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Tese

Ocorrência, mitigação e degradação de produtos fitossanitários no ar, água e solo

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OCORRÊNCIA, MITIGAÇÃO E DEGRADAÇÃO DE PRODUTOS FITOSSANITÁRIOS NO AR, ÁGUA E SOLO

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À minha amiga e namorada, Ananda

OFEREÇO E DEDICO

“How great you are, Sovereign Lord! There is no one like you, and there is no God
but you, as we have heard with our own ears.”

2 Samuel 7:22

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First and foremost, thanks to the God.

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Resumo

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A agricultura esta entre as principais atividades econômicas no Rio Grande do Sul (RS), onde as culturas da soja, milho e arroz são as principais espécies cultivadas durante o verão e o trigo durante o inverno. Os benefícios econômicos da agricultura são inquestionáveis, contudo, esse setor é também responsável por contaminação ambiental, principalmente devido ao manejo incorreto dos agrotóxicos, representando riscos para a qualidade da água e do ar. O processo de degradação tem função importante de atenuar os efeitos ambientais dos compostos orgânicos, sendo esse chave no destino ambiental dos contaminantes. Assim, os objetivos deste trabalho foram: (i) monitorar a ocorrência de 97 agrotóxicos na atmosfera em áreas rurais e urbanas em seis diferentes regiões geográficas no Estado do Rio Grande do Sul (Artigo I); (ii) monitorar a presença de 97 agrotóxicos na água utilizada para consumo humano em seis diferentes regiões geográficas no Estado do Rio Grande do Sul (Artigo II); (iii) avaliar a eficiência de diferentes métodos de tratamento de água residencial na remoção de 13 agrotóxicos com características físico-químicas distintas (Artigo III); e (iv), avaliar a taxa de degradação do herbicida fluazyfop-P-butyl e a taxa de formação e degradação de seus principais metabólitos em três diferentes solos dinamarqueses (Artigo IV). Com os resultados obtidos foi possível concluir que pelo menos um agrotóxico foi detectado em 60% das amostras de ar. Os mais frequentemente detectados foram chlorpyrifos, fenpropathrin, atrazine e azoxystrobin. Os agrotóxicos com maiores concentrações nas áreas rurais foram chlorpyrifos, fenpropathrin, malathion e atrazine, com concentração máxima de 75,8, 73,4, 27,8 e 20,2 ng m^{-3}, respectivamente. Nas áreas urbanas chlorpyrifos e fenpropathrin foram os mais frequentemente detectados com concentração máxima de 16,9 e 15,6 ng m^{-3}, respectivamente. Com relação presença de agrotóxicos na água de consumo, pelo menos um agrotóxico foi detectado em 100% das amostras. Os mais frequentemente detectados foram atrazine, azoxystrobin, carbendazim e imidacloprid. Os agrotóxicos com maiores concentrações nos rios e lagos foram azoxystrobin e 2,4-D, com a máxima de 14,3 and 1,94 μg L^{-1}, respectivamente. Na água da torneira propanil, 2,4-D, quinclorac e bentazone apresentaram as maiores concentrações, sendo a máxima de 4,11, 3,78, 2,57 e 1,45 μg L^{-1}, respectivamente. Com relação aos diferentes métodos de tratamento de água residencial, carbono ativado e osmose reversa foram 100% eficiente na remoção de agrotóxicos, seguido por resina de troca iônica e ultravioleta. Filtros de membrana, em geral, mostraram baixa eficiência, portanto, não são recomendadas para esse propósito. A degradação de fluazifop-P-butyl, em laboratório e sobre condições aeróbicas revelou que esse tem baixa persistência no solo. A sequência de degradação é: fluzifop-P-butyl, fluazifop-p, composto IV e composto X. Fluazifop-p é o principal produto da degradação, enquanto o composto IV é o com menor concentração e o composto X, o mais persistente.

Palavras-chave: Dinâmica de agrotóxicos. Contaminação ambiental. Atmosfera. Herbicidas. Qualidade

Abstract

SCHREIBER, Fabio. **Occurrence, mitigation and degradation of pesticides in air, water and soil.** 2016. 122f. Thesis (Ph. D.) – Department of Crop Protection. Federal University of Pelotas, Pelotas.

Agriculture is among the main economic activities in Rio Grande do Sul (RS), where soybean, maize and rice are cultivated as summer crops and wheat during the winter. The economical benefits of agriculture are undoubted, however, this sector is also responsible for environmental contamination mainly due to the incorrect management of the pesticides, threating the water and air quality. The degradation process has an important role in the environmental hazards associated with organic compounds and, it is a key process involved in the fate of these contaminants. Thus, the objectives of this study were: (i) to survey the presence of 97 pesticides in the atmosphere of rural and urban areas in six geographically different regions of the Rio Grande do Sul State (Manuscript I); (ii) to survey the presence of 97 pesticides in drinking water sources and tap water in six geographically different regions in Rio Grande do Sul State (Manuscript II); (iii) to evaluate the efficiency of different residential water treatments methods with regard to the removal of 13 pesticides with distinct physico-chemical characteristics (Manuscript III); and (iv), to clarify the degradation rate of the herbicide fluazifop-P-butyl and the formation and degradation rate of its major metabolites in three different Danish soils (Manuscript IV). According to the results, 60% of the air samples had traces of at least one pesticide. Among the monitored pesticides, the most frequently found were chlorpyrifos, fenpropathrin, atrazine and azoxystrobin. The pesticides with highest concentrations in rural areas were chlorpyrifos, fenpropathrin, malathion and atrazine, with maximum concentrations of 75.8, 73.4, 27.8 and 20.2 ng m^{-3}, respectively. In urban area chlorpyrifos and fenpropathrin were the most frequently detected with maximum concentrations of 16.9 and 15.6 ng m^{-3}, respectively. The water quality evaluation revealed traces of at least one pesticide detected in 100% of the samples. Among the monitored pesticides, the most frequently found were atrazine, azoxystrobin, carbendazim and imidacloprid. The pesticides with higher concentrations in drinking water source were azoxystrobin and 2,4-D, with maximum concentrations of 14.3 and 1.94 μg L^{-1}, respectively. In tap water propanil, 2,4-D, quinclorac and bentazone had the higher detected concentrations, with 4.11, 3.78, 2.57 and 1.45 μg L^{-1}, respectively. Regarding the different residential water treatments methods, activated carbon and reverse osmose were 100% efficient for pesticide removal, followed by ion exchange resins and ultraviolet. Membrane filters in general showed low efficiency and should, therefore, not be applied for this purpose. Fluazifop-P-butyl degradation results indicate the very low herbicide persistence in incubated soil under controlled and aerobic conditions. In the degradation pathway sequence fluzifop-P-butyl is followed by fluazifop-p, Compound IV and Compound X. Fluazifop-p is the major degradation product, while Compound IV is observed in minor concentrations and Compound X being the most persistent.

Keywords: Pesticides dynamic. Environmental contamination. Atmosphere. Herbicides. Quality

Sumário

Introdução geral

Na agricultura moderna os agrotóxicos (herbicidas, fungicidas e inseticidas) desempenham papel fundamental para a obtenção de altas produtividades, pois possuem como função proteger as espécies cultivadas das pragas que atacam a cultura e reduzir a presença de plantas daninhas. O Brasil está entre os maiores consumidores de produtos fitossanitários do mundo, tornando-se em 2008 o maior consumidor mundial (IBGE, 2014). Embora, segundo estudo realizado pela consultoria alemã Kleffmann, encomendado pela Associação Brasileira de Agronegócio (ABAG, 2015) o Brasil ocupa a sexta posição no ranking mundial de consumidores desses produtos quando o consumo é considerado por área cultivada. No entanto, não faltam razões para preocupações relacionadas ao consumo de agrotóxicos, e seus efeitos à saúde e meio ambiente, uma vez que o país não possui um sistema eficiente de monitoramento de agrotóxicos no ambiente e nos alimentos, bem como nenhum sistema de controle de qualidade. Além disso, o uso de agrotóxicos no país tem aumentado muito além do crescimento da área agrícola nos últimos trinta anos (SPADOTTO, 1996).

