Pesticides: yesterday, today and tomorrow

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Abstrakt

Ochrana vody ako strategickej suroviny štátu a nášho spoločného národného bohatstva a napĺňanie požiadaviek vodohospodárskej politiky na dosiahnutie environmentálnych cieľov, t. j. dosiahnutie dobrého stavu vôd, musia byť kontinuálne zabezpečované na všetkých úrovniach spoločnosti, naprieč všetkými odvetviami národného hospodárstva, ako aj jednotlivými občanmi Slovenskej republiky, a to ako prioritná súčasť každého infraštruktúrneho projektu, každej aktivity a činnosti, ktorá má priamy alebo nepriamy vplyv na útvary povrchových vôd alebo podzemných vôd.

Od polovice 50. rokov 20. storočia používanie pesticídov každý rok nepretržite stúpa, takže celkové množstvo používaných účinných zložiek pesticídov sa teraz pohybuje na hodnote okolo 2,5 milióna kilogramov ročne. Pesticídy spolu s hnojivami zohrávajú v poľnohospodárstve ústrednú úlohu a prispievajú k zvyšovaniu celosvetovej výroby potravín, majú však aj závažný negatívny vplyv na životné prostredie. Nadmerné používanie pesticídov môže viesť k ničeniu biodiverzity. Mnoho vtákov, vodných organizmov a zvierat je ohrozených škodlivými dopadmi nadmerného používania pesticídov.

Táto práca sa venuje štúdiu toxicity vybraných pesticídov z vôd (povrchových, podzemných a odpadových), kde sú prítomné v nízkych koncentráciách. Medzi vybrané pesticídy patria organochlórovaný pesticíd lindán, chlóracetoanilidový herbicíd alachlór a chlórtriazínový herbicíd atrazín. Všetky tieto látky sú na zozname sledovaných prioritných látok v Smernici 2013/39/EÚ. Ich negatívny dopad na životné prostredie (perzistentné a biologicky nedegradovateľné látky) a ľudské zdravie je dokumentovaný v mnohých prácach autorov celého sveta. Tieto látky sú karcinogény, mutagény, a tiež sa radia k endokrinným disruptorom a rizikovým faktorom životného prostredia (epidemiologické štúdie porúch autistického spektra).

Annotation

Every year, more than 200 000 kg of pesticides leak out into European environment. These chemicals threaten not only pests, but also useful organisms and human health, mainly children. This research is focused on theoretical aspects of pesticide problematics, their use, environmental impact and means of their removal. From a wide range of compounds, this work further focuses on atrazine, from the group of organochlorine pesticides.

Key words

pesticide, atrazine, toxicity

Anotácia

Každý rok uniká do životného prostredia Európy viac ako 200 000 kg pesticídov. Tieto chemikálie ohrozujú nie len „škodcov“, ale aj užitočné organizmy a zdravie ľudí, dospelých a predovšetkým detí. Táto práca je zameraná na teoretickú rešerš problematiky pesticídov, ich používania, dopadu na životné prostredie a možností ich odstraňovania. Zo širokej škály látok sa práca ďalej sústreďuje na látku atrazín, zo skupiny chlórovaných pesticídov.

Kľúčové slová

pesticídy, atrazín, toxicita

1 Pesticides – general overview

Pesticides are substances intended for pest and weed control. The term pesticide includes the following: herbicides, insecticides (which may include insect growth regulators, termiticides, etc.) nematicides, molluscicides, piscicides, avicides, rodenticides, bactericides, insect repellents, animal repellents, antimicrobials and fungicides. The most common of these are herbicides, which account for about 80% of the total pesticides. Most pesticides are intended to be plant protection products that generally protect plants from weeds, fungi or insects (Randall et al., 2014).
Pesticides can be classified according to the target organism (e.g. herbicides, insecticides, fungicides, rodenticides and pediculicides), chemical structure (e.g. organic, inorganic, synthetic or biological), and phase (e.g. gaseous (fumigant)). Biopesticides include microbial pesticides and biochemical pesticides. Pesticides derived from plants or "botanics" develop rapidly. These include pyrethroids, rotenoids, nicotinoids, and a fourth group containing strychnine and scilliroid (Gilden et al., 2010).
Important insecticidal families include organochlorinated pesticides, organophosphates and carbamates. Organochlorinated hydrocarbons (e.g. DDT) can be separated into dichlorodiphenylethanes, cyclodiene compounds and other related compounds. They work by disrupting the sodium and potassium balance in the nerve fiber, resulting in continuous transmission of impulses. Their toxicity varies widely but they have been phased out due to their persistence and bioaccumulation potential in organisms (US EPA, 2017). Organophosphates and carbamates have largely replaced organochlorinated pesticides. Both act by inhibiting the enzyme acetylcholine esterase, allowing acetylcholine to continuously transmit nerve impulses, manifested by symptoms such as weakness or paralysis. Organophosphates are toxic to vertebrate animals and in some cases have been replaced by less toxic carbamates.

