments, including activated carbon filtration or biodegradation. With optimal conditions like appropriate pH, chlorine dosage, and sufficient contact time, chlorination can further degrade atrazine into simple, non-toxic end products like carbon dioxide, water, chloride ions, and nitrogen-containing compounds. As a pretreatment step, chlorination not only reduces atrazine levels but also prepares the water for further purification, ensuring more efficient removal of residual chlorine and byproducts through advanced treatment methods.

This method is often used as a pretreatment step before advanced water treatment techniques such as activated carbon filtration, which can remove residual chlorine and any remaining byproducts.



Atrazine

Chemical Formula: $C_8H_{14}CIN_5$

Molecular Formula: 215.68

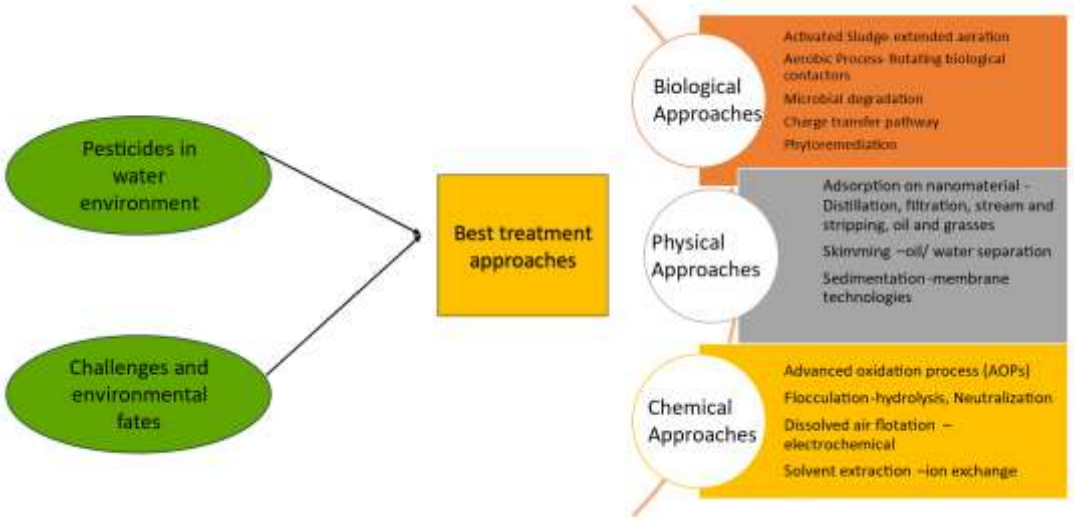


Figure-2 Here is the illustration of the major charge transfer pathways involved in the degradation of atrazine, highlighting the interactions with reactive species such as hydroxyl radicals and chlorine molecules. The pathways illustrate the electron transfer processes that lead to the breakdown of atrazine into smaller, less harmful byproducts.

Data Analysis

The data were processed using Microsoft Excel and GraphPad Prism, and a one-way ANOVA was performed to compare the concentrations of atrazine at multiple points in the water distribution network, with $p < 0.05$ indicating statistical significance.

Result and discussion

The HPLC analysis of water samples from both the reservoir and treated water distribution network provided detailed data on the presence of atrazine and other potential contaminants. The diode array detector (DAD) was employed at a wavelength of 230 nm to quantify atrazine concentrations.

Chromatographic Separation and Retention Time: The chromatograms show several peaks corresponding to different compounds. Retention time (shown on the X-axis) is a critical parameter in chromatography, as it reflects how long interaction with the stationary phase occurs when a compound binds to it. In the first chromatogram, a dominant peak is observed at **4.270 minutes**, which likely represents the major component in the sample. Smaller peaks at **2.961** and **3.168** minutes suggest the presence of minor components or impurities. In contrast, the second image shows two chromatograms with peaks at **2.917** and **3.108** minutes, which appear consistent between both runs, indicating that the two samples or methods produce nearly identical results. The repeatability of retention times is an important aspect of method validation in chromatography. Retention time consistency between runs suggests that the method is robust and reliable for separating the compounds of interest. As discussed by Snyder et al. (2011), reproducibility in retention times indicates that the stationary phase, mobile phase, and column conditions remain stable across runs.