O Rio Grande do Sul (RS) tem como base da sua economia a produção agrícola, dentro da qual as culturas da soja, milho e arroz são as principais cultivadas durante a estação quente do ano e o trigo durante a estação fria. Os benefícios econômicos da agricultura são inquestionáveis, contudo, esse setor é também responsável por contaminação ambiental, principalmente devido ao manejo incorreto dos agrotóxicos. Muitas vezes não são levadas em consideração as instruções e recomendações indicadas na bula dos agrotóxicos, além disso, a falta de conhecimento a respeito de suas características por parte dos usuários acaba causando possíveis danos ao ambiente e a saúde humana. O elevado consumo associado às condições climáticas do país resulta em grande preocupação quanto ao comportamento ambiental destas moléculas e possível contaminação do ar e dos corpos hídricos, inclusive água potável. O arroz irrigado, por exemplo, é apontado como uma cultura com elevado impacto ambiental, principalmente pelo elevado volume de água e agrotóxicos utilizados na lavoura e pelo risco de transporte desses agrotóxicos e nutrientes para locais não desejados no ambiente.

O potencial de impacto ambiental proveniente do uso de agrotóxicos depende da sua toxicidade ao ser humano e da sua ecotoxicidade, assim como, das concentrações atingidas nos diferentes compartimentos ambientais (solo, água, planta e atmosfera). As concentrações, por sua vez, dependem da carga contaminante e do comportamento e destino destes químicos no meio ambiente (SPADOTTO; GOMES; HORNSBY, 2002). Dessa forma, cada vez mais, o conhecimento dos processos envolvidos no destino ambiental dos agrotóxicos usados na agricultura torna-se essencial para que sua aplicação seja eficiente e ambientalmente segura, uma vez que existe a possibilidade de minimizar os processos considerados indesejáveis com pequenas precauções e adoção de técnicas simples.

Após a aplicação de um agrotóxico na lavoura, vários processos físicos, químicos e biológicos determinam o seu comportamento. A sua dinâmica no solo é governada pelo processo de sorção, que engloba os processos de retenção ou adsorção resultantes da interação entre a molécula do agrotóxico com as partículas coloidais do solo, podendo ser reversíveis ou não. A sorção é fator preponderante na disponibilidade desses compostos químicos. A maior ou menor adsorção define seus efeitos ecotoxicológicos, toxicológicos e sua capacidade de biodegradação e transporte por lixiviação, escoamento superficial e volatilização.

Os agrotóxicos podem sofrer transformações de natureza química (quebra da molécula por fotólise, hidrólise) ou biológica (degradação por microrganismos) e ainda podem ser transportados para locais não desejados no ambiente, através dos processos de volatilização, lixiviação e escoamento superficial (SILVA; FAY, 2004), ocorrendo exposição dos recursos hídricos ao risco de contaminação por agrotóxicos aplicados nas culturas comerciais.

A lixiviação e o escoamento superficial têm sido apontados como a principal via de contaminação da água potável com agrotóxicos, e o principal processo de controle é a degradação no solo. A degradação, de modo geral, reduz os níveis de resíduos do agrotóxico no solo (OLIVEIRA; BRIGHENTI, 2011). Esse processo refere-se à quebra das moléculas do agrotóxico em moléculas menores, de forma biótica ou abiótica. Estudos de degradação são essenciais para a avaliação da persistência de agrotóxicos e seus produtos de degradação, pois permitem avaliar o risco potencial associado à exposição aos resíduos, muitas vezes com o mesmo nível de toxidez da molécula original, ou até mais tóxicas (FRIGHETTO, 1997). Para muitos agrotóxicos amplamente utilizados atualmente em grandes áreas agrícolas o conhecimento da taxa de degradação, e formação de metabólitos não são conhecidos, como por exemplo, fluazifop-P-butyl.

Dentre outras formas de perdas de agrotóxicos para o ambiente a ocorrência de deriva tem seu destaque e sua importância. A deriva é considerada um dos maiores problemas da aplicação de agrotóxicos na agricultura (SUMNER; SUMER, 1999). O desvio da trajetória impede que as gotas produzidas pelos equipamentos de aplicação atinjam o alvo. Esse desvio está relacionado, principalmente, ao tamanho de gotas, velocidade do vento, temperatura e umidade relativa do ar (SILVA, 1999). Em suma, deriva é o movimento de um produto no ar, durante ou depois da aplicação, para um local diferente do planejado. Miller (2004) acrescenta ainda que o agrotóxico pode ser transportado da área alvo na forma de gotas ou vapor. A perda na forma de vapor pode ocorrer durante ou posteriormente à aplicação, sendo muito dependente da pressão de vapor e das características da formulação do produto. Assim, devido ao prejuízo resultante da perda de agrotóxico e dos danos que podem ser causados em culturas adjacentes, a deriva assume grande importância em relação à contaminação de recursos hídricos, alimentos, além de outras questões ambientais.

Outro processo a ser ressaltado é o fenômeno da volatilização, o qual representa uma importante fonte de perda de agrotóxicos para o ambiente (TAYLOR; SPENCER, 1990). Basicamente, baseia-se em um processo físico-químico pelo qual um composto é transferido da solução do solo e/ou da superfície do solo e plantas para a fase gasosa. Esse processo é fundamentalmente dependente das propriedades físico-químicas do composto como sua estrutura e peso molecular, pressão de vapor e também das condições climáticas locais.

Dessa forma, a atmosfera torna-se o provável destino dos agrotóxicos via processos de deriva e volatilização. Uma vez na atmosfera, o agrotóxico poderá ser novamente depositado à superfície por meio de vento (deposição seca) e/ou por precipitação (deposição úmida) (GAVRILESCU, 2005). A deposição seca ocorre quando a velocidade do vento é insuficiente para manter suspensa na atmosfera moléculas de agrotóxicos livres ou adsorvidas em partículas coloidais, ocorrendo a deposição sobre a superfície terrestre, em local não alvo. Já a deposição úmida é caracterizada pelo carregamento de partículas suspensas na atmosfera, pela ação das gotas da chuva, neve, neblina e/ou orvalho, em direção ao solo.

A saúde humana pode ser afetada pelos agrotóxicos por meio do contato direto ou indireto com estas substâncias. Não somente os moradores e trabalhadores do meio rural estão sujeitos a contaminação, os habitantes do meio urbano também se encontram sob risco, devido à contaminação ambiental e dos alimentos. A avaliação da contaminação ambiental é de fundamental importância para a compreensão da contaminação humana por agrotóxicos (MOREIRA et al., 2002), uma vez que os seres humanos podem receber resíduos provenientes de matrizes ambientais contaminadas, como água e ar.

Estudos têm relatado que existe uma relação direta entre a exposição humana a agrotóxicos e problemas de saúde, tais como aumento de certos tipos de câncer de mama e/ou do trato reprodutivo, redução da fertilidade masculina, anormalidades no desenvolvimento sexual entre outros (MEYER; SARCINELLI; MOREIRA, 1999). Assim, a questão da qualidade ambiental é um aspecto que deve ser investigado, com ênfase no que se refere ao impacto na saúde da população (NUNES; TAJARA, 1998). O uso de agrotóxico gera externalidades no meio ambiente e na saúde humana, sendo que muitos desses impactos ainda são desconhecidos a longo prazo. (SOARES; PORTO, 2007).