2 Pesticides – toxicity

Every year, more than 200,000 kg of pesticides are released into Europe's environment. These chemicals endanger not only 'pests' but also beneficial organisms and the health of humans, adults and especially children. Evidence of the harmfulness of pesticides to human health is increasing more and more. Recent results presented at the Annual Conference of the European Forum on Respiratory Diseases (European Respiratory Society, 2007) have shown that contact with pesticides increases the risk of respiratory diseases. A European study on Parkinson's disease shows that even small doses of pesticides can increase the risk of the disease. Canadian scientists have demonstrated the link between pesticides and cancer, including leukaemia and malignant lymphoma not classified as Hodgkin's disease. Although the EU has limits on pesticide residues in food and water, their definition does not yet consider important facts: the long-term impact and combination effect of several chemicals and stress factors that are common in today's food and everyday life (www.cepta.sk). Fig. 1 illustrates the consumption of pesticides in Slovakia compared to some other countries.

Important factors that affect the potential of a pesticide to cause water pollution are: the solubility of the pesticide; distance of application from water surface, resp. stream; the weather; soil type; the slope; presence and density of crop; method and technique of application of agrochemicals (Pál et al., 2011).

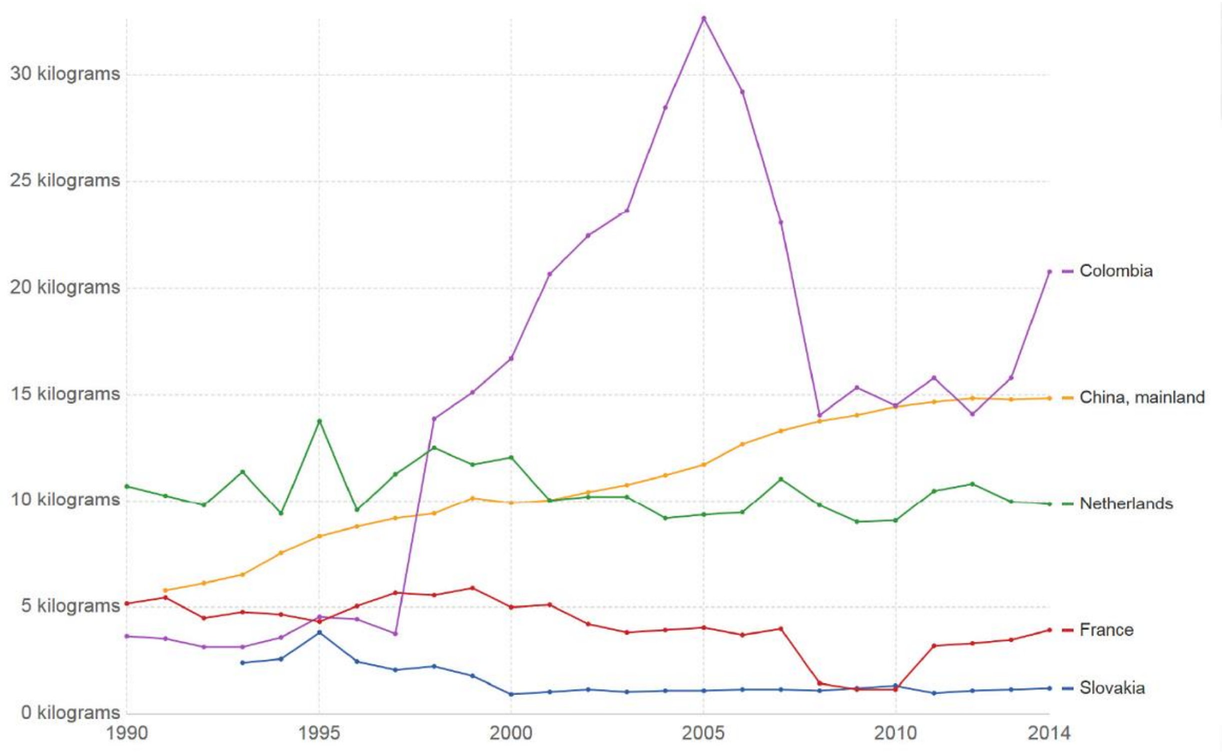

Figure 1: Average amount of pesticides used per hectare of agricultural land. Comparison of different countries of the world (Patschová et al., 2008).

Ecotoxicity

Pesticides cause serious damage to aquatic ecosystems. More than 98% of applied insecticides and 95% of herbicides do not reach the target pest but go further and damage the environment, aquatic ecosystems, air, soil and non-target organisms often pollinators, useful birds, soil organisms and the like. Pests can create resistance to reused pesticides. Therefore, either the dose should be increased (with all the negative effects) or a new, often more aggressive product should be administered. Perhaps the best-known example is the repeated use of the herbicide glyphosphate on GMO soy (Roundup ready soy), the consequent formation of so-called super weed, herbicide dose increase, soil, groundwater and surface water contamination, workers' health damage, etc. The washing of the pesticide from the soil surface during heavy rainfall most often causes the death of aquatic organisms, including fish in adjacent river basins. Herbicides cause the dying of aquatic plants, which subsequently rot and thus remove oxygen from the water, which in turn leads to the death of more sensitive fish. As in humans, the affected non-target organisms also affect life and health, the hormonal system, fertility, leaving nests and chicks, and so on. Pesticides naturally also affect the food chain of the affected ecosystem, either directly through a change in animal behaviour or through a change in the availability of its food - e.g. by eliminating zoo plankton in water as food for fish fry, or by destroying insects in the air, which is food for selected bird species (Pál et al., 2011).

