Use of Atrazine and groundwater availability in Brazil: case study Tianguá

Asdrúbal de Albuquerque Arraes[1]
Francisco Maurício de Sá Barreto[2]
José Carlos de Araújo[3]

Abstract. This paper focuses on the use of pesticides in Brazil, particularly Atrazine, and on the damage to groundwater and overall water availability resulting from this use. The paper gathers evidence from literature, pointing to the ultimate nocivity of this practice, both from the health perspective and from the social-environmental standpoint. The pollution-profit concept is debated, referring to its profound social and environmental unfairness. The economic evils of pesticide-intensive agribusiness are schematized under a chart. The fundamental conception that lies under pesticides is exposed, and linked to the root of the misuse of chemicals as agrarian panaceas. As a frequently used pesticide in Brazil, Atrazine, its characteristics, customary uses and essential dangers are described. The case study of the aquifer in the municipality of Tianguá, Ceará, Brazil, is presented. The two-year monitoring of the aquifer showed its contamination by Atrazine. The studied aquifer is an important source of water to Ceará, the driest State of the Country, and its pollution reduces considerably the water availability in the region. The discussion brought up in this paper is of great importance to the water management system, especially for the Brazilian semi-arid region, where conflicts for water are already a reality, and water quality effective regulation is still to be achieved.

Keywords. Water availability, groundwater, pesticide, Atrazine, Brazil

Topic. 1. Water availability, use and management / 1.2. Water quality management: surface and ground water

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[1] Chemical Engineer, Federal University of Ceará, Fortaleza, Brazil, asdrubal.arraes@gmail.com
[2] Professor, Faculdade de Tecnologia FATEC, CENTEC- Curso Saneamento Ambiental, Sobral, Brazil, maubarreto@oi.com.br
[3] Associate Professor, Department of Agricultural Engineering, Federal University of Ceará, Fortaleza, Brazil, jcaraujo@ufc.br

1. INTRODUCTION

The common and broad use of pesticides in Brazil is a major issue of concern among environmentalists and researchers in the Country, which is the fourth largest consumer of pesticides in the world (Caldas and Souza, 2000). The use of pesticides has been traditionally controlled either by agricultural or by health institutional frameworks. Only recently the Brazilian water management system has tackled the issue more consistently. Nonetheless, the historical misuse of pesticides might have generated long-term consequences to some water bodies in the Country, especially aquifers, whose depuration capacity is low. Of major concern are herbicides, especially Atrazine, banned from several countries, but still accepted by Brazilian authorities. The main objectives of this paper are to present Atrazine, its associated risks, and its use in Brazil; as well as to present a case study: the Serra Grande aquifer in Tianguá, in the State of Ceará.

2. PESTICIDES AND WATER QUALITY IN BRAZIL

2.1. Water quality management aspects in Brazil

Brazilian new Federal Water Law 9433 was approved in 1997, substituting the one that had ruled the subject since 1931. According to the new Law, water management counts on five instruments: information system, water plans, water use licensing, water tariff and water quality classification. The legislation of the water should be carried out by the Committees, whose executive secretariat should be an Agency. In case of serious conflicts within a Water Basin Committee or among them, the National Water Council is the deliberative body to take decisions.

One of the most important management instruments for the subject of this research is the water quality classification. According to the Regulation of the Brazilian National Environmental Counsel (CONAMA), approved in 2005, non-salty water bodies should be classified, regarding its noblest use, among five classes: special, 1, 2, 3 and 4. In case the Basin Committee has not classified a certain water body, it should meet the requirements of class 2, which does not allow Atrazine concentration higher than 2 µg per litre. Despite the new legislation, governmental action to control water pollution has been constantly delayed and very frequently important water bodies do not meet the requirements of class 2, as imposed by the legislation. An example: Sabiá and Araújo (in press) have monitored 60 km of the Salgado River, South of Ceará, Brazil, covering an area home to almost 500,000 inhabitants. The authors concluded that six important water quality parameters (DO, BOD, N, P, chlorophyll a and coliforms) were in disagreement with the legislation, but no governmental action had been taken whatsoever.

