The Contribution of Herbicides on River Water Pollution: the case of Beressa River, Ethiopia

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Abstract-**The survival of living things on Earth depends on three basic resources: water, air and soil. Among which water is the most important component as it forms the basic medium for origin of life.The quality of water is affected by human activities and is declining due to the rise of urbanization, population growth, industrial production, climate change, and the farmer activities like using of herbicides. The researcher is concerned to check the contribution of herbicides in water pollution at the study area. An herbicide is a substance used to kill unwanted plants; the different herbicides which are originated from factories, farm areas have different risks for human beings, land animals and aquatic mammals. For the purpose of this research antrazine and terbutryn were selected since recently and frequently used in the study area. The main objective of this research is to optimize the method and determine the quantities of herbicides (atrazine and terbutryn) those are used by the farmers farming near to beressa river stream. The chemicals and reagents used for this research were analytical grade. Water samples of the Beressa River were collected from five different points of the river in a kilometer breach. The extraction and proportion of solvent were optimized; mobile phase ratio was (acetonitrile (22%), water (45%) and methanol (33%)); finally, 20 µL was injected into HPLC-DAD system for analysis. The concentrations of atrazine and terbutryn were determined; 143.709 and 157.682µg/l respectively. This indicates that the herbicides have pollution effect for river water. The present research results on the status of river water tells us to establish water processing plants in future, the requirement of which increases at a tremendous rate due to growth of population, herbicide contamination in river water.**

***Keywords*: Atrazine, Herbicides, HPLC-DAD, Terbutryn, Water Pollution,**

1. INTRODUCTION

The survival of living things on Earth depends on three basic resources: water, air and soil, nature's three valuable gifts to mankind. Among which water is the most important component as it forms the basic medium for origin of life. The quality of water is affected by human activities and is declining due to the rise of urbanization, population growth, industrial production, climate change, the farmer activities like using of herbicides for their land and other factors. The resulting water pollution is a serious threat to the well-being of both the Earth and its population [1].

Water pollution may be defined as any impairment in its native characteristics by addition of anthropogenic contaminants to the extent that it either cannot serve to humans for drinking purposes and/or to support the biotic communities, such as fish. Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater by human activities [2]. All water pollution affects organisms and plants that live in these water bodies and in almost all cases the effect is damaging not only to the individual species and populations but also to the natural biological communities. It occurs when pollutants are discharged directly or in- directly into water bodies without adequate treatment to remove harmful constituents [2]. Water pollution is a major cause of global concern as it leads to onset of numerous fatal diseases [3]**.**The researcher is concerned to check the contribution of herbicides in water pollution at the study area.

An herbicide is a substance used to kill unwanted plants. Selective herbicides kill specific targets while leaving the desired crop relatively unharmed. Some of these act by interfering with the growth of the weed and are often synthetic "imitations" of plant hormones. Herbicides used to clear waste ground, industrial sites, railways and railway embankments are non-selective and kill all plant material with which they come into contact. Smaller quantities are used in forestry, pasture systems, and

management of areas set aside as wildlife habitat. Many of them are species specific to the target plant pests [4]. For the purpose of this antrazine and terbutryn were selected since recently and frequently used in the study area.

Atrazine is a selective triazine herbicide used to control broadleaf and grassy weeds in corn, sorghum, sugarcane, pineapple, Christmas trees and other crops, and in conifer reforestation plantings. It is also used as a non-selective herbicide on non-cropped industrial lands and on fallow lands. It is available as dry flowable, flowable liquid, liquid, water dispersible granular and wet table powder formulations [5, 6].

Atrazine is an herbicide and inhibits the photosynthesis in the target plants. It is water-soluble and can be transported in dissolved form [7]. Atrazine has been detected consistently in water bodies [8]. It is quite susceptible to leaching and/or runoff. Atrazine has also been reported in precipitation, so it can lead to contamination of pristine water resources. Approximately 1 to 6% of the applied herbicides are released to the aquatic environment. Aged and persistent herbicides can become recalcitrant due to increased sorption and decreased bioavailability over time [9].The presence of atrazine in different spheres of environment causes severe effects on human health. These range from those on nervous system, immune system, kidney, heart and liver as well as on hormones and enzymes. Even low doses of atrazine can increase health risks. In humans, nausea and dizziness were reported after ingestion of contaminated well water containing an unspecified concentration of atrazine [10]. A National Toxicology Program study of immune system function in mice concluded that “atrazine was found to adversely affect the immune system and, thus, is considered to be an immune toxic compound [11].