Endocrine disruptors

As defined by the World Health Organization (WHO), endocrine disruptors (EDs) are exogenous substances that alter the function of the endocrine system, with adverse effects on the health of the intact organism, its progeny or (sub) populations (WHO / IPCS, 2002). A more detailed definition is provided by the Environmental Protection Agency (EPA): Endocrine disruptors are substances that affect the synthesis, secretion, transport, binding, effect or breakdown of natural hormones that are responsible for homeostasis, reproduction, development and behaviour in the body (US EPA, 1997).

The endocrine-related group of chemicals is constantly expanding from year to year as new substances are investigated, and therefore the exact number is unknown. In his 1999 paper, N. Salgueiro-González lists more than 680 labelled and banned endocrine disruptors. In 2013, approximately 800 chemicals were known or suspected to interfere with hormone synthesis and conversion, hormone receptor activity, and thus the entire endocrine system (Bergmann et al., 2013). Endocrine disruptors, such as exogenous estrogens, mimic the function and response of natural hormones as they are realized by the same cellular mechanisms.

The presence of endocrine disruptors in the environment, even at low concentrations, has a significant impact on living organisms, ranging from metabolic and reproductive disorders to mutagenic, carcinogenic and teratogenic effects. Sources of these substances are contained in a large number of daily use products such as food, plastic bottles, metal food packaging, toys, cosmetics, cleaning agents, pharmaceuticals, pesticides and industrial products. This suggests that exposure to EDs is permanent (Kujalova et al., 2007).

Endocrine disruptors, as persistent substances, occur in virtually all environmental compartments, in the atmosphere, in marine and inland waters, in soil, sediments and vegetation. ED distribution occurs not only at environmental level, but also within more distant regions of the Earth's surface. Such global residue transport has been observed under Arctic conditions (Annamalai et al., 2015).

Atrazine, one of the most commonly used herbicides in the world, affects the reproductive system of various animal species, e.g. adult and larval amphibians, young fish, alligators and peripubertal male and female rats. The mechanism of endocrine effects of atrazine is not yet described, but it is believed that atrazine exhibits estrogenic activity in ovarian cancer cells via the G-protein receptor 30 (Kucka et al., 2012).