Brazil is one of the world's largest consumers of pesticides, particularly Atrazine (Knight, 1997), one of many herbicides, which are, by their turn, just a fraction of synthetic pesticides used in the country. Pesticides can be replaced by innovative agricultural techniques, biological agents and organic products - and this replacement is both ecologically and commercially attractive. Atrazine is particularly used in corn and sugarcane crops, both important Brazilian cash crops. The reason to oppose pesticides is its high financial, social and environmental costs, which are cumulative with time. Such costs represent damage to lives and to the environment, some irreversible. Although "Brazil possesses the largest river drainage system in the world, the most extensive wetlands" and "the water in Brazil represents an astounding 12% of our planets supply of fresh water" (CNBB, 2004), one should consider that many countries are already facing water scarcity (Loucks et al 2005). This is also the case of Brazil’s semi-arid region, where this research was developed: Araújo et al. (2004) have analyzed four global-changing scenarios in the region, concluding that global warming is expected to worsen its water scarcity. The use of pesticides, then, adds to the responsibility of environmentalists, researchers and decision-makers not only from Brazil, but also from all agricultural lands (see, for instance, Trupp, 1988).

2.2 Impact of use of pesticides in Brazilian agribusiness

It is believed that the wealth generated by polluting economic activities would compensate the society for the losses resulting from pollution. Should intensive use of pesticides boost the productivity of Brazilian agribusiness, it would be profitable, despite the resulting pollution. From the last decades of the 20th century, economical research has been finding that the profits resulting from such pesticide use tend to concentrate in the hands of few, while its associated costs are largely dumped on the local population.

The diagram of Figure 1 shows how the misuse of pesticides spreads losses, even on purely economic terms. Pesticides are petroleum derivatives, and to depend on them is to depend on a non-renewable resource (1 in Figure 1). Intensive pesticide use results in water contamination, which damages the overall population health, resulting in productivity loss and heavy social security expenses (Loucks and van Beek, 2005; see 2 in Figure 1). Intensive pesticide use contaminates the agri-product, which devalues it as an export commodity (3 in Figure 1). Also, as the agri-product is also (frequently) consumed locally, its contamination will also result in more damage to the local population health (2 in Figure 1), with associated loss of productivity and increase of social security expenses. As pesticides unavoidably get carried beyond the point of application, they damage the local environments and wildlife (Caza and Bailey, 2000; see 4 in Figure 1). The losses resulting from this range from proliferation of plagues (from destruction of their local predators) with associated damages to the population health, to business loss from devalued real estate. Last, but not least, one must consider the damage caused to agri-worker's health by pesticides (Maroni et al, 1999; see 5 in Figure 1). Even from a purely economic point of view, productivity losses and social security expenses are strong negative entry against the pesticide-intensive agri-business (Shiva, 2002).

Perhaps the worst impact of the misuse of pesticides on the agribusiness is the addictive effect of using (or misusing) pesticides as if they were some irrefutable solution to pest control problem. In fact, the very "pest control" label exposes the dangerous underlying concept, which does nothing about the disharmony between the cultivation and the global environment. This disharmony may not be abolishable, at least now, but neither should it be ignored, blamed on "misbehaved" species nor reduced to the problem of eliminating such species. Instead, the pest problem should be recognized for what it is, a symptom of the much wider problem of harmonizing the human agrarian activity with the overall surrounding environment. Once that view is adopted, the disharmony can be, if not eliminated, at least minimized, leaving the poisoning approach to be used in emergencies or even not at all (Frey, 1995). Presently, in Brazil, this organic approach is certainly minority. Most agribusiness managers are addicted to the view of pesticide as a "magical bullet" to solve the "pest problem". Like most addictions, this one leads to a vicious circle, where the addicted is compelled to applying more and more to obtain less and less satisfaction (van de Fliert, 1997). As a result, of course, the environment gets more and more loaded with poisons, a horrible parallel to what happens with the body of the human drug addict (Frey, 1995).

Figure 1. Schematic diagram of impacts of pesticides use

Another impact is the reverse side of the damage done to the population by the agribusiness. One should not forget that with misuse of pesticides, the owner of the agribusiness is, however unwittingly, poisoning the population. It stands to reason that this poisoning cannot go on indefinitely without considerable consequences.