Terbutryn(2-(t-butylamino)-4-(ethylamino)-6 (methylthio) s-triazine) belongs to the group of triazine herbicides. Triazines inhibit photosynthesis by interrupting the electron transport system, and are powerful tools for weed control in agriculture [12]. Terbutryn is an active ingredient in many past and current plant protection products. These herbicides are still preferentially applied in maize, pea and cereal culture. Terbutryn is slightly toxic to humans, but has been shown to have moderate toxicity to aquatic organisms, including algae. The triazine herbicides were banned during the last decade (atrazine 1991, simazine 2000) because of their persistence in aquifers and the resulting threat to drinking water resources. Terbutryn was one of the last triazine compounds for which authorization for use as an herbicide was revoked [13].

The different herbicides which are originated from factories, farm areas have different risks for human beings, land animals and aquatic mammals. The effect of open defecation is that herbicides would be washed into water sources during rainstorms, or transferred to the water source by wind, people or animals.Many of the communities in Ethiopia use unprotected water sources especially the rural communities who use unprotected springs and hand-dug wells. Other groundwater sources for some communities include shallow-drilled and boreholes, ponds, lakes, streams and rivers. Roof water-harvesting techniques are used to capture rainwater, which is easily exposed for contamination from human activities like using of herbicides. As a result it needs to quantify in the consumption of live hoods like environmental water. So the main objective of this research is to optimize the method and determine the quantities of herbicides (atrazine and terbutryn) those are used by the farmers farming near to beressa river stream.

2. EXPERIMENTAL

2.1. Chemicals and Reagents

All the solvents used in this study were of HPLC grade, and the chemicals and reagents were also of analytical grade. The disperser and extraction solvents were obtained from different sources: methanol was purchased from Acros organics (New Jersey, USA); acetonitrile from Sigma-Aldrich Chemie GmbH (Buchs, Switzerland), extra pure sodium chloride was purchased from Oxford laboratory (Mumbai, India), Toluene was purchased from Beijing Chemical Works (Beijing, China), distilled water. The standards atrazine and terbutryn are of analytical

reagent grade and were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

2.2. Sample Area and Sampling

This retrospective study used beressa river water which is found near to Debrebrehan town that is around 130kilometers away from Addis Ababa, the capital city of Ethiopia in north- east direction.

Water samples of the Beressa River were collected from fivedifferent points of the river in a kilometer breach. Various water quality parameters were monitored and a detailed field survey has been conducted. Proper sampling procedure was followed while collecting the samples.Appropriate sample handling and preservation is essential to ensure data quality. Factors considered were: clean amber glass containers were used since the analytes are organic compounds; proper sample preservation is important if accurate and representative results are to be obtained from the sampling efforts, all samples are placed on ice in the dark and analyses has been initiated as soon after collection to avoid sample deterioration.Selection of sampling depth varies with the purpose of work and the parameter to be tested. In this study, the sampling depth was taken up to 2.5m. This was because; the main point offocus of this study was river water pollution. Generally, water soluble analyte concentration analysis needs sample from all section.

2.3. Sample preparation and analysis

2.5mg weight of terbutryn was measured and dissolved with methanol as a solvent by shaking 50 times. Then the solution was diluted to 25 ml volume to have 100ppm analyte. By the same procedure and the same amount of atrazine solution was prepared. From each prepared solutions 2.5ml was measured and mixed together then diluted to 25ml volume by distilled water to get 10ppm solutions of each analyte.

2.5g of NaCl weighed and dissolved with distilled water to have10 %(m/v) in a volume of 25ml NaCl. Aqueous solution of 5 mL NaCl (10% w/v) was spiked into appropriate quantity of the standard solution containing the mixture of the model compounds under study. A mixture of 50 µL toluene and 0.60 mL methanol was injected rapidly into the sample solution through the 1-mL syringe. An emulsion (water, extraction solvent, and disperser solvent) was formed in the volumetric flask. After 10 min, another 0.6 mL of methanol, used as the de-emulsifier, was injected slowly into the aqueous bulk to break up the emulsion. The emulsion was then cleared into two phases in 5 to 10 s. This was followed by collection of the upper layer (organic phase) using a micro syringe. The collected organic phase was dried in vacuum oven and the residue was reconstituted in 25 µL methanol. The extraction and proportion of solvent were optimized; mobile phase ratio was (acetonitrile (22%), water (45%) and methanol (33%)); finally, 20 µL was injected into HPLC-DAD system for analysis.

