Pesticides in the Pantanal

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Abstract This chapter presents a brief discussion on the potential for contamination of the Pantanal by pesticides and reviews the studies, which evaluated these substances in different matrices in the Pantanal and its surroundings. Agricultural activities occur mainly in the highlands around the floodplain and represent the main source of pesticides to the Pantanal. It is evident that they can be transported to the lowlands, but the pesticides were detected in low frequency and concentrations so far. There is no monitoring program, and a few studies regarding this contamination are limited in sampling frequency and spatial distribution as well as in analyzed substances that considered the large spectrum of pesticides used. Moreover, only water and sediment have been subject to analysis, and no biological indicators have been studied. Also, to the moment, no risk analysis has been carried out indicating the need for more studies in the region in order to prevent future damages to this important ecosystem.

Keywords Agriculture, Herbicides, Insecticides and fungicides, Land use

Contents

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1 Agriculture and Cattle Breeding in the Pantanal and Its Surroundings

The Pantanal is a unique area influenced by activities developed in the high areas surrounding it, particularly those carried out in areas drained by many rivers that feed this ecosystem. It comprises, in Brazil, two states – Mato Grosso and Mato Grosso do Sul – whose economic base is agriculture and cattle breeding.

Presently, Mato Grosso shows a large expansion in the area under cultivation for soya bean, cotton, maize, bean, and sugarcane in the highlands surrounding the Pantanal, mainly in the drainage basins of Casca, Manso, Sepotuba, Paraguay, Vermelho, and São Lourenço rivers. In Mato Grosso do Sul, this growth is also observed in the highlands surrounding the Pantanal, mainly in the drainage area of Alto Taquari, Miranda, Aquidauana, and Negro rivers, except for cotton that is not grown in this region and for sugarcane, whose increase forecast is more significant than in Mato Grosso [1]. A land use map in the Upper Paraguay basin is shown in [2] of this book. The decree n. 6,961 from the Brazilian Presidency published in 17 September 2009 approved the agroecological zoning for sugarcane in Brazil, and this activity was forbidden in the Pantanal and the High Paraguay river basin [3].

Productivity in these cultures has increased greatly due to the use of modern technologies. In general, these cultures are grown in extensive areas (monoculture systems) demanding mechanization and intensive inputs of agrochemicals, particularly, pesticides and fertilizers.

According to the Brazilian National Sanitary Vigilance Agency (ANVISA) [4], between 2000 and 2010, the pesticides Brazilian market increased 190%, a growth rhythm much higher than the registered in the world market (93%). In the crop period 2010/2011, pesticides consumption in Brazil reached the mark of 936,000 tons.

Pesticides (herbicides, insecticides, and fungicides) constitute a large spectrum of chemical compounds with different chemical structures which present variable behavior in the environment and consist on one of the main technologies used to control insects, fungus, plant diseases, and invasive weeds in the plantations and grasslands aiming to guarantee high productivity. Due to the extremely variable chemical properties of these molecules, the estimation of their dynamics in the environment is difficult, and no generalization is possible.

After application in the plantations, the major destination of pesticides is the soil, where it can undergo several processes which can lead to off-site transportation reaching nontarget areas particularly the water courses.

The mobilization of large amounts of sediment as a consequence of deforestation, soil tilling, and animal trampling to lower lands can make available to the aquatic environment elements or substances present in the sediment such as the pesticides.

The headwaters of the rivers in the Upper Paraguay basin are localized in the highlands, where monocultures of agriculture or pasture are developed in large scale. Transported sediments can eventually be contaminated by pesticides and settle down in the Pantanal lowlands, where water velocity is reduced due to the low declivity of the terrain [5]. Frequently, good agricultural practices are not observed, increasing soil erosion and sediment transportation to rivers.

In the lowlands, the main economic activity in large scale is extensive cattle breeding. The hydrological regime and low natural soil fertility were responsible for the establishment of the low-impacting extensive cattle breeding in the Pantanal floodplain. In 2010, among the municipalities in the Pantanal lowlands, cattle breeding was developed in 84% of the farms; only 10% were used for agriculture and 6% for both [6]. However, changes in the last years with implantation of soya plantation in the Pantanal borders (see also [7]) have increased the concern of potential impacts of pesticide contamination. Although incipient, the soya production has shown good profitability that has stimulated the farmers in the region to invest in this culture [8].

2 Transportation of Pesticides to the Pantanal

After having contact with the soil, several physical, chemical, and biological processes determine the behavior of pesticides. According to Spadotto et al. [9], pesticide dynamics in soil is driven by process of retention, transformation, transport, and by the interaction of these processes.

