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Environment

Chemical Residues in Rice Culture: A Bibliographic Review

Resíduos Químicos na Cultura do Arroz: Uma Revisão Bibliográfica

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ABSTRACT

Rice is the most cultivated cereal in the world and the main component of human food. Due to the particularity that this crop develops in rainfed areas, irrigated and, mainly, flooded, associated with intense agricultural activity. The final product becomes a potential vehicle, directly or indirectly, of innumerable diseases caused by pesticides used during the phase vegetative; absorption of various cations that, in excess, cause disturbances in man and, percolation in the soil carrying elements or chemical compounds that will contaminate rivers, springs and groundwater. In addition to receiving significant amounts of post-harvest pesticides in search of better storage and conservation. Given the above, the objective of this work is to search the literature for reports of contamination of rice in human food, indicating the need for greater control of the product in the final stage of the production chain, that is, in the stages of culture, harvesting, storage and marketing. Therefore, a way to reduce the possibility of causing diseases to humans due to the load of pesticides applied during their production.

Keywords: Contamination; Agrotoxics; Side-effects; Pesticides

RESUMO

O arroz é o cereal mais cultivado no mundo e o principal componente da alimentação humana. Pela particularidade de que essa cultura se desenvolve em áreas de sequeiro, irrigada e, principalmente, inundada, associada à intensa atividade agrícola. O produto final passa a ser veículo em potencial, direta ou indiretamente, de inúmeras doenças causadas por agrotóxicos utilizados durante a fase vegetativa; absorção de vários cátions que, em excesso, causam distúrbios no homem e, percolação no solo carreando elementos ou compostos químicos que irão contaminar rios, mananciais e águas subterrâneas. Além de receber significativas quantidades ainda de pesticidas pós-colheita na busca de melhor armazenamento e conservação. Diante do exposto, o objetivo deste trabalho é buscar na literatura relatos de contaminação do arroz na alimentação humana, indicando a necessidade de maior controle do produto no estágio final da cadeia produtiva, ou seja, nas etapas de cultivo, colheita, estocagem e comercialização. Portanto uma forma de reduzir à possibilidade de provocar doenças ao ser humano em função da carga de agrotóxicos aplicada durante sua produção.

Keywords: Contaminação; Agrotóxicos; Efeitos secundários; Pesticidas

1 INTRODUCTION

As a result of technological development and world demographic growth, especially in recent decades, industrial and agricultural activities have intensified, well as mineral extraction and urbanization, which have caused a considerable increase in the levels of contamination in the environment, especially in relation to soil - water, from a productive perspective.

Rice is the most produced cereal in the world and belongs to the *Oryza* genus (SOUZA, 2012), which has about 20 known species worldwide (FIORAVANTI, 2016). In the world scenario, it is characterized as the third largest grain crop (WALTER, 2014).

Among other species, *Oryza sativa L*, which belongs to the vast majority of rice varieties commercially cultivated in the world, according to Lourenço (2009), originated in southwest Asia. It is a plant belonging to the grass family and is responsible for feeding half of the human population.

In Brazil, according to data from a survey by the National Supply Company (CONAB, 2020), the area planted with rice in the 2020/2021 harvest reached 1.7 million hectares, whose expected production, added upland to irrigated rice, should remain at 11 million tons.

Looking at the species, the three most important subspecies, according to Weber (2012), are: (i) the *indica*, with long and fine grains, cultivated in warmer regions, such as southwestern Asia itself and tropical regions of America and from Africa; (ii) *japonica*, with short, rounded grains, the best adapted to colder regions, such as Korea, Japan and northern China; and, (iii) *javanica*, with long and thick grains.

As described by Yoshida (1981), and corroborated by Santiago et al. (2013), the rice plant can take 3 to 6 months from planting to maturity, depending on the variety and environment. However, most varieties have a cycle of 110 to 150 days. And that, regardless of the subspecies, as verified by Zilio (2009), rice is present in the daily menu of Brazilian workers in an average amount of 350 grams at each meal.

Cereal husks represent approximately 20% of the dry mass of the harvest, being an abundant lignocellulosic residue. The husk covers and protects the grain during its growth, and consists of layers, which comprise the outer epidermis, coated with a thick cuticle layer of highly silicified cells (SOUZA, 2018). Another relevant point of the residue is the superior calorific value (PCS) equal to 0.89 Mtoe, where the unit is represented in mega ton of oil equivalent (HORST, 2013). The chemical composition of the rice husk can be seen in Table 1.