Como forma de intervir em qualquer impacto antrópico no ambiente, o primeiro passo é diagnosticar e quantificar esse impacto, avaliando-se a extensão do problema de contaminação e em seguida buscando-se alternativas para minimizá-los. Dessa forma, faz-se necessário estudar os impactos ambientais causados pelas culturas de arroz irrigado, soja, milho e trigo assim como dos processos que possam reduzir o impacto ambiental e a contaminação do ar e da água.

Em vista do exposto, os objetivos gerais deste trabalho foram: (i) monitorar a ocorrência de agrotóxicos em amostras de ar em áreas rurais e urbanas, no Estado do Rio Grande do Sul (Artigo I); (ii) monitorar a presença de agrotóxicos na água utilizada para consumo humano em diferentes regiões do Rio Grande do Sul

(Artigo II); (iii) avaliar a eficiência de diferentes métodos de tratamento de água residencial na redução da contaminação por agrotóxico (Artigo III); (iv) avaliar a taxa de degradação de fluazyfop-P-butyl e a formação de metabólitos em solos. (Artigo IV).

Manuscript 1 - Science of the Total Environment *

Occurrence of pesticides in the atmosphere on Rio Grande do Sul, Brazil

*Manuscript formatted according to the Journal’s guidelines.

Occurrence of pesticides in the atmosphere on Rio Grande do Sul, Brazil

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Abstract

Rio Grande do Sul (RS) state is situated in Southern Brazil, which is one of the largest states in the country with approximately 281.730 km^2 and 11.207.274 habitants. Agriculture is among the main economy activities in RS, covering approximately 70% of the state area. Moreover, monitoring studies dealing with pesticides contamination levels in air samples have been very limited and scarce, leading to a lack of knowledge about the air quality in this region. Thus, the aim of this study was to survey the presence of 97 pesticides in the atmosphere in rural and urban areas in six geographically different regions in Rio Grande do Sul State. The sampling was performed in six cities: Porto Alegre, Vacaria, Ijuí, Santa Maria, Alegrete and Pelotas. Two samples were collect in each locality per season (spring, summer, fall and winter), one from the rural and other from urban area. According to the results, residues at low concentrations of 15 pesticides were detected in the air samples analyzed, with 60% of the samples contained traces of at least one pesticide. Among the monitored pesticides, the most frequently found were chlorpyrifos, fenpropathrin, atrazine and azoxystrobin. The pesticides with highest concentrations in rural areas were chlorpyrifos, fenpropathrin, malathion and atrazine, with maximum concentrations of 75.8, 73.4, 27.8 and 20.2 ng m^{-3}, respectively. In urban areas chlorpyrifos and fenpropathrin were the most frequently detected with maximum concentrations of 16.9 and 15.6 ng m^{-3}, respectively. Contamination frequency and levels in rural samples were higher than in urban areas

Keywords: air; environment; chlorpyrifos; fenpropathrin; atrazine; seasonal; contamination

Introduction

Volatilization represents the overall result of all physical and chemical processes by which a compound is transferred from the soil solution and/or the plant surface to the atmosphere (Bedos et al., 2002). Once in the atmosphere, the pesticide may be transported over long distances and be redeposited on the surface (soil, water and plants). Pesticides can reach the surface via dry deposition (wind) and wet deposition (rain, dew, snow and fog) (Gavrilescu, 2005), targeting undesirable organisms and consequently contaminating the environment (Schreiber et al., 2015). Once in the environment, pesticides can affect the biota, the water and air quality, productivity and food quality from animal and plant source, which may make them unsuitable for consumption (Schreiber et al., 2013).

Nowadays, more than 900 pesticide active ingredients are used to control pests (weeds, insects) and diseases (Casida, 2012). Although the majority of the currently used pesticides is considered to be less persistent and more biodegradable compared with the ones used in the past (pesticides banned by Stockholm Convention), they have been frequently observed in air samples of agricultural and urban areas (Coscollà et al., 2010; Gouin et al., 2008). Furthermore, pesticides have been detected in remote areas like high mountains, the Pacific Ocean, and the Arctic (Bradford et al., 2010; Ruggirello et al., 2010; Zhong et al., 2012), which indicate their potential for long-range transport.

High-volume active samplers is a new method that allows to assess the concentrations of persistent toxic pollutant in the atmosphere. The majority of atmospheric monitoring programs rely on the use of active air samplers (AAS), deployed for short periods but in high frequency. This technique has shown to be a very effective tool as it allows the monitoring of pesticides in the different atmospheric phases (particle and gas). Moreover, this method also allows the study of spatial and temporal variations of pesticide concentrations in the air (Sanusi et al., 1999, 2000; Schummer et al., 2010). In the ASS system the air is pumped through a glass-fiber filter and a resin plug where the molecules are adsorbed (Dobson et al., 2006). XAD-2 resin-based is the most popular sampler available in the market (Schummer et al., 2012).

Yusà et al. (2009), reviewing the presence of pesticides in air, detected approximately one hundred pesticides using ASS. In general, the reported values are the sum of the pesticides present in both the gas and particle phases, although some studies reported them separately. Concentrations of pesticides in air ranged from small to large amounts, given in pg and ng per m^3. Several of the active ingredients detected are currently banned pesticides according to EU regulations (CEU, 1991).

Brazil is one of the world's top exporters of food, but to support the high production together with the climate conditions that favor pest and diseases the country became an enticing market for pesticides, even legacy pesticides (no longer in use around the world due to bans or restrictions). Although there is still a large knowledge gap regarding the environmental levels of pesticides in the majority of the Brazilian States, some studies have been reporting the presence of pesticides in both abiotic and biotic environmental matrices (Souza et al., 2008; Lailson–Brito et al., 2010; Oliveira et al., 2015; Campanha et al., 2015). However, only few studies have been investigating the occurrence and transport of pesticides in air. Meire et al. (2012) reported the occurrence of endosulfan, chlorpyrifos, hexachlorocyclohexanes, dieldrin, heptachlor epoxide and DDT in Brazilian tropical and subtropical mountains. Nevertheless, it is not possible to find any other study referring to the occurrence of pesticides in air in Rio Grande do Sul (RS) State.

RS is situated in Southern Brazil, which is one of the largest states in the country with approximately 281.730 km^2 and 11.207.274 habitants (IBGE, 2014). Agriculture is among the main economy activities in RS, covering approximately 70% of the state area. Soybean, rice, maize and wheat, are the most important crops, representing the largest portion of the agricultural activities (IBGE, 2014). However, crop activities are strongly dependent on the use of pesticides due to climatic and soil conditions. RS consume a total of 50.000 tons of pesticides active ingredients, which represents about 10% of the national consumption (IBAMA, 2013).

The occurrence of pesticides in atmosphere has been widely studied in many countries. However, these studies are still very limited and scarce in RS, as well in Brazil, creating a lack of knowledge about the air quality. Therefore, it is necessary to identify their source and quantify their presence in air. Identify and monitor the presence of pollutants in air is of critical importance in an attempt to keep a safe air quality for the health of human beings. Furthermore, gives valuable information to develop national and international control strategies on emission, production and usage of pesticides. Thus, the aim of this study was to survey the presence of 97 pesticides in the atmosphere on rural and urban areas in six geographically different regions in RS. The present work represents the first screening of pesticides in the atmosphere in RS. Thus, these data may be very useful for future epidemiological and environmental studies.

Material and methods

Reagents and chemicals

Analytical standards of the pesticides were obtained from Dr. Ehrenstorfer (Augsburg, Germany), with purity above 95%. Full-scan mass spectrometric analysis revealed no contamination. In total 97 pesticides were analyzed, which are listed in Table 1. HPLC grade methanol (MeOH), acetonitrile (MeCN), and optima grade acetic acid (HAc) from J. T. Baker (Phillipsburg, USA) were purchased for this study. Ammonium acetate was purchased from Merck (Darmstadt, Germany). Ultrapure water was obtained with a Milli-Q Direct UV3® system from Millipore (Molsheim, France). Vortex mixer model QL-901 was acquired from Microtécnica (Curitiba, Brazil). The polymeric SPE sorbent cartridges Oasis® HLB (60 mg; 3 mL) was acquired from Waters (Wexford, Ireland).