These processes depend largely upon the physical-chemical properties of the molecules, physical characteristics of the environment (relief, soil type, and climate) as well as the management practices of the cultures.

The transport of pesticides can occur in several ways, including migration in water (suspended or dissolved), in soil particles (sorbed), or in vapor state [10]. Among the transportation processes between the environmental compartments, the movement from soil to water via runoff and/or leaching is the most important.

Runoff is the movement of pesticides along the soil surface by rain or irrigation water to river, lakes, or areas of lower elevation. Runoff constitutes the main route of surface water contamination either associated to suspended particles or dissolved in water [11].

Runoff is highly dependent on pesticide use system, pesticide chemical properties, climate, and topography associated to soil physical and chemical properties. Dabrowski et al. [12], studying the application of modeling to estimate runoff, emphasize that the most important catchment variables determining runoff seem to be buffer strip width, presence of erosion rills, and slope.

One of the properties that greatly influence pesticide runoff is the retention in soil, which is generally denominated sorption, and depends mainly on the organic matter content and texture of surface soil, as well as on the molecular structure of the pesticide. The greater the sorption, the higher the potential for runoff associated to suspended material [13].

The adoption of conservation practices in soil preparation such as no-tilling and direct sowing can be good alternatives for the central region of Brazil that in addition to the positive impacts on soil fertility can reduce runoff. Among the facts that contribute to the sustainability of these practices is the maintenance of vegetable residues on the soil associated to little utilization of agriculture machinery implicating in high efficiency in hydric erosion reduction and, consequently, less soil, nutrient, and pesticide loss by runoff [14, 15].

The knowledge about pesticides transport processes in the environment is essential to orientate the elaboration of management plans. The variety of pesticides used from many different chemical classes makes the interaction forms of these compounds with different environmental components also extremely variable.

Leaching through the soil tends to result in groundwater contamination, and in this case, the chemical substances are transported in solution together with percolating water. Contaminated groundwater in the Pantanal may represent a risk to surface water since water table is very shallow in the lowlands.

In a literature review, Carter [16] reported that for herbicides, losses of up to 0.25% of applied quantity by runoff and 5% by leaching have been reported. In Center-Western Brazil, Dores et al. [17] determined herbicide loss of 3% and 1% by runoff adsorbed to soil particles and dissolve in water, respectively. On the other hand, Matallo et al. [18], based on experimental data, reported that 52% of applied amount of a herbicide used in sugarcane in Southern Brazil leached through the first 50 cm of a sandy soil during a year-end. Using a mathematical model, these authors estimate that 96% can leach below 12 cm (depth where there is a desired weed control) in 67 days.

A pesticide property that is very important to the potential impacts in the environment is the persistence. Laabs et al. [19] concluded that a medium-term accumulation in the sediment of tropical ecosystems can be expected for chlorpyrifos and endosulfan isomers (11–35% of applied amount still extractable at 50 days after application).

The evaluation of pesticide dissipation in two different Brazilian soils (Ustox and Psamments) demonstrated that persistence was mostly greater in the clayey than in the sandy soils. In comparison with temperate regions, dissipation of pesticides was 5 to 10 times faster, except for alachlor, deltamethrin, and λ-cyhalothrin, which exhibited a less reduced persistence than under temperate conditions [20].

Another route of off-site pesticides transportation that may be more important in tropical regions is the movement in the atmosphere. Volatilization of pesticides may be enhanced due to the high temperatures, and studies that analyzed pesticides in rainwater in Mato Grosso detected significant pesticide concentrations near the agricultural areas [21].

In rainwater samples collected in the highlands around the Pantanal, substantial insecticide (endosulfan, profenofos, monocrotophos) and herbicide (metolachlor, alachlor, trifluralin) concentrations were found by Laabs et al. [22], showing a high deposition rate in this region. In the lowlands, at about 75 km distance from the next application areas, maximum pesticide concentrations in rainwater were about fivefold, and deposition was about tenfold lower than in the highlands surrounding them. Despite the lower deposition in the lowlands, this study showed that transportation by the atmosphere may be an important route of pollution of areas distant from application sites.

3 Organochlorine Pesticides in the Pantanal

Organochlorine pesticides, forbidden in Europe and United Sates in the seventieth decade and in agriculture in Brazil since 1985, due to their high environmental persistence and bioaccumulation potential, can still be found in several environmental compartments in Brazil [23–29].