Another important impact affects the reputation of the agrarian products. The growing bad name of those is reflected in the growing popularity of the so-called organic products, to be grown free of pesticides. There is also the growing awareness of agrarian products contamination that is reflected in the issuing of more and more restrictive regulations by the countries which import agrarian products (UNEP, 2004). This is an impact that can be felt right in the agribusiness's finances (UNEP 2005). Last, but not least, there is an increasing international conscience that the overall environmental health of the planet is unavoidably dependant on the individual behaviour of each nation, bringing the need for each nation being accountable to the global community for globally consequent transgressions (UNEP, 2005).

3. ATRAZINE

3.1. Description of Atrazine

Atrazine is the industrial denomination for 6-chloro N-ethyl, N'-(1-methylethyl) 1,3,5-Triazine 2,4-diamine (see Figure 2). As the chemical denomination implies, it is a derivative of 1,3,5 Triazine. Triazine derivatives have been used in analytical chemistry (as complexation agents) (Giacomelli et al, 2004) and as pesticides in agriculture. Many other uses, actual and potential, are being researched (Wallick et al, 1969). The versatility of the derivatives of 1,3,5 Triazine ensures that they will interact with a large range of chemical reagents in a wide variety of conditions. This very same versatility makes these triazine derivatives very likely to interfere in potentially ruinous way with the components of biological systems. It is this interference that makes some of them useful as pesticides. Atrazine, for instance, will interact with plastoquinones, inhibiting photosynthesis - what is in the basis of its extensive use as an herbicide. Alas, atrazine will also interfere with the neuropeptide somatostatin (Buttery and Dawson, 1990). Given the importance of somatostatin to vertebrate metabolism (Sheridan et al 2000), that makes it toxic to practically all vertebrates. Also, given the role of somastatin in hormone control (Buttery and Dawson, 1990), this toxicity should be expressed as hormone disruption, as indeed is seen in (Giusi et al., 2006).

The World Health Organization (WHO) sets 2 μg per litre as maximum allowed concentration of Atrazine on water, the same as in the UK, for instance (UNEP 1996), whereas the United States Environmental Protection Agency (EPA) considers that the maximum contaminant level for Atrazine is 3 μg per litre (PAN, 2007). Simply put, for WHO, one kg of Atrazine is enough to destroy the potability of nearly 500,000 m^3 of water.

Many countries have banished Atrazine completely from use. The main objections to Atrazine, however, are founded in its persistence in the ecosystem. Its low solubility on water (70 mg/L), combined with its density (1.269 g/cm3), and relatively high fusion temperature (175oC), result in a rather low availability to the natural degradation agents, both biological and non-biological, to be found on the soil, which results in a slow degradation (Erickson and Lee, 1989; Nakagawa and Andréa, 2000; Wells, 1972).

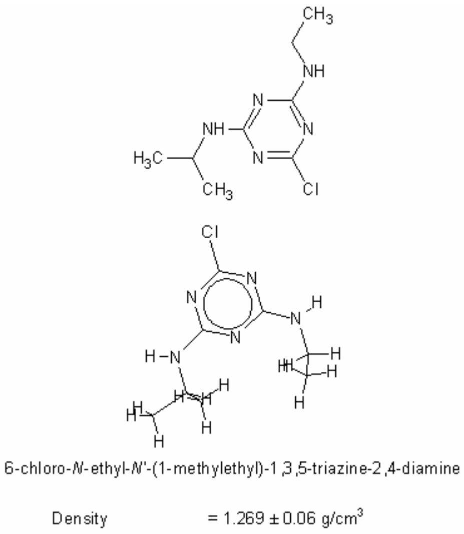

Figure 2. Two representations of the Atrazine molecule

According to the literature, the most used methods for Atrazine determination are as follows: (1) Chromatographic methods: High performance liquid chromatography (Pinto and Jardim, 2000.) Reversed-phase high performance liquid chromatography (Wenheng et al., 1991). It has the advantage of high sensitivity, and the disadvantage of being work intensive and usually time-demanding; (2) voltammetric methods: square wave voltammetry (Santos et al., 2006); with the advantage of being relatively fast and simple, and the disadvantage of being generally less sensitive than chromatography; (3) eletrochemical sensors: Atrazine sensor based on molecularly imprinted polymer-modified gold electrode (Shoji et al., 2003), a new method, potentially fast and sensitive, with the disadvantage of being less well-known.