Table 1. Analyzed pesticides.

Fungicides				
Azoxystrobin	Bitertanol	Boscalid	Bromuconazole	Carbendazim
Carboxin	Dichlofluanid	Difenoconazole	Epoxiconazole	Fenarimol
Fenpropimorph	Fluquinconazole	Flutolanil	Imazalil	Iprovalicarb
Mepronil	Metalaxyl	Metconazole	Myclobutanil	Propiconazole
Pyraclostrobin	Pyrazophos	Pyrimethanil	Quinoxyfen	Tebuconazole
Tetraconazole	Thiabendazole	Thiophanate	Tolclofos-methyl	Triadimefon
Triadimenol	Tricyclazole	Trifloxystrobin	Triflumizole	
Herbicides				
2,4 - D	Atrazine	Azimsulfuron	Bentazone	Bispyribac-sodium
Chlorimuron-ethyl	Chlorpropham	Ethoxysulfuron	Fluroxypyr	Imazapic
Imazapyr	Imazethapyr	Linuron	Metsulfuron	Monolinuron
Pendimethalin	Picloram	Propanil	Propazine	Pyrazosulfuron-ethyl
Pyridate	Quinclorac	Simazine	Sulfentrazone	
Insecticides				
Azinphos-ethyl	Azinphos-methyl	Buprofezin	Carbaryl	Carbofuran-3-OH

Carbofuran	Chlorpyrifos-ethyl	Chlorpyrifos-methyl	Deltamethrin	Diazinon
Dimethoate	Fenthion	Fipronil	Imidacloprid	Lufenuron
Malathion	Mecarbam	Methiocarb sulfone	Methiocarb methyl	Mevinphos
Monocrotophos	Oxamyl	Paraoxon	Pirimicarb	Pirimiphos-ethyl
Pirimiphos-methyl	Profenofos	Propargite	Propoxur	Pyridaben
Pyridafenthion	Sulfathiazole	Terbufos	Thiacloprid	Thiamethoxam
Thiodicarb	Triazophos	Trichlorfon	Vamidothion	

Sampling locations and procedures

RS state is located in Southern Brazil, as shown in Figure 1. Lies within the South temperate zone and its climate is predominantly humid subtropical (Cfa, according to the Köppen climate classification). There are four relatively well-marked seasons and rainfall is well distributed throughout the year, with an annual average ranging from 1300 to 1800 mm (Table 2).

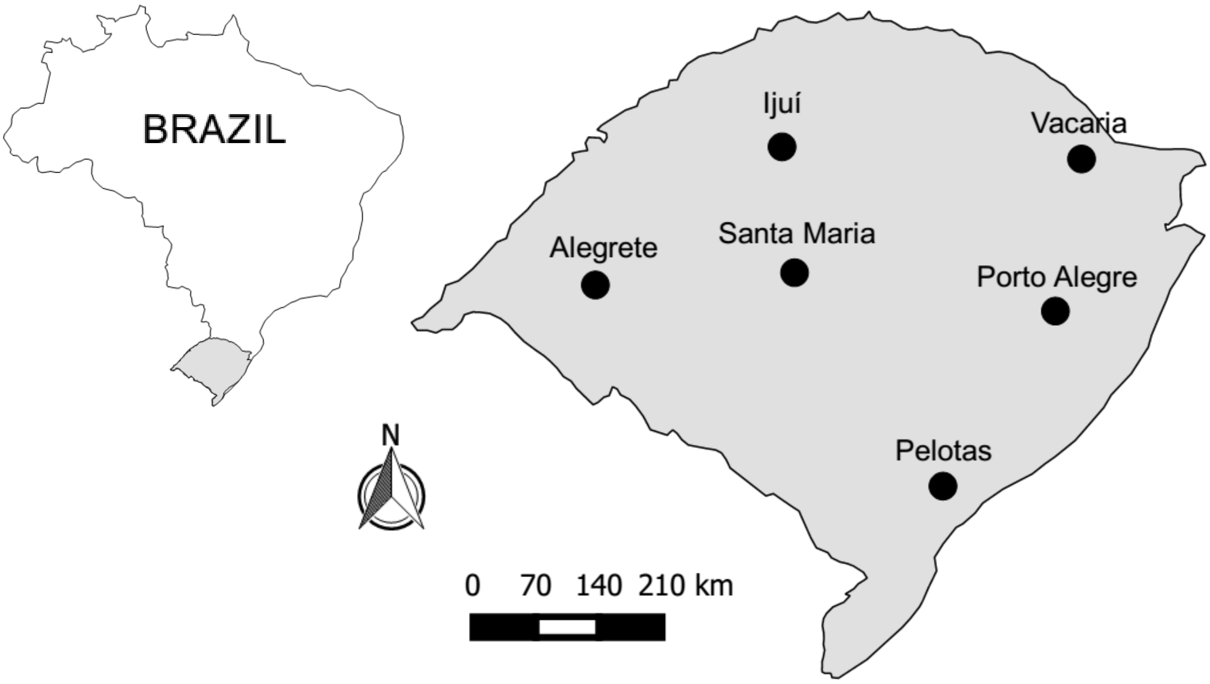

Figure 1. Sampling sites in Rio Grande do Sul.

Air samples from rural and urban areas were collected in September and December 2013 and February and June 2014, which were considered as four sampling seasons (spring, summer, fall and winter). Sampling was performed at six locations in RS: Porto Alegre, Vacaria, Ijuí, Santa Maria, Alegrete and Pelotas

(Figure 1). The sites were selected on the basis of their geographic distribution and agricultural influence covering a wide range of features, which could represent the air quality in the whole State. Therefore, several pollution levels, pesticides, regions and crops were covered. Corn, soybeans and wheat are the main crops cultivated in Northern region of RS (Ijuí, Vacaria), while in the South rice, soybean and cattle production cover the majority of the agricultural activities (Alegrete, Santa Maria, Porto Alegre and Pelotas).

At least two samples were collected in each locality, one from the rural (a radius around 20 km from the edge cities) and other from the urban area (always in the center of the cities), per season. In total 48 samples were collected. Air samples were collected using OVS (OSHA Versatile Sampler) tubes containing XAD-2 (glass fiber filter) sorbent (140/270 mg sorbent), 8 X 75-mm size, connected to a SKC air sampling pump (PCXR8KD) operated at a flow rate of one liter per minute (LPM) for 24 hours. Samples were taken two meters (m) above the ground. All samplers were equipped with calibrated SKC pumps. XAD-2 resin and glass fiber filters were chosen, respectively, for sampling the atmospheric gas and aerosol phases because they are proven to be effective for a large range of compounds (Billings and Bildeman, 1983; Kaupp and Umlauf, 1992; Haraguchi et al., 1994).

Table 2. Geographic coordinates of rural (R) and urban (U) areas, average temperature (AT) and cumulative rainfall from six sampling sites in Rio Grande do Sul State during the studied period.

City	Geographic coordinate		Spring		Summer		Fall		Winter	
	Urban	Rural	AT (°C)	CR (mm)	AT (°C)	CR (mm)	AT (°C)	CR (mm)	AT (°C)	CR (mm)
Ijuí	28°23’24.94’’S 53°55’55.49’’W	28°07’22.28’’S 53°54’38.44’’W	20	566	25	559	19	721	15	731
Alegrete	29°47’34.80’’S 55°48’04.70’’W	29°42’32.63’’S 55°51’53.77’’W	20	433	25	395	19	546	15	319
Santa Maria	29°41’01.37’’S 53°48’35.76’’W	29°45’51.80’’S 54°03’30.67’’W	19	497	25	487	19	546	15	712
Vacaria	28°30’19.10’’S 50°56’22.23’’W	28°25’12.12’’S 50°51’40.66’’W	17	571	22	500	17	552	13	599
Porto Alegre	30°01’42.25’’S 51°11’22.92’’W	30°02’43.40’’S 51°22’33.27’’W	20	453	26	304	20	284	16	630
Pelotas	31°46’10.72’’S	31°48’39.53’’S	18	456	24	550	19	320	15	419

	52°20’19.09’’W	52°31’37.76’’W

After each sampling procedure the samples were closed, placed in a cooler box and transported to the laboratory for further extraction and analysis. The pesticides analyzed were some of the frequently used in the main crops in RS.