These pesticides belong to the dirty dozen substances (to which endosulfan has been recently added) included in the Stockholm Convention, ratified by 178 countries and the European Union, where a joint effort to elimination/reduction of the use of these substances is proposed [30].

The Latin America Regional Report on POPs monitoring reported that scarce information regarding POPs in the environment in this region is available [31]. Although there is no continuous monitoring program of these pesticides in Brazil, particularly in the Pantanal, punctual studies have detected organochlorine in water and sediments in the floodplain and in rivers whose riverheads are located in highlands and that go downward to the plains.

Although the use of organochlorine pesticides in agriculture was forbidden in Brazil since 1985, DDT was used in health campaigns for vector control up to 1997 [32]. Only endosulfan had its use allowed in agriculture up to July 2013 since its persistence was much lower than the other organochlorines. In 2011, the National Sanitary Vigilance Agency, following the inclusion of endosulfan in the Stockholm convention, determined its total ban in agriculture up to July 2013.

In a study carried out by Laabs et al. [22], five organochlorine pesticides and two metabolites were analyzed in water and sediment samples collected in tributaries of the São Lourenço River (e.g., the Tenente Amaral) and the São Lourenço River itself in the highlands and in the Cuiabá River, the mouth of the Mutum River at the Sia Mariana lake, and the Sia Mariana lake itself in the floodplain. The sampling period began on 10 November 1999 and ended on 2 March 2000. The authors did not find detectable concentrations of formerly used organochlorine pesticides (lindane, p,p′-DDT, quintozene) in water samples but detected p,p′-DDT and p,p′-DDE at low concentrations in sediments either in the sampling points in the highlands and in the lowlands with concentrations slightly higher in the lowlands showing potential for accumulation. Regarding endosulfan, its isomers were detected in stream water and in river waters in the highlands near application areas in less than 14% of analyzed samples while the metabolite endosulfan sulfate was detected in 50% of river water samples in the highlands and in 10.5% in the lowlands. In sediments, β-endosulfan and endosulfan sulfate were detected only in the highlands.

Troli [33] analyzed 16 organochlorine (ten pesticides and six metabolites) in 66 water and 64 riverbed sediment samples collected in 2002/2003 in points divided in what the author called of three routes. Route 1 comprised points in the rivers Aquidauana, Miranda, and Negro collected in the dry season (September 2002); route 2 comprised points in Cuiabá, São Lourenço, Piquirí, Paraguay-Mirim, Branco, Abobral, Miranda, Negro, and Apa rivers, all of which are affluents of Paraguay river, in the beginning of the rainy season (December 2002); and route 3 whose sampling points were localized in Taquari River Basin (São Lourenço, Vermelho, Taquari, Coxim, Itiquira, Piquirí, Correntes rivers, and Gaucho creek) in the rainy season (January 2003). In water samples, the author detected only heptachlor epoxide (a metabolite of heptachlor) in five samples in concentrations ranging from 0.15 to 0.62 μg L^{-1} and the DDE isomers (o,p′- and p,p′-DDE) in concentrations varying from 0.78 to 14.65 μg L^{-1}. No pesticides were detected in the points in route 1 that comprises sites located in the Pantanal, far away from agricultural areas. The DDE isomers were detected in the points situated along route 2 and heptachlor hepoxide in route 3. Both DDE and heptachlor epoxide are metabolites which present high persistency in the environment. In sediments, the only detected pesticide was lindane ranging from 20.00 to 71.11 μg kg^{-1} in three points located along routes 2 and 3. Sediments were collected using core samplers and were subsampled at three depths. In two of the sampling points, lindane was detected in the three subsamples while in one sampling point was detected in only one subsample. The detected concentrations may represent risks to the biota according to Brazilian legislation; however, as the detection was eventual and the study was carried out in a short time period, more studies are necessary to analyze the real risk to the Pantanal ecosystem.

Miranda et al. [34] detected p,p′-DDT (3.6 μg kg^{-1}) in only one riverbed sediment sample collected in the Miranda river, in a study where sampling was performed in 17 rivers from the highlands/lowlands transition area from November to March 2004. The authors determined aldrin, dieldrin, endrin, endosulfan isomers, endosulfan sulfate, methoxychlor, p,p′-DDE, and p,p′-DDT.