Table 1 – Chemical composition of lignocellulosic biomass for rice crops

Residue	**Chemical composition of rice husks in (%)**						
	Celulose	**hemicellulose**	**lignin**	**extractives**	**Gray**	**protein**	**Total**
Casca de arroz	34,0	13,0	29,0	3,0	17,0	2,0	98,0

Source: Hickert (2010)

Thus, the objective of this study was to search the scientific literature for reports of contamination by chemical elements or compounds, using rice as a vehicle, when used in human food.

2 METHODOLOGY

For the classification of this study, according to the taxonomy proposed by Gil (2017) and Vergara (2003), there are two categories for the methodology:

regarding the ends and regarding the means. Thus, as to the ends, the research is descriptive; and, as for the means, it is a bibliographic and documental research.

Thus, the present work consisted of an intense bibliographical survey, approaching rice as an essential food for the population all over the world and as a vehicle for contamination of chemical elements or compounds (organic and/or inorganic) resulting from agricultural management, cultural treatments and post-harvest treatments that the crop is subjected to, directly or indirectly affecting the human being.

As a database, the consultation of works published in various scientific journals and/or available on the internet (SILVEIRA *et al.* 2011) was used, relating the issue of pesticide application in the rice production chain, according to Lacerda *et al.* (2012).

The established criteria can be the same used in Treinta's (2011) research, where the articles were evaluated for relevance in relation to four main axes: articles, authors, journals and theme.

Finally, according to Treinta *et al.* (2013), it should be remembered that the bibliographic research process must be continuous and dynamic, where researchers must always be aware of new possibilities and natural evolutions of science. So the bibliographic search will be very consistent.

3 ANALYSIS OF RESULTS

The results obtained allowed the prioritization of the researcher's reading to be carried out with a guarantee that the articles were firstly aligned with the theme and that they met the quality criteria presented by the academic society. Thus, they are listed in four themes: (3.1) Contaminants via soil / pesticides; (3.2) Contamination by chemical elements; (3.3) Characteristics of the rice crop; and, (3.4) Agrochemicals in rice culture.

3.1 Contaminants via soil / pesticides

Contamination comes from anthropogenic activity or from accumulation resulting from biogeochemical processes occurring in nature (SANTANA, 2017).

The amount of agrochemicals that reach water resources varies significantly between regions and depends on the dosage, the chemical characteristics of the product and the environmental conditions during application (HUBER *et al.* 2000; RIBEIRO *et al.* 2007; OLIVEIRA, 2019).

Polluted soil (ACCIOLY and SIQUEIRA, 2000; MOREIRA and SIQUEIRA, 2006), is that which contains concentrations of a certain contaminant that affect the biotic components of the ecosystem, compromising the functionality and sustainability of the entire environment considered.

Agricultural pesticides, such as pesticides, are generally applied in large quantities, over large areas, characterized by their persistence in the environment, generating serious problems in the quality of surface and groundwater (BAIRD and CANN, 2011), in addition to resulting in the toxicity of many non-target species (CARR and CHAMBERS, 1996; MACHADO, 2016). Any commonly used pesticide falls into two main groups: organophosphate compounds and organochlorine compounds (SANTOS *et al.* 2007).

Currently, according to Maluf and Flexor (2017), it is estimated that approximately 85% of synthetic pesticides used in the world are destined for the agricultural sector. As presented by INCA (2019), the assessment of the degree of soil contamination by pesticides, that is, agrochemicals, chemical pesticides, agricultural pesticides or pesticides, is of high relevance, due to the transfer of these contaminants to food, via absorption by the roots or aerial system.

As presented by Carvalho (2000), he states that the most persistent compounds, such as organochlorine insecticides, are deposited in soils as well as in water, and their residues progressively accumulate in food chains. However, according to Vinhal and Soares (2018), organophosphate compounds are responsible for most cases of poisoning in the population.

Also considering organophosphates, Babu *et al.* (2003) and Royte (2021), state that chemical pesticides belonging to this group were and still continue to be, also, widely used in agricultural production. Its residues can remain present in the soil and can accumulate in vegetables, especially cereals and many of those used for human consumption, including rice, potentially causing health problems for consumers.

According to D'Amato *et al.* (2002), samples of the pesticides DDT and HCH (their isomers and metabolites) were analyzed in soil samples and in different parts of rice. As described by Babu *et al.* (2003) concluded that all four isomers were present, including in rice grains.

According to Dimond and Owen (1996), the DDT used in the USA, in the 50s of the 20th century, to control forest pests, is still detected in quantities of 1.6 mg.kg-1 of soil in the 1 to 6 cm layer.