3. Result and Discussion

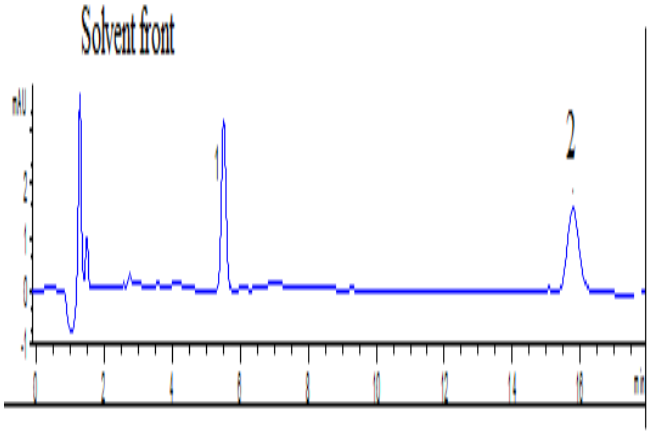

Figure1: The chromatogram of the analytes

The peak area of peak 1 and 2 are 198 and 204mAU respectively, regression equations are Y = 1.259x + 17.07 for atrazine and Y = 1.208x + 13.52 for terbutryn, where Y is peak area in mAU, retention times (t_{r1} and t_{r2}) of peak1 and 2 are 5.5 and 15.75 minutes respectively, dead time(t_m) for solvent front is 1.3 minute, baseline width(W)of peak1and2 are 0.4 and 0.8 minutes respectively, sample volume, 5 mL; spiked concentration, 50 µg L^{-1}; extraction solvent, 50 µL toluene; disperser and terminating solvent, 1.2 mL methanol; pH = 6; 10% NaCl (w/v);1, Atrazine; 2, Terbutryn.

Table1: Experimental results

Analytes	Concentration (µg/L)	Retention factor(k)	Separation factor of the two peaks (α)	Resolution(Rs)
Atrazine	143.709±0.4	3.3077	3.3605	35.4167
Terbutryn	157.682 ±0.7	11.1154		

The extraction of atrazine and terbutryn from water was done. The concentrations of atrazine and terbutryn were determined i.e. 143.709 and 157.682µg/Lrespectively. This indicates that the herbicides have pollution effect for river water.

As shown from the chromatogram or from calculated retention factor, atrazine spend more time in mobile phase than terbutryn did this is due to atrazine is slightly polar than terbutryn, as a result the physical interaction between MP & atrazine is higher. On the other hand, terbutryn spends more time on stationary phase than atrazine did again this is due to terbutrynis slightly non polar than atrazinei.e. the adsorption, ion exchange etc. physical interaction between stationary phase and terbutryn is higher.

Resolution (R_s) between the two samples was calculated, the combined effects of solvent (i.e.the extent to which substances are separated on account of differences in their rates of migration with reference to a particular set of solvent & stationary phase) andcolumn efficiency (i.e. ability to achieve prevention of remixing of theseparated substances) is expressed in terms of resolution of the column. Thus, R_s = 35.4167 which is greater than 1.5, would tell us a complete recovery of each components.

The selectivity factor(α), which is the ability of the column to separate the two sample components (the ratio of the retention factor of more strongly retained sample component to less retained) is greater than one i.e. 3.3605 shows the column is efficient to separate atrazine and terbutryn.

In general the given situation (the optimized extracted sample, solvent component and type of column) are perfect to separate atrazine and terbutryn which are extracted from water by low density organic extraction solvent.

4. CONCLUSION

The present research results on the status of river water tells us to establish water processing plantsin future,therequirementofwhichincreasesat a tremendous rateduetogrowthofpopulation, herbicide contamination in river water.From this study, the river water quality of the major rivers around Debrebirhan town, is a great threat to ecosystem though some parameters may not in the depreciate level but the condition of the river side urbanization and industrialization may cause all kind of water pollution in the near future.Even the presence of atrazine and terbunylin this river causes severe effects on human health and the life span of aquatic animals.

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