Calheiros and Dores [35] analyzed riverbed sediment samples collected in the main tributaries of Miranda and Aquidauana rivers in 21 sampling points throughout the watershed distributed in the highlands and in the floodplain. Dieldrin which is a pesticide and also a metabolite of aldrin was detected in all sediment samples collected in May 2005 in concentrations ranging from 9.5 to 10.8 mg kg^{-1} and in 88% of the samples collected in December 2005 from 9.3 to 15.4 mg kg^{-1}. The insecticide p,p′-DDT was detected in only one sample in the Miranda river and one sample in an irrigation channel in May 2005 which is a period shortly after the rainy season when water level is reducing. This insecticide was detected near irrigated cultures of rice, sorghum, and bean at 1.0 mg kg^{-1} and in the irrigation channel at 20.3 mg kg^{-1}. On the other hand, its main metabolite p,p′-DDE was detected in all sediment samples from 1.2 to 14.4 mg kg^{-1}. Since the use of DDT is no longer authorized in Brazil since 1997, the concentration ratio DDE/DDT is an indicator of the contamination period, where a high ratio indicates past contamination, while when the contamination is recent, this ratio is low. Since in most samples where

DDE was detected DDT was not, this contamination is likely related to past use except for the point located in the irrigation channel whose DDT concentration was particularly high. Coincidently, the irrigated crops are developed in the medium Miranda river where there are high densities of fish eggs and larvae [36], which are particularly sensitive to contaminants [37].

The most recent study reporting organochlorine in this region analyzed water samples collected in three rivers from the Alto Paraguay river basin, Cuiabá, Perigara/São Lourenço, and Piquirí rivers. A total of 188 samples were collected in the dry season in June and July 2012. Samples were collected while traveling downstream on the rivers. A total of 24 sampling points were located along Cuiabá river, 18 along Perigara/São Lourenço rivers, and 21 along Piquirí river. Each river was sampled three times from 17 to 20 June 2012, 11 to 13 July 2012, and 17 to 18 July 2012. There were only ten contaminated samples all of which were from the second sample set and from the downstream portion of the Rio Cuiaba. Endosulfan sulfate – the most important metabolite of endosulfan which is the only organochlorine pesticide whose use was authorized in agriculture in Brazil until July 2013 – was detected in only one sample, while the p,p′-DDT metabolites (p,p′-DDD and m,p′-DDD) were detected in nine samples in concentrations ranging from 0.7 to 3 μg L^{-1} [38]. The author [38] attributed the overall low incidence of pesticide pollution to the period of sample collection (dry season with consequent low runoff) and the prohibition of organochlorine pesticides usage in agriculture since 1985 (except for endosulfan at the time of this study). Endosulfan sulfate and DDD are very stable compounds, so it is unknown whether their occurrence in the water samples from the second collection was due to recent application or runoff processes. Endosulfan sulfate has been shown to bioconcentrate and possess high toxicity [39]. As nonpoint source pollution, pesticide contamination is difficult to trace. This author also emphasizes the urge that Brazilian policymakers look to sad examples such as the problems with Everglades in Florida, USA, where farmland expansion and increased development of the wetland caused severe impacts among them contamination by pesticides.

4 Currently Used Pesticides (CUP) in the Pantanal

In contrast to organochlorine pesticides, currently used pesticides (CUP) are much less persistent in the environment, but due to their intensive use in the surrounding areas of the Pantanal, they may also pose a risk to this environment. As endosulfan is an organochlorine pesticide that was currently and intensively used up to July 2013, it was also included in this discussion.

As well as the organochlorine, CUP has not been monitored frequently, and a few studies [22, 33–35, 38, 40] have analyzed these pesticides in the Pantanal, most of them carried out by researchers at the Brazilian universities. Those studies indicate that there is a potential for pesticide transport from the highlands to the lowlands mostly associated to suspended matter in waters.

Laabs et al. [22] showed in a pilot monitoring study evidence of occurrence of several pesticides of different chemical classes (29 pesticides and 3 metabolites) in the northeastern Pantanal basin. From the investigated substances, 22 were detected at least once, leading to an overall pesticide detection frequency of 68% in surface water samples ($n = 139$), 87% in rainwater samples ($n = 91$), and 62% in sediment samples ($n = 26$). Pesticides were detected in stream and river waters in concentrations below 0.1 μg L^{-1} and in sediments below 10 μg kg^{-1}.

Pesticides with higher detection frequency and/or persistence in that study region were triazines (atrazine, simazine, ametryn), acetanilides (alachlor, metolachlor), trifluralin, and endosulfan compounds (especially β-endosulfan and endosulfan sulfate). Some organophosphorus pesticides (e.g., monocrotophos, profenofos, triazophos) showed higher peak concentrations in environmental samples but were rarely detected outside the application regions, presumably due to their low persistence. In the lowlands, the pesticides alachlor, endosulfan sulfate, malathion, metolachlor, simazine, and trifluralin were detected in more than 10% of the water samples. In sediments collected in the Pantanal area, only the formerly used organochlorine pesticides p,p′-DDT and p,p′-DDE were detected in 25% of the samples. Higher percentage of detection was found in the rivers in the highlands near the agricultural areas.