3.2. Environmental and health risks associated with Atrazine

The compound Atrazine presents physical and chemical properties that favor, in special, the contamination of the underground resources. Its high flow potential that results of its low adsorption potential to organic substances; moderate solubility in water, high half-life in the ground and slow hydrolysis, constitute determining factors for the contamination of aquifers.

The interaction of Atrazine with the environment is tied with its stability and low solubility.

Having become sorbed in the soil, Atrazine's availability to the potential degrading factors lowers considerably, leading to a situation of steady-state equilibrium, in which the "reserve" Atrazine (sorbed in the soil particles) keeps its concentration in the infiltrated water above a certain minimum. Depending on the amount of Atrazine sorbed (that depends on the amount of applied Atrazine, and on the characteristics of the soil itself), this situation can last for years, with the minimal Atrazine concentration in water above tolerable levels. In other words, Atrazine can make the aquifers on a region unfit to drink for years.

Atrazine affects the vertebrate organisms as a hormone disrupter, particularly as a somatostatin represser, which implies that Atrazine poisoning will disturb the mechanisms regulated by somatostatin which include the growth of nervous tissue. As Colborn (2006) details in his article "...most developmental effects cannot be seen at birth or even later in life." The author adds that, "... brain and nervous systems disturbances are expressed in terms of how an individual behaves and functions, which can vary considerably from birth through adulthood". The present systems for determining the safety of pesticides are not sufficiently effective at detecting long term effects of pesticide exposure, focusing instead on immediate effects. There is clear evidence that such long term effects exist and are significant (Colborn, 2006). Besides, one should consider that somatostatin has a distinct masculinizing effect (Hasegawa et al 1992), which indicates why Atrazine (that repress the effects of somatostatin) would exert a feminizing influence over mice and frogs (Hayes et al 2002, Low et al 2001). The pervasiveness of somatostatin in vertebrate metabolism leads to the conclusion that the differences effective toxicity on different vertebrates is partially a result of Atrazine's poor solubility interacting with diverse metabolic rates and different intervals of contact with contaminated matter (particularly food being digested). That would tend to explain why birds are so little affected by Atrazine (Eason and Scanlon, 2002) and why ruminants are so intensely affected, and also explain why young rats are less affected than adult ones (UNEP 1996). Once Atrazine does reach the blood stream, then there should be little diversity of its susceptibility among vertebrates.

4. AQUIFER CONTAMINATION BY ATRAZINE: CASE STUDY TIANGUA

4.1. Description of the study area

The study area is the municipality of Tianguá, which encompasses an area of 854 km^2 and is situated in the northwest of the State of the Ceará. Its main cash crops, irrigated with groundwater, are carrot, tomato, beans and lettuce, with a production of around US$ 12 million a year, exporting to consuming markets in the nearby States. The researched area is part of the Serra Grande aquifer, where the exploitation of groundwater is made mainly through wells, to balance its demand. The municipality of Tianguá is formed by three distinct hydrogeological districts: crystalline bedrock (fissural aquifers), sedimentary bedrock and alluvial deposits. In Tianguá groundwater is extracted through 70 wells, 93% of which located in the sedimentary bedrock. The pesticide use in Tianguá is among the most intense in the State and is object of public health concern. Besides the health problems associated to the use and the manipulation of pesticides, the indiscriminate application of these compounds can result in serious problems of contamination of its aquifer. Approximately 50 compounds, according to data of the Tianguá Secretariat of Health, are applied in its irrigated area, including herbicides, fungicides, insecticides, acaricides and bactericides (Barreto, 2006).

4.2. Material and methods

The Atrazine was chosen to be investigated based on a survey of the types of pesticides used in the researched area, considering the following criteria: commercialized amount, available laboratorial techniques, relevance in literature, and physical and chemical properties of the compound. The selection of the monitored wells was based on the records of the Brazilian Geological Service CPRM and on field investigations. The information collected from the CPRM database was checked by ground-truthing. The sampling of the underground water for Atrazine determination on the monitored wells were made from November 2003 to January 2006, totaling 14 campaigns. The water samples were collected on amber glasses with one liter capacity, prepared with a 24h immersion in Merck detergent solution followed by rinse with deionized water. After the sampling, the glasses were packaged on ice-filled boxes and transported to the laboratory, where they were stored on refrigerator. The procedure adopted on the collection and sample transport followed the standard sampling methodology adopted on the laboratories. Nine wells were investigated for the presence of Atrazine.