Lindane, as a hormone-active organochlorinated pesticide, is subject to high regulatory pressures worldwide. On 13 July 2000, the EU regulatory office voted on banning the agricultural use of lindane in Europe. Lindane, however, is still used in some other products. Lindane, one of the persistent pollutants (POPs), was also present in breast milk. The estrogenic properties of lindane have been demonstrated in several systems, e.g. in the production of vitellogenin (egg yolk protein) and zonaradiata (egg shell protein), and in primary hepatocytes (liver cells) of Atlantic salmon. Lindane damages human sperm at very low concentrations (www.lindane.org).

Environmental risk factors

The increasing incidence of autism suggests a significant environmental impact on the etiology of autism spectrum disorders (ASD). For more than a century, it has been believed that autism is a genetic and hereditary disease. Many misinterpretations, methodological misrepresentations and erroneous approximations, not to mention overstated media reports, have been discovered by thoroughly reviewing the results and claims that support the strong genetic origin of autism. Hallmayer et al. (Hallmayer et al., 2011) conducted one of the largest studies of twins (192 pairs) and saw that a high degree of ASD risk was due to environmental factors and a lower risk was due to heredity or genetics (Sealey et al., 2016). Epidemiological research has suggested many possible environmental triggers and the genetics of ASD-associated genes. In Carter and Blizard paper (2016a) 206 autism susceptibility genes were selected from the Autworks database and over a million different interactions between these genes and chemicals associated with ASD etiology were examined. Many investigated substances such as: benzo (a) pyrene, heavy metals, valproate, acetaminophen, SSRI, cocaine, bisphenol A, phthalates, polyhalogenated biphenyls, flame retardants, gasoline components, terbutaline, oxytocin showed a high degree of affinity for ASD-associated genes, and endogenous substances such as retinoids, sex steroids, thyroxine, melatonin, folate, dopamine and serotonin. Among the endocrine disruptors, many have selectively targeted ASD-associated genes e.g. parkvat, atrazine, and other pesticides whose effects on ASD genes have not been studied, as well as many compounds used in food, cosmetics and household products (tretinoin, soy phytoestrogens, titanium dioxide, aspartame and sodium fluoride). Autistic polymorphisms affect sensitivity to some of these substances, while the same genes play an important role in the functionality and control of biological barriers (Carter, 2016b). Pesticides, heavy metals and pollutants also damage respiratory barriers (cilia, algae) that are regulated by sex steroids and sweet / bitter taste receptors. Some examples of mechanisms of environmental risk factors (pesticides) in the body are given in Tab. 1.

Table 1: Mechanisms by which gestational exposure to certain class of pesticides may induce observed pathophysiologic symptoms of autism (Shelton et al., 2012)

Mechanism of action/ route to autism pathophysiology	**Observed effects**	**Pesticides**
Developmental neurotoxicity		
Alternation of excitation/ inhibition mechanisms	Decrease in GABA receptors Inhibition of GABA Inhibition of AChE	dieldrin OCPs OPs
Mitochondrial dysfunstion		
Oxidative stress	Apoptosis of neuronal cells Inhibition of mitochondrial respiration	dichlorovos methoxychlor
Immune toxicity		
Immunosupression Neuroinflammation	Decreased DTH and antibody production Activation of human fetal astrocytes, increased expression of proinflammatory cytokines	atrazine cyfluthrin, chlorpyrifos
Maternal hypothyroxinemia		
Insufficient gestational thyroid hormones	Decreased T_4, inhibition of T_4 deiodination to T_3, prevention of iodine uptake	acetochlor, alachlor, 2,4-D, endosulfan, aminotriazole

3 Selected pesticide – atrazine

"What is the use of a house if you haven't got a tolerable planet to put it on?"
Henry David Thoreau

Water is an essential natural resource for man and all ecosystems. The water crisis that already exists is aggravated by increasing consumption and wastage of water, the irregular distribution of water as a component of the environment, climate change and the constant increase in anthropogenic activities. Agriculture is one of the important sources of micropollutants, in the form of pesticides, in waters. The continuous but not yet described effects of these micropollutants can gradually accumulate, leading to irreversible changes in ecosystems, and on human health. (Sousa et al., 2018). For these reasons, it is important to address micropollutants and to develop new water purification procedures. Fig. 2 lists the number of scientific articles dealing with the issue of pollution in different types of water since 2012 by substances mentioned in Directive 2013/39/EU.