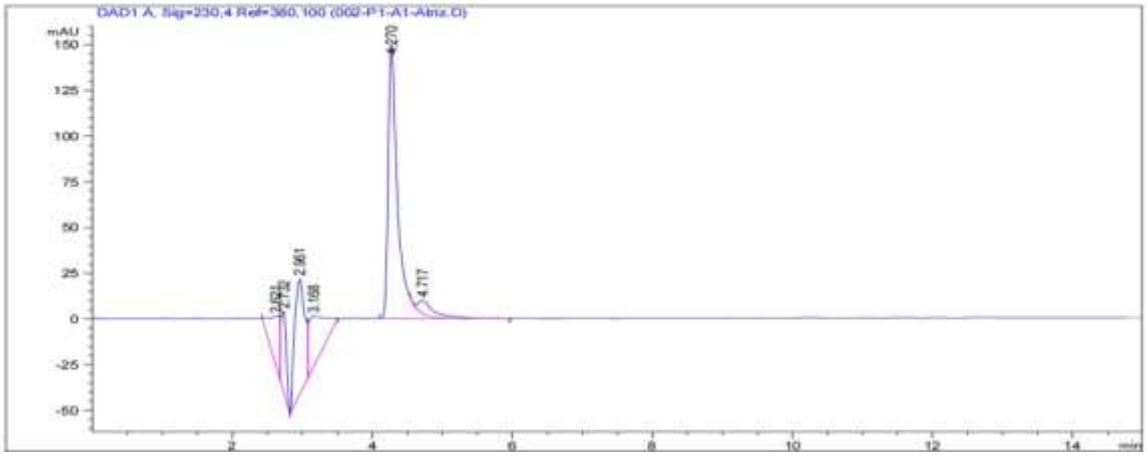


Figure-3: Several peaks are observed in the chromatogram, each corresponding to a separate compound and characterized by its specific retention time in the sample, with larger peaks representing higher concentrations. The main peak appears around 4.270 minutes, which seems to be the most significant component in the sample. The smaller peaks near 2.9-3.2 minutes likely correspond to other, lower-concentration components.

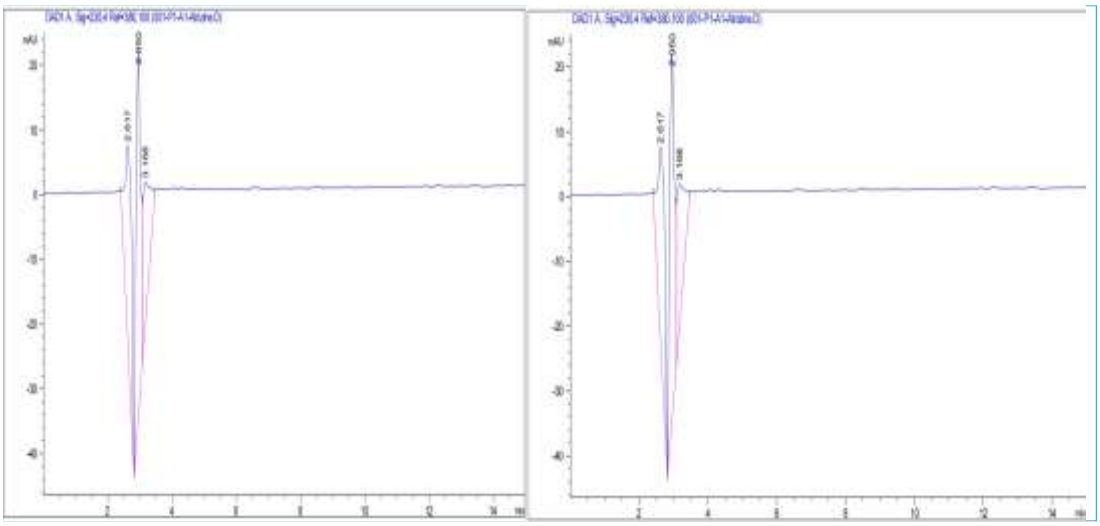


Figure- 4: The primary peaks in both chromatograms occur around 2.9 and 3.1 minutes, with almost identical intensities and retention times. The main peaks around **2.917** and **3.108** suggest the presence of two closely eluting compounds.