However, those authors detected in highlands rain water substantial insecticide (endosulfan, profenofos, monocrotophos) and herbicide (metolachlor, alachlor, trifluralin) concentrations, leading to a high deposition rate in this region. Conversely, in the lowlands, at about 75 km distance from the next application areas, maximum pesticide concentrations in rainwater were about fivefold, and deposition was about tenfold lower than in the highlands surrounding them.

Miranda et al. [34] analyzed riverbed sediments of 17 rivers that drain to the Pantanal, in the beginning of the floodplain, in November 2004. They identified three currently used active ingredients (pyrethroids) at the following concentrations: λ-cyhalothrin (1.0–5.0 μg kg^{-1}), deltamethrin (20.0 μg kg^{-1}), and permethrin (1.0–7.0 μg kg^{-1}).

Another study carried out in the Cuiabá watershed analyzed pesticides in sediments collected monthly in 15 sampling points located along the Cuiabá and São Lourenço rivers from the highland areas to the Pantanal floodplain, from August 2010 to July 2011. From a total of 216 samples, only ten presented detectable concentrations of at least one pesticide. The pesticides chlorpyrifos, endosulfan (α- and sulfate), λ-cyhalothrin, malathion, metolachlor, and permethrin were detected at concentrations ranging from 5.7 to 79.3 μg kg^{-1}. Although detected at low frequency, samples collected in the Pantanal floodplain presented residues of metolachlor, λ-cyhalothrin, endosulfan sulfate, and malathion indicating that there is a potential for transportation of pesticides used in agriculture carried out in the high areas reaching the lowlands [40].

Pyrethroid insecticides have been detected in riverbed sediments in several countries [41–44] with emphasis to cypermethrin, deltamethrin, bifenthrin, λ-cyhalothrin, and permethrin. The last two pyrethroids were detected in the abovementioned studies carried out in the Pantanal [34, 35]. This is probably due to the intensive use of insecticides of this chemical class in several crops associated to their high soil sorption coefficient (Koc from 100,000 to 1,000,000 mL g^{-1}) that contribute to their transport associated to particulate carried in runoff.

Other pesticides frequently detected in sediment by several authors in different regions around the world are endosulfan (alpha and beta isomers and their main metabolite endosulfan sulfate) and chlorpyrifos [26, 43, 45, 46]. As the pyrethroids, these pesticides present high soil sorption coefficients, low water solubility, and moderate persistency.

A dissipation study developed by Laabs et al. [19] in the Pantanal using mesocosms pointed out that β-endosulfan followed by metolachlor, atrazine, simazine, and chlorpyrifos were the most persistent ones among the nine studied pesticides and tended to accumulate in the sediment. This observation explains the detection of some of these pesticides in the studies described above.

5 Potential Risks to the Pantanal from Pesticides Pollution

Most studies regarding pesticide transport to the Pantanal have been carried out using periodic sampling plans, usually monthly or less frequently. This sampling strategy is not the most appropriate for risk evaluation since the entry of pesticides in the aquatic environment is not continuous but episodic, mainly associated to intensive precipitation events that cause runoff. In this way, peak concentrations of pesticides are missed due to rapid dissipation dynamics of pesticides in the aquatic environment, either as a consequence of dilution, degradation, absorption by living organisms, or sorption to particulate. Also, no studies determined pesticide concentration in aquatic organisms.

Moreover, there is no study regarding acute impact of peak concentrations to aquatic organisms in water in this ecosystem, making it very difficult to evaluate the actual risks to the Pantanal environment.

Nevertheless, the studies published so far indicate that pesticides can be transported to the Pantanal, and so, mitigating measures should be stimulated in order to prevent significant impacts to occur.

Examples of possible mitigating measures are the use of less persistent and toxic pesticides, reduction of chemical pesticide usage in the highlands, use of soil conservation measures with particular attention to erosion reduction measures as well as maintenance and recovery of the riparian vegetation which function as a buffer to runoff, complying with the current Brazilian legislation [47].

As a result, although detected with low frequency and relatively low concentrations, pesticides may interfere in the Pantanal ecosystem, and little is known about the potential effects indicating that more research is needed in this regard.

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