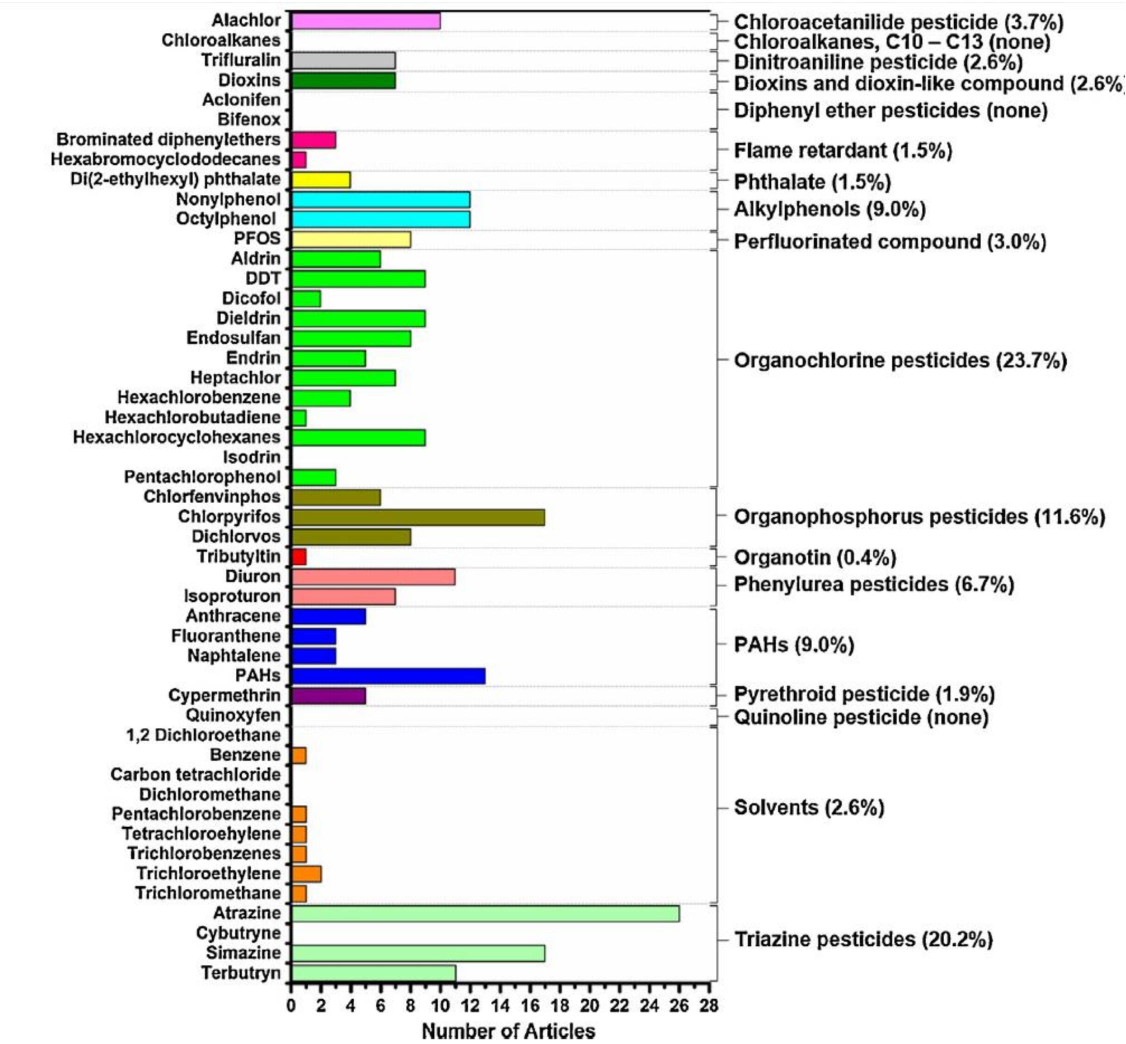

Figure 2: Number of reports monitoring 41 priority substances and 8 other substances under Directive 2013/39 /EU, broken down by substance and class of substances, published from 2012 (until 2018). The search was conducted in Scopus, using as a keyword the name of each of the listed compounds listed in Directive 2013/39 / EU and the terms "groundwater", "surface water", "river", "estuarine water", "lake water" and "coastal water" (Sousa et al., 2018).