Standard solutions and calibration curves

Stock solutions were prepared by dissolving an exact amount of each pesticide in methanol. A stock mixture of pesticides with the same concentration was obtained from individual stock solutions by measuring and combining the desired volumes. An aliquot from this mixture was then diluted in methanol to obtain concentrations of 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 50.0, 100.0, 200.0 µg L^{-1} used for calibration. Standard solutions were all stored at -18 °C prior be used. Pesticides concentrations (µg L^{-1}) in the samples, mentioned in the following sections, were quantified based on the standard curves. Subsequently the data was adjusted for the final calculations of the compounds in µg L^{-1} of water.

Analytical procedures

Air samples (filters and solid-phase cartridges of XAD-2) were ultrasonically extracted twice with 3 mL of acetonitrile solvent during 20 min in each occasion. Subsequently, the extract was dissolved in 1 mL to be injected in the UHPLC-MS / MS system. For each time point, aliquots of treatments, controls, and blanks were combined prior to analysis.

LC-MS instrumentation and conditions

The chromatographic analyses were performed using UHPLC-MS/MS system (Waters, Milford, USA) equipped with Acquity UPLC^{TM} liquid chromatography; Xevo TQ^{TM} MS/MS triple quadrupole detector equipped with electrospray source, an autosampler, a binary pump and a column temperature controller (Waters, Milford, USA). The separation was achieved using an Acquity UPLC^{TM} BEH C18 (50 x 2.1 mm i.d., 1.7 µm particle size) analytical column at 40 °C. MassLynx 4.1 software

(Waters, Milford, USA) was used for instrument control and data processing. The mobile phase consisted of 98% water, with 2% of methanol (A) and 100% methanol (B), both containing 0.1% formic acid and 5 mmol L^{-1} ammonium formate. The chromatographic method began with an initial mobile phase composition of 5% for solvent B, increased to 100% for 7.5 minute and decreased to 5% for 1 minute, held constant for a further 1.5 minutes. The total run time was 10 min with a flow rate of 0.225 mL min^{-1} and injection volume of 10 µL. Compounds quantification was operated in electrospray ionization positive mode (ESI+) using selected reaction monitoring (SRM). The MS source conditions were as follow: capillary voltage, 2.0 kV; source temperature of 150 °C; desolvation temperature of 500 °C; desolvation gas (N_2) flow, 600 L h^{-1} and cone gas (N_2) flow, 80 L h^{-1}.

Limit of detection (LOD) and limit of quantification (LOQ)

The LOD and LOQ were estimated using the method of signal-to-noise ratio, and the LOD was defined as the lowest concentration at which the analytical signal could be reliably differentiated with a signal-to-noise ratio of 3:1. The LOQ was established as the lowest spiked level concentration, which produced a signal-to-noise ratio of 10:1 with acceptable recovery and precision according to legislation (SANCO, 2013).

Data analysis

In order to evaluate pesticides levels in different water sources and identify their distribution, the water quality dataset was analyzed via descriptive statistics, where the data was transformed to percentage (%) values. The data was presented based on the frequency of pesticides detection in rural and urban areas, as well in the different season along the study.

Results and discussion

The selectivity of the method was assured in the LC analyses, as no interference peaks were detected for the blank samples. The analytical curves presented good linearity with R^2 higher than 0.99 for all the compounds studied. The instrumental limit of detection (LOD) and limit of quantification (LOQ) were 0.31 and 1.04 ng m^{-3}, respectively. Good recoveries of the analytes (77.9 – 102.7%; RSD ≤ 16.7) were obtained for all compounds at the 500 ng g^{-1} fortification level.

In total 97 pesticides were analyzed and 15 were detected, where 2 were herbicides, 7 fungicides and 6 insecticides, which are listed in Table 3, with their use and main physicochemical characteristics. Pesticides were detected in 60% of the air samples, where at least one compound was detected. Considering the total number of samples with pesticides (29), 74 and 22% of them showed the presence of at least 2 and 4 pesticides, respectively.

Table 3. Physico-chemical properties of the 15 pesticides detected in this study (IUPAC, 2015).

Pesticide	Type	Molecular weight (g mol^{-1})	Water solubility (mg L^{-1})	Log K_{ow}[a]	K_{oc} (mL g^{-1})	Soil half-life (days)	P_V (mm Hg)	K_H (atm m^3 mol^{-1})
Atrazine	Herbicide	215.68	35	2.6	100	6-108	2.93x10^{-07}	1.48x10^{-09}
Azoxystrobin	Fungicide	403.4	6.7	2.5	589	121-262	8.25x10^{-13}	7.30x10^{-14}
Carbendazim	Fungicide	191.21	8.0	1.5	350	11-78	6.75x10^{-07}	3.58x10^{-08}
Carbofuran	Insecticide	221.26	322	2.3	22	5.7-60	6.00x10^{-07}	4.94x10^{-10}
Chlorpyrifos	Insecticide	350.89	1.05	-[b]	8151	2-65	1.07x10^{-05}	4.72x10^{-06}
Diazinon	Insecticide	304.35	60	3.8	609	7.5-30	8.98x10^{-05}	6.01x10^{-07}
Epoxiconazole	Fungicide	329.76	7.1	-	-	44-124	7.50x10^{-08}	4.65x10^{-09}
Fenpropathrin	Insecticide	349.42	0.33	-	5000	34	5.70x10^{-06}	1.79x10^{-06}
Malathion	Insecticide	330.36	148	-	1800	1	2.33x10^{-05}	9.87x10^{-09}
Pyraclostrobin	Fungicide	387.80	1.9	-	9304	8-102	1.95x10^{-10}	5.24x10^{-11}
Profenofos	Insecticide	373.63	28	-	2016	7	1.90x10^{-05}	1.63x10^{-08}
Simazine	Herbicide	201.66	5	2.1	130	27-102	6.08x10^{-09}	5.53x10^{-10}
Tebuconazole	Fungicide	307.82	36	3.7	>470	25-365	9.75x10^{-09}	9.87x10^{-11}
Tricyclazole	Fungicide	189.24	596	1.4	169	240-842	2.03x10^{-07}	5.78x10^{-12}
Trifloxystrobin	Fungicide	408.37	0.61	4.5	2377	0.3-3.6	2.55x10^{-08}	2.27x10^{-08}

[a] http://pubchem.ncbi.nlm.nih.gov/; [b] Not determined

In 67 and 45% of the rural and urban samples, respectively, pesticides were detected. Furthermore, the frequency of pesticides was also higher in the rural than urban samples for the majority of them (Table 4). It is important to note, that though the frequency difference between samples from rural and urban areas source were small, the average concentrations in rural area was twice higher for the majority of the pesticides. This behavior was also observed when the maximum concentration is considered. These results were expected, once in RS is not allowed to apply any pesticide in urban areas, which indicates that the source of contamination comes from the rural areas.

Chlorpyrifos and fenpropathrin had the highest frequency, being detected in more than 40% of the samples in rural areas and more than 37% in urban areas. The average and maximum concentrations of these pesticides ranged from 14.6 to 22.9 and from 73.4 to 75.8 ng m^{-3}, respectively in rural area. While in urban areas the average concentration ranged from 5.51 to 8.80 and the maximum concentration from 15.6 to 16.9 ng m^{-3}. Atrazine and azoxystrobin concentrations showed a frequency of 20.8, while the other pesticides had frequencies inferior to 12.5% (Table 4).