The samples were previously subjected to solid phase extraction to interferent elimination and pre-concentration of the compounds, using mini speed reverse phase cartridge

C18/14% as extracting material and a vacuum system Supelco Visiprep. The determination of defensive in the water samples was done with a High Performance Liquid Chromatograph Shimadzu (LC-10AD) equipped with a UV-VIS Diode array (SPD-10AVP) detector, plus two SL-10AVP pumps, operating with two solvents. The separation of the compounds was made after the injection of 20 µL concentrated sample in a Supelco C18 (25 cm x 4.6 mm DI; particles de 5 µm) column in the elution of mobile phase composed of water (A) and acetonitryl (B) in constant flux of 0.8 mL/min with the following programming: from 0 to 2.00 min 50% of B; in 5.00 min 80% of B; in 10.00min 50% of B. The measurement of the analyzed pesticide concentration was done by the external standard method, so that the calibration curve was obtained by the linear regression of the areas of the standard solutions with 0.1; 0.5; 1.0; 5.0 e 10.0 mg/L of Atrazine.

4.3. Results and discussion

The results of the samples collected in the first year (November 2003 to November 2004) showed that, out of the 51 analyzed samples, Atrazine was detected in 39 (76%); and in 25 samples (49%), the detected concentration was higher than the maximum allowed value (2 µg per Liter). The results of the second year sampling (December 2004 to January 2006) corroborated the same trend, i.e., that almost half of the samples (47%, or 17 out of 36 samples) presented higher Atrazine concentration than allowed. In one of the wells, the concentration (maximum value 9.95 $\mu g.L^{-1}$) was in disagreement with the legislation for all the monitored period, whereas in only two of the nine monitored wells Atrazine concentration did not, in average, exceed the maximum allowed value. The map of Figure 3 shows that the highest levels of Atrazine concentration are in the northeastern, southeastern and southwestern portion of the researched area. In the central region (wells 4, 6 and 7), where the urban area is located, Atrazine concentration presented the lowest values in the groundwater.