Thus, its high persistence can be observed, since certain xenobiotics have been constituted for continued detection in the environment and for the existence of areas contaminated with these compounds or metabolites and their degradation (COSTA et al. 2008).

Depending on the application rate and biodegradation, the accumulation of pesticides in the soil can reach, under certain circumstances, 500 $kg.ha^{-1}$ (PISQ, 2008).

3.2 Contamination by chemical elements

According to Nellessen and Fletcher (1993), Oliveira (2008) and Schmidt et al. (2009), among others, the heavy metals commonly associated with toxicity or pollution are As (Arsenic), Cd (Cadmium), Co (Cobalt), Cr (Chrome), Cu (Copper), Pb (Lead), Hg (Mercury), Mo (Molybdenum), Ni (Nickel), Se (Selenium) and Zn

(Zinc), where it can be observed that Mo, Cu, Zn and Se are micronutrients and are commonly added during the development stage of the culture and it can be present in substances such as organometallics, which make up the structure of various agrochemicals.

Once released into the soil solution, according to Lima (2013), metals can be leached underground, reaching the water table, with serious consequences for humans (either by drinking, or by consuming contaminated fish or this water is still used for irrigation purposes). Another route of these metals can also cause toxicity to plants, either through the absorption process or mass flow of soil organisms or being adsorbed on clays and complexed to organic matter, representing a potential polluting source (CHARLESWORTH *et al.* 2003; LOPES *et al.* 2006; SILVA *et al*. 2007).

Specifically regarding the contamination of rice production water via fish, Copatti et al. (2009), demonstrate that pesticides leave residues in the water used for rice culture, which can even come into contact with several nearby water systems, affecting aquatic life, especially fish, as they act as organisms at the top of the food chain, as they are supplied by an intricate lower trophic network of various animal or plant organisms that serve as food subsidies. In addition, fish (as well as other aquatic life beings) serve as food for human populations, and may serve as an indirect route to such contaminants.

Vargas (2010) defines trace elements as those chemical elements that occur in natural systems and are disturbed by the unfriendly presence of human beings, that is, an anthropic process, even in small quantities and which, when present in sufficient concentrations, is oxidized or from their ionic speciation, are toxic to living human, animal and plant organisms.

As described by Yaron *et al.* (1996) and Silva *et al.* (2006), one of the main sources of pollution and contamination by trace elements, via soil, comes from the use of animal waste, whether in solid or liquid states, in addition to disposal, that is, application of raw effluent in cultivated areas.

For a deeper understanding of the relationships and interactions of these trace elements, the Table of the effects of trace elements on plant and animal nutrition is transcribed Table 2.

Table 2 – Effects of trace elements on plant and animal nutrition

Element	**Essential or beneficial to**		**potentially toxic to**		**Comments**
	Plants	**Animals**	**Plants**	**Animals**	
Ag	No	No		Yes	
As	No	Yes	Yes	Yes	Phytotoxic before animal toxicity. May be carcinogenic
B	Yes	No	Yes	-	Narrow margin, especially on plants
Ba	No	Possible	-	-	Insoluble; relatively non-toxic.
Be	No	No	Yes	Yes	Carcinogenic
Bi	No	No	Yes	Yes	Relatively non-toxic
Cd	No	No	Yes	Yes	Narrow margin. Adds to the food chain. Carcinogenic. Itai-itai disease
Co	Yes	Yes	Yes	Yes	Relatively non-toxic. Carcinogenic
Cr	No	Yes	Yes	-	Very toxic. Carcinogenic
Cu	Yes	Yes	Yes	-	Easily complexed in soil. Narrow margin for plants
F	No	Yes	Yes	-	Accumulatively toxic to plants and animals
Hg	No	No		Yes	Water accumulation. Minamate disease
Mn	Yes	Yes	<pH 5	-	Wide margin. Toxic in acidic soils
Mo	Yes	Yes	-	5-20 ppm	Highly enriched in plants
Ni	No	Yes	Yes	Yes	Very mobile in plants. Carcinogenic
Pb	No	No	yes	yes	Aerial dispersion and deposited on the surface. poisonously cumulative
Sb	No	No	-	Yes	Insoluble. Relatively non-toxic
Sc	Yes	Yes	Yes	4 ppm	Interacts with other metallic trace elements
Sn	No	Yes	-	Yes	Relatively non-toxic
Ti	No	Possible	-	-	Insoluble. Probably carcinogenic
Tl	No	No	-	Yes	Very mobile in plants
V	Yes	Yes	Yes	Yes	Highly toxic to animals. Carcinogenic
W	No	No	-	-	Very mobile in plants
Zn	Yes	Yes	-	-	Easily complexed in soils. Relatively non-toxic

Source: Adriano (1986)

The phytoavailability of nutrients and other potentially toxic elements, as described by Berton (2002) and Villanueva *et al.* (2012), mainly from soils that receive urban-industrial waste, that is, composed of garbage and sewage, as well as hydroponic solutions, agricultural soil substrates and ecosystems in general, has been shown to be highly correlated with chemical species of the elements present in solution, according to their ionic speciation for certain pH values.