Table 4. Frequency (%), maximum (MC) and average (AC) concentrations of the detected pesticides in rural (R) and urban (U) areas from six sampling sites in Rio Grande do Sul State during the studied period.

Pesticides	Frequency (%)		MC (ng m^{-3})		AC (ng m^{-3})	
	R	U	R	U	R	U
Atrazine	20.8	12.5	20.2	1.55	7.21	1.36
Azoxystrobin	20.8	4.17	1.50	1.04	1.38	1.04
Carbendazim	12.5	12.5	9.14	1.80	3.98	1.60
Carbofuran	8.33	-[a]	3.13	-	3.13	-
Chlorpyrifos	50.0	37.5	75.8	16.9	22.9	8.80
Diazinon	4.17	-	1.04	-	1.04	-
Epoxiconazole	4.17	-	1.04	-	1.04	-
Fenpropathrin	41.7	37.5	73.4	15.6	14.6	5.51
Malathion	4.17	4.17	27.8	1.04	27.8	1.04
Pyraclostrobin	12.5	-	1.04	-	1.04	-
Profenofos	4.17	-	2.31	-	2.31	-
Simazine	4.17	-	4.15	-	4.15	-
Tebuconazole	4.17	-	10.3	-	10.3	-
Tricyclazole	8.33	-	7.62	-	7.62	-
Trifloxystrobin	8.33	-	2.08	-	2.08	-

[a] Not detected

Chlorpyrifos has been detected and listed as a pesticide of potential concern in many parts of the world. In a study carried out by Arinaitwe et al. (2016) in Lake Victoria, Africa, chlorpyrifos was the predominant pesticides in air samples, with average concentrations of 93.5, 26.1 and 3.54 ng m^{-3} for 2008, 2009, 2010 sample sets, respectively. The highest concentrations in these periods were 520 and 349 ng m^{-3}. Therefore, these results corroborate with the ones obtained in this study. Furthermore, this insecticide was detected in localities far from the spray site, showing its transport potential in the atmosphere. Jantunen et al. (2015) detected this pesticide in 85% of the samples with an average of 0.41 (± 0.37) pg m^{-3} in the Western Arctic Ocean. Chlorpyrifos was also detected in Bering, Chukchi Seas and the North Pacific (Zhong et al., 2012).

Chlorpyrifos is a broad-spectrum chlorinated organophosphate insecticide and the fifth most widely used pesticide in Brazil (IBAMA, 2013). It is registered for the control of cutworms, corn rootworms, flea beetles and flies, presents in beans, maize, coffee, cotton and wheat cropping fields. In RS is used mainly in wheat and maize. This compound has short to moderate persistence in the environment as a result of several pathways of dissipation, including volatilization (Williams et al., 2014; Pinto et al., 2015). It has a moderate vapor pressure and an intermediate Henry's Law constant (Table 3) in the range of 4.72 x 10^{-06} atm m^3 mol^{-1} (Mackay et al., 2014). According to Lyman et al. (1990) for compounds with Henry's constant (H) between 10^{-07} and 10^{-06} atm m^3 mol^{-1} the volatilization rate is controlled by the slow rate of diffusion through the air. Therefore, its volatilization is slow but possible. The rate at which chlorpyrifos volatilizes in the environment depends on its physical–chemical properties, but also on the properties of the environmental matrix in which it is released.

Fenpropathrin is among the most popular pyrethroid insecticides used to control a range of insects, especially mites and flies, in fruits, vegetables, beans, coffee and mainly in soybean in RS. As for chlorpyrifos, fenpropathrin has a moderate vapor pressure and an intermediate Henry's Law constant (Table 3). Furthermore, it has been proven that continuous use of fenpropathrin causes widespread environmental contamination problems. There are few data available on air levels for fenpropathrin, however, recent reports showed that its residues have been detected in nearly all the tested samples from agricultural zones and urban area (Kuivila et al., 2012; Lao et al., 2010). This scenario indicates a high potential of human exposure to fenpropathrin, which can damage their reproductive, nervous, respiratory, and immune systems (Meeker et al., 2009; Thiphom et al., 2013).

Atrazine was detected in 20.8 and 12.5% of the samples, with the average concentration of 7.21 and 1.36 ng m^{-3} in rural and urban areas, respectively. The maximum concentration was 20.2 in rural and 1.55 ng m^{-3} in urban areas. These results corroborate with the ones obtained by Scheyer et al. (2007) in France before this herbicide was banished, with maximum atmospheric concentrations of 2.5 ng m^{-3} in urban areas and 25 ng m^{-3} in rural areas.

Atrazine belongs to the triazines chemical family and is classified as moderately persistent. Its occurrence has been documented in the United States for a long time in both, air and rain samples, with a frequency higher than 50% of the samples (Majewski et al. 2014). Based on the inability to keep environmental contamination in low levels European Union has banned this herbicide. In Brazil, atrazine is ranked in the third position as the most consumed product (IBAMA, 2013). In RS, this compound has been on the market for many years and rather high amounts are applied over wide areas, mainly in maize and sorghum fields. Therefore, its detection in air samples was expected.

Azoxystrobin and carbendazim are broad spectrum fungicides approved for the use on a wide variety of crops in Brazil, including soybean, wheat and maize, which are widely cultivated in RS. Consequently, due to favorable climate to fungal developments, these fungicides are often used. Therefore, even though they have low vapor pressure and Henry's Law constant they were detected in considerable frequencies in air samples. In February 50% of the samples had both pesticides in rural area (Table 5), which represents an interesting result, since only few data is available for the air concentrations of these fungicides.

Table 5. Pesticides frequency (%) in rural (R) and urban (U) areas from six sampling sites in Rio Grande do Sul during the studied period.

Pesticides	Frequency (%)							
	September 2013		December 2013		February 2014		June 2014	
	R	U	R	U	R	U	R	U
Atrazine	50	33	33	17	-[a]	-	-	-
Azoxystrobin	17	-	17	-	50	17	-	-
Carbendazim	-	-	-	-	50	5	-	-
Carbofuran	-	-	17	-	-	-	17	-
Chlorpyrifos	67	33	33	33	83	67	17	17
Diazinon	-	-	-	-	17	-	-	-
Epoxiconazole	-	-	-	-	17	-	-	-
Fenpropathrin	33	17	50	50	83	67	17	17
Malathion	-	-	-	-	17	17	-	-
Pyraclostrobin	-	-	17	-	33	-	-	-
Profenofos	-	-	-	-	17	-	-	-
Simazine	-	-	17	-	-	-	-	-
Tebuconazole	-	-	-	-	17	-	-	-
Tricyclazole	-	-	-	-	33	-	-	-
Trifloxystrobin	-	-	-	-	33	-	-	-

[a] Not detected

The air vulnerability to contamination by compounds can differ seasonally. Pesticides like chlorpyrifos and fenpropathrin, which were detected in all seasons, had their higher frequencies matching with the spray occasions on the main crops in RS. In general the frequencies and average concentration (Figure 2) of the most pesticides were higher during December and February, which corresponded to spring and summer in RS, and in rural areas. In June, concentrations were generally very low or no detectable. Probably this is due to seasonal patterns (increased diseases and pest infestation) which result in an increased spraying frequency during the warm seasons.