Atrazine

Atrazine or 2-chloro-4-ethylamino-6-isopropyl-amino-1,3,5-triazine is a herbicide belonging to the group of substituted triazines. Atrazine is used to control broad-leaved and grassy weeds in corn, sorghum, sugar cane, pineapple, Christmas trees and other crops, and in planting coniferous forests. It is also used as a non-selective herbicide on non-cultivated industrial plots and on uncultivated fields (Meister, 1992). In 2014, atrazine was the second most widely used herbicide (immediately after glyphosphate) in the US with an annual application of approximately 35,000 tonnes. It belongs among the most used herbicides is also in Australian agriculture (www.apvma.gov.au). The use of atrazine in the EU was banned in 2004, when high levels of this herbicide were detected in groundwater (Decision 2004/248 / EC).

Atrazine is prepared from triazine, which is successively treated with ethylamine and isopropylamine. As with other triazine herbicides, the efficiency of atrazine lies in binding to the plastochynone-binding protein in photosystem II. Plant death is caused by hunger and oxidative damage resulting from an electron transfer disorder (Appleby et al., 2001).

Atrazine is a highly persistent herbicide in the environment. Atrazine is moderately to highly mobile in soils, particularly in soils with low clay or organic content. Since it is only slightly adsorbed to soil particles (K_{OC} = 100 g·l^{-1}) and has a long half-life in soil (60 to more than 100 days), there is a high risk of groundwater contamination (US EPA, 1988). Therefore, it is important to understand how atrazine affects non-target aquatic organisms. Atrazine, as an endocrine disruptor, targets in particular the hypothalamic-pituitary-adrenocortical axis (HPG-axis), which functions in the developmental and reproductive system (Wirbisky et al., 2015).

Atrazine toxicity

Studies have shown that atrazine caused decreased egg production, reproductive disorders and morphological changes in the Japanese medaka *Oryzias latipes* and in the zebra *Danio rerio*. In addition, atrazine induced feminization during development and a change in the sex ratio in amphibians. In the case of invertebrates, atrazine accelerated the time of development of the fruit fly *Drosophila melanogaster*, while inducing developmental malformations in marine cephalopods *Amphias custenuiremis* (Yoon et al., 2019).

Cleary et al. (Cleary et al., 2019) investigated the transgenerational effect of atrazine on the reproductive system of *Oryzias latipes*. The atrazine concentrations observed were consistent with the concentration's atrazine present in the environment. Cleary et al. observed that exposure to atrazine during the early stages of "grand-parent" fish resulted in disorders of the reproductive system in their grandchildren. The transgenerational effects of atrazine were accompanied by a change in gene expression regulating reproduction and DNA methylation.

4 Pesticides – means of removal

The removal of pesticides from water (waste, surface, underground) is an important process, as many of them are persistent substances in the environment, capable of bioaccumulation, and are transported over long distances due to adsorption to soil particles.

Biological processes

Numerous studies have been carried out to determine whether biological wastewater treatment plants (with activated sludge activation process) are capable of degrading micropolutants, or whether they can be modified to increase the degradation of micropolutants (e.g., by increasing the sludge age). This was because the efficiency of biodegradation can be increased by cultivating slow-growing microorganisms (MO). As the age of the sludge increases, an increased biodegradability has been observed, but can only be applied to certain substances. The results show that at 5 and 15 days of sludge age the removal of micropolutants was more effective than at 1 to 3 days of sludge age. Increasing the sludge age to 50 days or more has little effect on the complete removal of organic micropolutants (Burns, et al., 2010).

Very few studies deal with biological removal of atrazine from drinking and waste water. Most of the literature refers to the presence of atrazine, adsorption and removal in soil systems or pure crops, or chemical and physical removal methods (Buttiglieri et al., 2011). In their study, Baghapour et al. (Baghapour et al., 2013) investigated the possibility of atrazine biodegradation by the microbial community in the aquatic environment. The degradation of atrazine in synthetic waste water (atrazine and sucrose) took place on a submerged biological aerated filter (SBAF) at various hydraulic retention times. The result of their work is atrazine removal with 90% efficiency at higher initial atrazine concentrations (10 mg·l^{-1}), and 60% removal efficiency at 0,01 mg·l^{-1} concentration of atrazine (6 hours hydraulic retention time).