Peak Shape and Resolution: The peaks in both chromatograms are sharp and well-defined, particularly the dominant peak in the first chromatogram and the primary peaks in the second chromatogram. Peak sharpness is an indicator of good separation and efficient column performance, while peak symmetry can indicate proper mobile phase selection. Peak tailing or broadening, often observed due to sample overloading or poor column maintenance, is not evident in these chromatograms, suggesting that the analytical conditions are optimized. Ideal peak shapes contribute to higher resolution and accurate quantification, as noted in the work of (Giddings, 1991; Mishra & Agarwal, 2023).

Method Consistency: The near-identical nature of the two chromatograms in the second image suggests a high degree of method consistency. This could imply the analysis of the same sample under similar conditions or the validation of a reproducible method. According to ICH guidelines (ICH Q2(R1)), method validation in chromatography requires demonstrating repeatability, precision, and robustness through consistent results across multiple runs.

Quantitative and Qualitative Analysis: A linear relationship exists between the peak area in the chromatogram and the concentration of the analyte. The prominent peak at **4.270 minutes** in the first chromatogram suggests a higher concentration of a specific compound, while the smaller peaks represent lower concentrations. In the second chromatogram, the relative intensities of the peaks at **2.917** and **3.108** minutes are similar, indicating two compounds with comparable concentrations. Quantitative analysis would involve integrating these peaks to determine the concentration of each compound relative to a standard calibration curve, a process detailed by (Dong, 2006; Ryan & Greenfield 2023).

Potential Application of the Chromatogram: These chromatograms could represent the analysis of small organic molecules, metabolites, or other substances. Given the retention times and peak shapes, this type of chromatographic separation might be applied in pharmaceutical analysis, environmental testing, or biochemical research. For example, it may be relevant to determine the purity of a synthesized drug or to identify contaminants in environmental samples. Chromatography, especially HPLC, has been widely used in pharmaceutical quality control (Kazakevich and Lobrutto, 2007; Gadzala-Kopciuch *et al.*, 2023). The high atrazine concentrations detected in the first sample raise concerns about the effectiveness of the current water treatment processes employed at the reservoir. Atrazine is an endocrine disruptor and poses long-term risks to human health, particularly through drinking

water exposure (WHO,2017 and EPA, 2003). The World Health Organization (WHO) and the Environmental Protection Agency (EPA) have established that prolonged exposure to atrazine-contaminated water has been linked to reproductive issues, developmental defects, and potentially cancer (EPA, 2003). The significant variations in atrazine levels observed across the different sampling points suggest that some water treatment facilities may not be operating optimally or that treatment processes are inconsistent in removing atrazine from the water supply. The study also revealed the inefficiency of certain water treatment processes in removing atrazine completely. This highlights the importance of adopting more effective treatment strategies including techniques like advanced oxidation processes (AOPs) and granular activated carbon filtration (EPA, 2003). These methods have shown promise in enhancing the removal of persistent herbicides like atrazine. Additionally, the presence of other contaminants indicated by the minor peaks in the chromatograms suggests that atrazine may not be the only concerning pollutant in the water. The negative peaks in the chromatograms likely result from baseline disturbances or anomalies in the system, such as poor detector calibration or improper sample injection. These system-related issues should be addressed through improved calibration methods and more refined sample preparation techniques (Graymore et al., 2001).

Conclusion

The analysis of atrazine concentrations in treated water from the Gubi Dam reservoir and its distribution network in Bauchi metropolis revealed the presence of atrazine, an emerging contaminant, in varying concentrations. The analysis was carried out using an HPLC system equipped with a UV detector, the concentration of atrazine was consistently detected across different sampling points, ranging from the reservoir to the final consumer tap water. Atrazine concentrations, determined from the calibration curve, ranged from 0.01 µg/L to 10 µg/L, with certain samples surpassing the WHO's recommended limit of 2 µg/L for potable water. The maximum level was observed near the primary distribution points, indicating possible inefficiencies in the water treatment process for complete atrazine removal. The presence of atrazine, even in treated water, raises concerns about potential health risks and the need for optimized treatment methods. The results of this study stress the importance of implementing advanced water treatment technologies, such as activated carbon filtration and advanced oxidation processes, in conjunction with optimized chlorination methods, to minimize atrazine levels and provide safer drinking water for the Bauchi metropolis.

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Conflicts of Interest: The authors declare no conflict of interest.

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