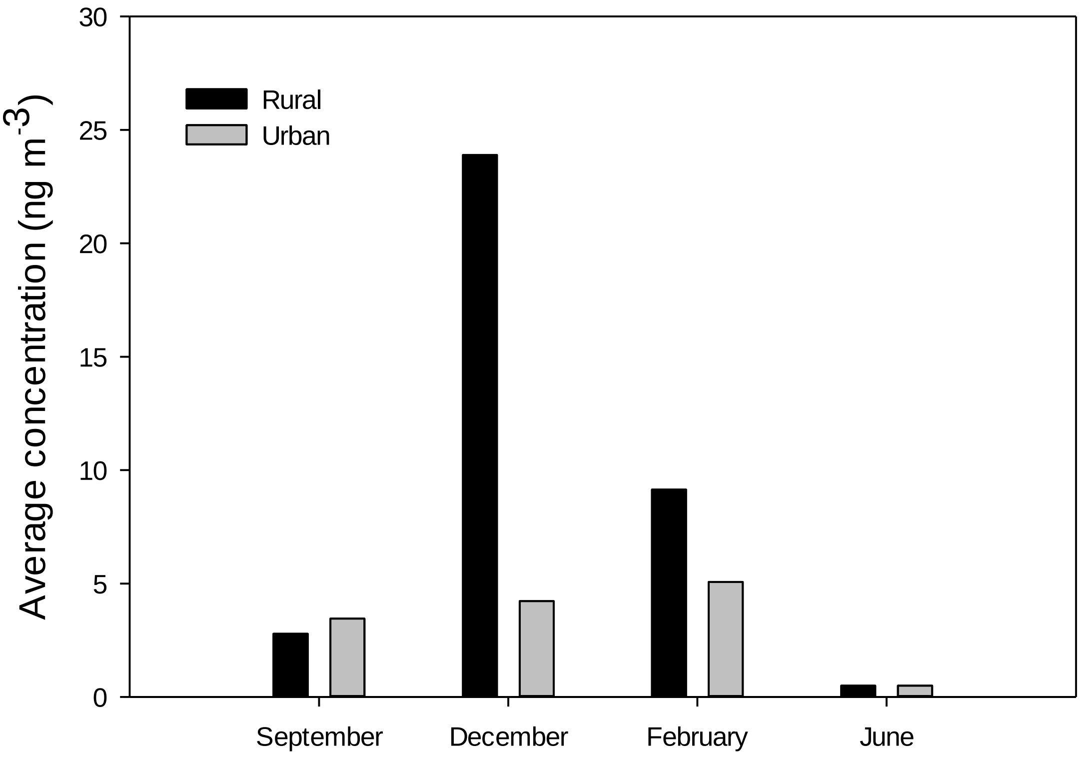

Figure 2. Pesticides concentration average detected in rural and urban areas in four different seasons.

Concentrations lower than 5.00 ng m^{-3} were quantified for 73% of the pesticides detected, whereas in 35% of these the concentration was lower than 1.04 ng m^{-3}. Concentration between 5.00 and 20 ng m^{-3} were quantified for 20% of the pesticides detected, whilst less than 7% had more than 20 ng mL^{-3} (Figure 3). The pesticides with highest concentrations in rural areas were chlorpyrifos, fenpropathrin, malathion and atrazine, with maximum concentrations of 75.8, 73.4, 27.8 and 20.2 ng m^{-3}, respectively. In urban areas chlorpyrifos and fenpropathrin were the most frequently detected with maximum concentrations of 16.9 and 15.6 ng m^{-3}, respectively.

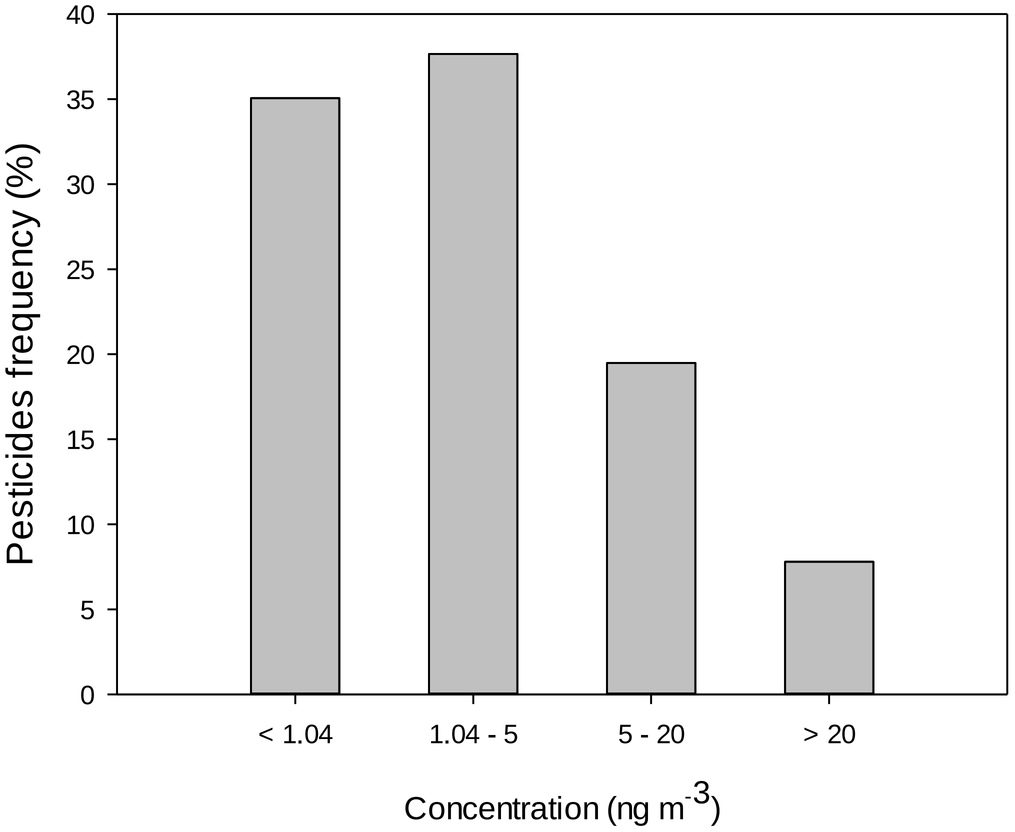

Figure 3. Pesticides frequency and concentrations in all samples during the studied period.

There was not observed significantly differences between the sampling locations (data not shown). In general, the same pesticides were presented in each site in similar concentrations.

In general, the cities are located nearby highly populated areas or intensive agricultural production sites in RS, conditions that are favorable for air contamination by pesticides and can be exacerbated due to tropical climate conditions. The pesticides detected in the air samples demonstrated that there is a contamination issue which creates human health hazard.

The pesticides detected in this study, as atrazine, fenpropathrin and chlorpyrifos are highly toxic to bees, birds, mammals, aquatic life and algae (IUPAC, 2015). Moreover, in humans they are associated with reduced birth weight and birth length (Whyatt et al., 2005), increased risk of mental and motor delay (Rauh et al., 2006), and increased number of problems related to attention and brain structural development (Rauh et al., 2012). Persistent effects due to continuous exposure on cognitive outcomes have been reported for both, rural (Bouchard et al., 2011) and urban populations (Rauh et al., 2011). Results show that volatilization, associated with the great use of pesticides in RS, is an important pathway for their dissipation which consequently becomes a public concern due to human and environment health hazards.

Conclusions

During the experimental period 15 pesticides were detected in the air samples with 60% of the air samples containing traces of at least one pesticide. From the 97 pesticides evaluated approximately 16% were detected. The most frequently pesticides detected were chlorpyrifos, fenpropathrin, atrazine and azoxystrobin. Contamination frequency and levels in rural samples were higher than urban areas. The pesticides with highest concentrations in rural areas were chlorpyrifos, fenpropathrin, malathion and atrazine, with maximum concentrations of 75.8, 73.4, 27.8 and 20.2 ng m^{-3}, respectively. In urban areas chlorpyrifos and fenpropathrin were the most frequently detected with maximum concentrations of 16.9 and 15.6 ng m^{-3}, respectively. The observed pesticide residue levels in air samples correlate with current pesticide applications and rates.