Physical processes – adsorption

Gao et al. (Gao et al., 2019) investigated the adsorption properties and kinetics of atrazine adsorption on four types of biochar. The results of their work showed that atrazine adsorbed on the biochar BC_{800B} according to the pseudo-second order kinetic model. The adsorption capacity of the biochar BC_{800B}, mixed from two separate biochars at 800 °C, was 37,2 mg·g^{-1}, the highest of all biochars studied. The biochar used in this work was prepared from corn straw and sawdust mixed 1:1 (w:w) at

300 and 800 °C, by co-pyrolysis (BC_{300A} and BC_{800A}) and by mixing separate biochars (BC_{300B} and BC_{800B}).

Chemical processes

In the work of Arnold et al. (Arnold et al., 1995) atrazine was degraded by the Fenton reaction. The optimal amount of fenton reagent ($FeSO_4 : H_2O_2$ = 1:1) for atrazine degradation at 140 μmol·l^{-1} was 2,69 mmol·l^{-1}. Furthermore, emerging intermediates and the effect of pH on FR were investigated. Atrazine degradation efficiency decreased from 99% at pH 3 to 37% at pH 9. FR can rapidly degrade atrazine, but further treatment may be required to eliminate chloro-s-triazine intermediates.

Rubio et al. (Rubio et al., 2006) degraded six water-soluble pesticides (alachlor, atrazine, chlorfenvinphos, diuron, isoproturon and pentachlorophenol), priority substances under the Water Framework Directive (2000/60/EC) of the European Union, by homogeneous photocatalysis by photo-Fenton reaction. All tests were performed in a 35 L solar pilot plant with compound parabolic collectors (CPC) in natural sunlight. The initial test concentration for all compounds was 50 mg·l^{-1} except those that were less soluble in water. Two different iron concentrations were tested, 2 mg·l^{-1} and 1 mmol·l^{-1}. All pesticides have been successfully degraded and largely mineralized.

Beltran et al. (Beltran et al., 1994) investigated the ozonation process to remove the priority pollutant - atrazine. The results of their work have shown that ozonation of atrazine at neutral pH is mainly via a radical (indirect) mechanism. The overall rate constant of the direct reaction with ozone is very low (6,3 mol^{-1}·s^{-1} at 20 °C), so even at neutral pH the radical mechanism can be dominant. In addition, this process is dependent on the presence of impurities that promote the decomposition of ozone and/or promoters releasing superoxide radical anions and hydroxyl radicals.

Ormad et al. (Ormad et al., 2009) studied the effect of hydrogen peroxide and titanium dioxide on ozone-based processes in the degradation of 44 organic pesticides present in natural water, systematically detected in the Ebro basin (Spain). The pesticides studied were alachlor, aldrin, ametryn, atrazine, chlorfenvinphos, chlorpyrifos, pp'-DDD, op'-DDE, op'-DDT. pp'-DDT, desethylatrazine, 3,4-dichloroaniline, 4,4'-dichlorobenzophenone, dicofol, dieldrin, dimethoate, diuron, α-endosulfan, endosulfan sulfate, endrin, α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, heptachlor-epoxide A, heptachlor-epoxide B, hexachlorobenzene, isodrine, 4-isopropylaniline, isoproturon, metolachlor, methoxychlor, molinate, methyl parathion, ethyl parathion, promethone, promethrin, propazine, simazine, tert-butylazine, tercutyl, tetradifon and trifluralin. Ozonation using 3 mg_{O3}·l^{-1} leads to the removal of pesticides with an efficiency of almost 23%, while in O_3/H_2O_2 and O_3/TiO_2 systems the degradation efficiency is lower than in ozonation. However, the application of the $O_3/H_2O_2/TiO_2$ process significantly improves the degradation of pesticides and achieves an average degradation efficiency of 36%.

5 Conclusion

This work provides results of theoretical research focused on pesticides toxicity and means of removal. Pesticides, along with fertilizers, play a central role in agriculture and contribute to increasing global food production, but also have a significant negative impact on the environment. Excessive use of pesticides can lead to the destruction of biodiversity. These substances have genotoxic effects and belong to the group of endocrine disruptors. For these reasons, there is a need to develop and apply new degradation processes. Some of newly developed processes are included in this work. Among wide range of pesticides, more focus is put on organochlorine pesticide atrazine.

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