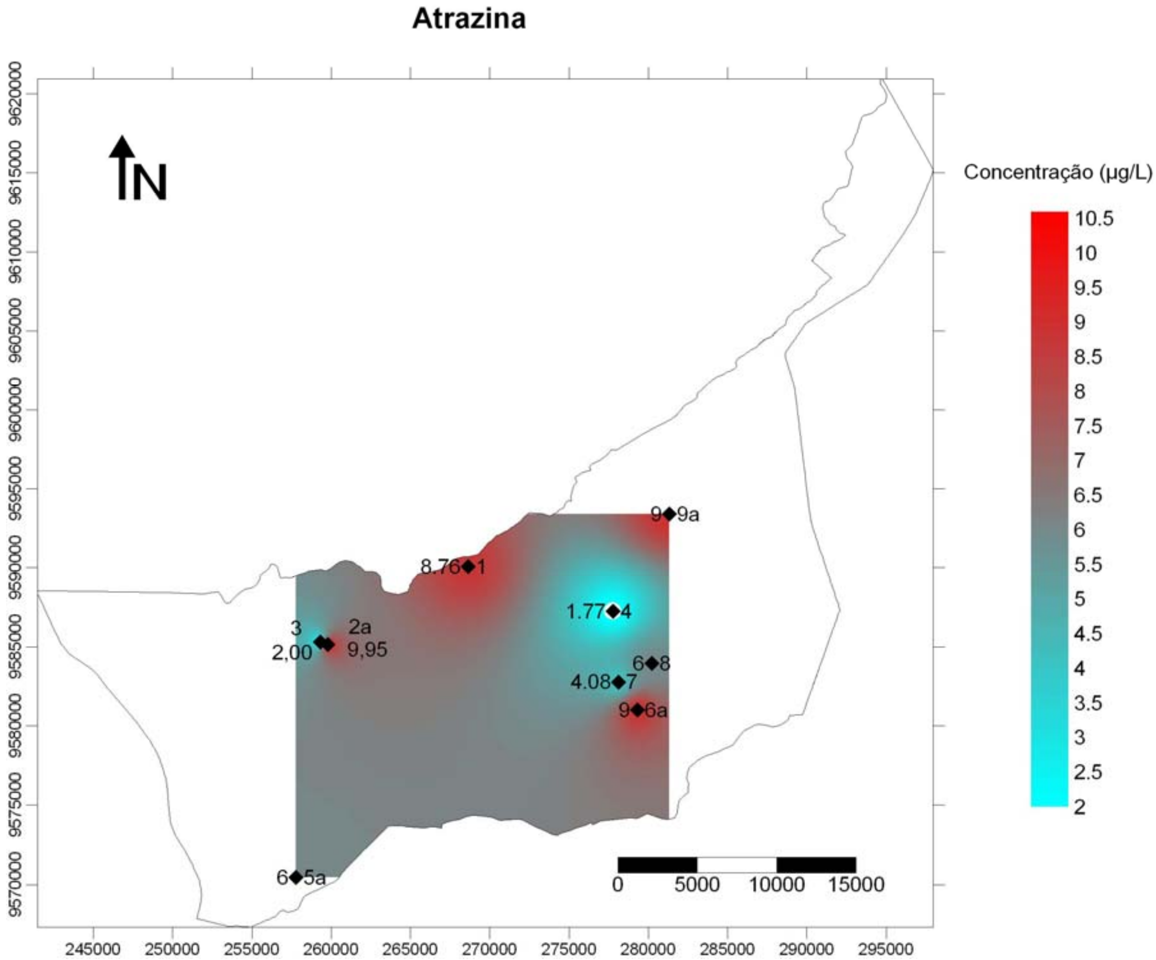

Figure 3. Spatial distribution of the maximum Atrazine concentrations in the wells monitored in Tianguá, Brazil. The black spots represent the location of the monitored wells; the real numbers refer to the maximum Atrazine concentration (µg.L^{-1}); and the integer numbers represent the well identification number.

The presence of Atrazine in the Serra Grande aquifer in Tianguá may have been affected by high rates of application; characteristics of the geology, solubility of the pesticide in water, adsorption to ground particles, persistence and mobility. The contamination of the groundwater of Tianguá by Atrazine shows that pesticides can indeed reduce significantly water availability in semi-arid regions. Such is the case of Brazilian Northeast, where the research area is located. Tianguá functions as an oasis amidst semi-arid municipalities in the State. Nonetheless, the indiscriminate use of pesticides led to the contamination of groundwater, which can have serious impacts in the coming decades. The case of Tianguá should be taken as an example not to be followed and, more, as a challenge to public and societal institutions to recover this relevant environmental resource.

5. CONCLUSIONS

From the research, the following conclusions can be drawn:

(i) Given the difficulties of diagnosis of developmental effects resulting from long term defective growth of nervous tissue, it becomes difficult to connect Atrazine with low-intensity, long term poisoning, which makes statistical analysis on the consequences of pesticide use extremely difficult to compile;

(ii) Given the characteristics of Atrazine toxicity, short-lived, small-bodied animals with faster metabolism are also the least affected by it, which makes them inadequate test subjects to model the long term interaction of Atrazine with the human body;

(iii) It is questionable to assert that the wealth generated by pesticide use would compensate the society for the losses resulting from its pollution, such as water contamination, petroleum dependency, impact on public health; and wildlife damage, among others.

(iv) The groundwater of the case study (Tianguá, Brazil) shows signs of contamination by Atrazine: its presence was found in ¾ of the samples; its concentration was higher than maximum allowed value (2 $\mu g.L^{-1}$) in 48% of the samples; and concentrations up to 10 $\mu g.L^{-1}$ were detected; and

(v) Water contamination by pesticide is already a reality in Northeast Brazil, as shown in the case study. Lack of a firm environmental policy can lead to a considerable decrease in water availability, damaging even more the water balance in a region with expectation of rainfall decrease (Gaiser et al., 2003) and increasing demand (Araújo et al., 2004).

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