The US Environmental Protection Agency (EPA-US, 2020) considers the metal content that causes a 50% reduction in plant growth to be toxic, while in Switzerland only 25% is considered to have a drop in growth (CUNHA et al. 2008).

An important ecological modification is introduced when rice is cultivated in flooded soils where, according to Evald (2016), it needs ethanol in the process to create an oxidative zone, obtained by cell elongation, to develop the air parenchyma, aiming for respiration or oxygen demand in the root system. The essential chemical element both for this cell elongation as well as for the growth hormone synthesis, activator of the AIA enzyme, that is, the idoleacetic acid, which is very sensitive to the oxidation process, is zinc (CLARKSON and HANSON, 1980; CASTRO *et al.* 2012).

3.3 Characteristics of the rice crop

In addition to climatic variables caused by latitude or altitude, rice is now cultivated all over the world. It is cultivated in Slovakia at 50ºN, in Uruguay at 35ºS, in Kerala, India, at sea level and in Nepal, at more than 2000 m altitude (FAO, 2021; EMBRAPA, 2016).

However, about 90% of all rice produced in the world is located in Asia and of this, the vast majority is cultivated under flooded areas, naturally or artificially, according to Prochnow (2002), causing a continuous flow of percolation of water, nutrients and pesticides to deeper layers of soil beyond the water table. When analyzing only the nitrate parameter, it appears that high concentrations of this compound in water from irrigated rice fields and used for drinking can cause methemoglobinemia, the "blue baby" syndrome in children and stomach cancer in adults (BOUMAN *et al.* 2002; NASCIMENTO *et al.* 2008).

However, in the tropics, for example, as verified by Santos et al. (2011), 500 to 600 diseases linked to rice culture are known, while in temperate zones, 54 related diseases are known, basically caused by fungi (PRABHU *et al.* 2006).

As described by Lazzari (2001), foreign matter, impurities and broken grain affect the quality of the product, as in addition to reducing the value of the grain, they increase the risk of fungi and insect growth and interfere with conservation during storage. As described by Lins *et al.* (2014), they state that the process of grain infection by fungi begins in the field, at maturation and continues during harvesting, drying, storage, transport and processing.

As described by Ferreira (2002), rice that is in a poor state of conservation, including fermentation and mold processes, is considered unfit for consumption; strange odor; substances harmful to health; content of mycotoxins, fungicides and herbicides above the limit established by legislation.

Another relevant aspect related to rice, since its association is closely linked to human consumption as food, is its potential for phytoremediation (KRAEMER, 2008). According to a more current definition, bioremediation is the use of living organisms or their derivatives (eg enzymes) to degrade polluting compounds (Van DILLEWIJN *et al.* 2009).

Phytoremediation is a bioremediation strategy that consists of procedures that involve the use of plants and their associated microbiota and soil softeners, in addition to agronomic practices that, according to Huang et al. (2005), if applied together, remove, immobilize or render the contaminants harmless to the ecosystem. Its functional conception is based on plant physiology, soil biochemistry and contaminant chemistry, according to several authors, including Nyer and Gatliff (1996), Hinchman *et al.* (1997) and Marques *et al.* (2011).

In this reasoning, according to Pires et al. (2003), rice is effective as a plant used in the phytoremediation of contaminated soils for the removal of Selenium (Se).

C4 grasses have a lower amount of chlorophyll molecules per chloroplast, especially chlorophyll b, as they develop well in light saturated environments, not needing to invest energy in the production of energy-collecting pigments (PAULILO *et al.* 2015). The same result does not apply to rice, where there is a decrease in the levels of chlorophyll a and b according to the increase in the dose of Pb, with the amount of 360 $mg.kg^{-1}$ having the lowest value related to chlorophyll a and b (IRINEU *et al.* 2016).

Phytoremediation techniques are based on the use of plants to remove, stabilize and degrade contaminants in soil and sediment (RIBEIRO, 2013).

Also considering the existence of specific accumulator species for application as phytoremediation in different biomes, being a low-cost alternative with the use of green technology that does not impact the environment (TAVARES, 2009).

3.4 Agrochemicals in rice crops

Agrochemicals, such as insecticides, are most commonly used in the culture of cotton, rice, fruits and vegetables; 70% of the demand for herbicides falls on cereals, especially corn, wheat, barley and rice (AGROEMDIA, 2020). Small grain cereals, such as (wheat and barley), corn, rice and cotton, are responsible for use in world of half of the phytosanitary products (ELIAS *et al.* 2017).

ANVISA (2017) found trifluralin herbicide residue in a rice sample in an amount three times greater than the limit allowed by legislation. This herbicide causes (or prudently may cause) mucosal irritation. However, according to Santos *et al.* (2021), according to international bodies such as (EPA, DCEA and others), trifluralin [2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)-benzamine] is considered among the 10 most detrimental to the environment and human beings on all 14 lists of harmful substances promoted by government agencies and NGOs around the world.

The IDEC (2000) in another analysis, this time fungal, found in three samples of rice from the most commercialized brands, residues of folpet [N-(trichloromethylthio)-phthalimine], a fungicide not allowed for this crop. This fungicide is suspected to be carcinogenic.

As reported by Kim and Smith (2000), they claim that more than 3,500 tons of organochlorine pesticides were released on rice cultivated soils in South Korea between 1946 and 1980. And that, due to their chemical properties, according to Flores *et al.* (2004), more than twenty years after the last applications, residues of these pesticides are still detected today in high quantities.

Several authors, such as Newsome *et al.* (1998); Schade and Heinzow (1998) and Silva (2009), among many others, state that due to this high resistance to degradation, organochlorines contaminate some agricultural products until the stage of animal and human consumption, among cultures, mainly rice.

In rice culture, just like any other, pesticides can directly affect the plant and, consequently, the fruit that will be consumed, not least the industrial processing received by the rice, making it essential to analyze the active principles, that is, the residues of agrochemicals in grains as a way to ensure food safety and quality (JARDIM *et al.* 2009).

Pesticides have certain physicochemical characteristics, such as solubility, surface chemistry, ease of reacting with plant media and persistence in the plant, according to active ingredients found in rice samples after analysis (ANVISA, 2020), considering maximum residue limit (LMR), as shown in Table 3.

Table 3 – Presence of active principles in samples analyzed by the LMR, established by the Health Surveillance Agency (ANVISA, 2020), by agrochemicals in rice crops

	Active principle (*)	LMR (mg.Kg^{-1})
1	2,4-D acid	0,2
2	acetamiprid	0,3
3	Azoxystrobin	0,7
4	beta-cypermethrin	0,3
5	bifenthrin	0,7
6	Carbendozin	0,5
7	Carbofuran	0,2
8	Carbosulfan	0,5
9	Cyproconazole	0,4
10	Chlorothalonil	2,0
11	Deltamethrin	1,0
12	Diphenoconazole	1,0
13	dithiocarbamates	3,0
14	esfenvalerate	1,0
15	Etofemprox	3,0
16	lambda-cyhalothrin	1,0
17	Melathion	8,0
18	Myclobutanil	0,5
19	Pyrimphoz-methyl	5,0
20	tetraconazole	1,0
21	thiamethoxam	1,0

(*) Also indicated in the literature as an active ingredient
Source: authors (2021)

The presence of certain pesticide residues in industrialized rice has been a matter of concern on the part of consumers and, consequently, there has been an increase in demand for products free of pesticide residues, such as products marketed with the slogan "Organic product" (IPARDES, 2007; MELON, 2007).

Faced with a great challenge in the search for technologies to promote the degradation of agrochemical residues in food, it is possible to verify the use of technologies that include ultra-violet (UV) radiation, action of oxidizing agents, such as the use of hydrogen peroxide and gas ozone. Ozone gas has been presented as an alternative due to its oxidative action and ease of obtainment, as described by Ikeura *et al.* (2011).

4 CONCLUSION

It is concluded that, as rice is consumed worldwide, it becomes a vehicle for the contamination of chemical elements or compounds, harmful to human beings and, for this, it must be better monitored and there is a greater level of control, determination of analysis and performance of responsible government agencies so that such effects are minimized.

As a vegetable, rice is subject to carrying chemical compounds inherent to the application of pesticides (herbicides, fungicides, insecticides), that is, agrochemicals for the rational development of production.

Specifically because a large part of the amount produced comes from flooded areas, with an absence or amount of oxygen below normal in the soil, rice absorbs reduced cations by mass flow where, in excess, these elements can be toxic to humans when consumed.

Furthermore, rice already as a product, post-harvest, is subject to contamination by agrochemicals in order to better adapt it to storage, with a view to its commercialization in a timely manner from an economic perspective.

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