Considering the precautionary principle, continuous monitoring and stronger air quality control are advised in order to gain a more complete knowledge of the environmental status. This is very important if a representative picture of air quality is wanted, mainly because pollutants levels vary both spatially and temporally. Additionally, pollutants monitoring should be complemented with studies dealing with the determination of the effects caused by the contamination, such as risk assessment.

Acknowledgments

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Manuscript 2 – Water, air and soil pollution*

Occurrence of pesticides in drinking water sources of Rio Grande do Sul, Brazil

*Manuscript formatted according to the Journal’s guidelines.

Occurrence of pesticides in drinking water sources of Rio Grande do Sul, Brazil

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Abstract

Monitoring studies dealing with pesticides contamination levels in water in Rio Grande do Sul (RS) State, Brazil, has been very limited and scarce, leading to a lack of knowledge about the water quality in this region. Moreover, most of the pesticides in use in the country are not yet regulated by the environmental or drinking water laws. Thus, the aim of this study was to survey the presence of 97 pesticides in drinking water sources and tap water in six geographically different regions in Rio Grande do Sul, as well to monitor the marked water bottle quality. The sampling was performed in six cities; Porto Alegre, Vacaria, Ijuí, Santa Maria, Alegrete and Pelotas. At least two samples were collect in each locality per season (spring, summer, fall and winter), one from the drinking water source (lakes or rivers) before treatment and other from the tap water after being treated by the municipal water company. According to the results, residues of 33 pesticides occurred in the samples analyzed. The 12 brands of mineral water analyzed did not show the presence of pesticides. In water source and tap water, traces of at least one pesticide were detected in 100% of the samples. Among the monitored pesticides, the most frequently found were atrazine, azoxystrobin, carbendazim and imidacloprid. The pesticides with higher concentrations in drinking water sources were azoxystrobin and 2,4-D, with maximum concentrations of 14.3 and 1.94 μg L^{-1}, respectively. In tap water propanil, 2,4-D, quinclorac and bentazone were the ones with higher concentration detected, being the maximum concentration of 4.11, 3.78, 2.57 and 1.45 μg L^{-1}, respectively. Contamination frequency and levels in tap water and drinking water source were similar, which suggest that the municipal water treatments are not able to remove pesticides. The majority of the samples in this study exceed the regulated drinking water concentration thresholds for pesticides in EU.

Keywords: environmental; seasonal; atrazine; azoxystrobin; contamination; quality

Introduction

Rio Grande do Sul (RS) State, situated in Southern Brazil, is one of the largest states in the country with approximately 281.730 km^2 and 11.207.274 habitants (IBGE, 2014). One of the main economy activities in RS is agriculture. In the national territory soybean, rice, maize and wheat, are the most important crops representing the largest portion of the agricultural activities. RS is responsible for approximately 68% of the national rice, 7% of maize, 40% of wheat and 10% of soybean production (IBGE, 2014). However, these crop practices are strongly dependent on the use of pesticides due to climatic and soil conditions.

Pesticides provide incontrovertible benefits to obtain high crop yields, however, it has been verified that their use cause widespread contamination, which is harmful to environmental safety and human health (Bhanti and Taneja 2007; Zhang et al. 2010). Therefore, pesticides are a vast class of organic compounds with enormous impact in the environment, especially as contaminants of surface and groundwater resources, being considered an increasing threat worldwide (Plakas and Karabelas, 2012).

The presence of pesticides in water occurs mainly due to transport of these compounds via runoff and/or leaching from the field to other environmental compartments. Furthermore, the careless disposal of empty containers and the cleaning process of spraying equipment are also important sources of contamination (Reichenberger et al., 2007). Pesticides physicochemical properties like half-life, solubility in water and organic solvents determine their transport potential and character to reach the surface and ground waters (Brown and Beinum, 2009).

Decades of monitoring studies have documented the occurrence of pesticide residues at trace concentrations (on the order of mg L^{-1} and lower) in water resources around the world (Moschet et al., 2014). Loos et al. (2009) reported the occurrence of persistent organic pollutants in European rivers, where samples from over 100 rivers from 27 European countries were analyzed for 35 compounds. Only 10% of the samples analyzed could be classified as “very clean” in terms of chemical pollution. The fifth Global Environment Outlook by the UNEP (2014) reported the contamination level of the main rivers and streams in United States, where one or more pesticides were detected with a frequency higher than 90%.

The harmful effects of pesticides for human health and environment have led to the adoption of stringent legislation with the objective of preserving, protecting an improving the quality and purity of drinking water. Different international legislations such as the European Union (EU), United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) established maximum concentrations for pesticides in drinking water. Particularly, the EU settled very strict limits for pesticides in drinking water of 0.1 µl l^{-1} for individual compounds and 0.5 µl l^{-1} for the sum of pesticides (Council of the European Communities, 1998). However, despite these legislations, pesticides frequently exceed regulated drinking water concentration thresholds (Benner et al., 2013).

Furthermore, drinking water sources contaminated with pesticides represent a risk to the tap water supply by the municipal pipeline, as well to the bottle water marketed. Therefore, during the water treatment some cost-effective techniques are used for cleaning in order to increase the water quality. The most commonly available and traditionally used water treatment processes in the municipal level are flocculation, filtration, sedimentation, activated sludge and chlorination. However, these are not effective in totally eliminate the pesticides (Benner et al., 2013; Ternes et al., 2005; Rivera-Utrilla et al., 2013). Consequently, monitoring the occurrence of pesticides in the marketed water bottle and tap water are also important to allow an integrative assessment and an appropriate evaluation of the risk to human health.

The occurrence of pesticides in aquatic ecosystems has been widely studied in many countries. However, these studies are still very limited and scarce in RS, as well in Brazil, creating a lack of knowledge about the water quality. Moreover, the majority of the pesticides are not yet regulated by the environmental or drinking water laws. Therefore, there is the need in identify the source and quantify their presence in the drinking water. Identification and monitoring of these pollutants is of critical importance in an attempt to keep drinking water quality safe for human beings health. Thus, the aim of this study was to survey the presence of 97 pesticides in drinking water sources and tap water in six geographically different regions of the RS, as well in marketed water bottle, consequently assessing the efficiency of municipal drinking water treatment processes to remove pesticide. The data obtained from the analysis of water samples collected in these regions may be very useful for future epidemiological and environmental studies.

Material and methods

Reagents and chemicals

Analytical standards of the pesticides were obtained from Dr. Ehrenstorfer (Augsburg, Germany), with purity above 95%. Full-scan mass spectrometric analysis revealed no contamination. In total 97 pesticides were analyzed, which are listed in Table 1. HPLC grade methanol (MeOH), acetonitrile (MeCN), and optima grade acetic acid (HAc) from J. T. Baker (Phillipsburg, USA) were purchased for this study. Ammonium acetate was purchased from Merck (Darmstadt, Germany). Ultrapure water was obtained with a Milli-Q Direct UV3$^{®}$ system from Millipore (Molsheim, France). Vortex mixer model QL-901 was acquired from Microtécnica (Curitiba, Brazil). The polymeric SPE sorbent cartridges Oasis$^{®}$ HLB (60 mg; 3 mL) was from Waters (Wexford, Ireland).

Table 1. Analyzed pesticides.

Fungicides				
Azoxystrobin	Bitertanol	Boscalid	Bromuconazole	Carbendazim
Carboxin	Dichlofluanid	Difenoconazole	Epoxiconazole	Fenarimol
Fenpropimorph	Fluquinconazole	Flutolanil	Imazalil	Iprovalicarb
Mepronil	Metalaxyl	Metconazole	Myclobutanil	Propiconazole
Pyraclostrobin	Pyrazophos	Pyrimethanil	Quinoxyfen	Tebuconazole
Tetraconazole	Thiabendazole	Thiophanate	Tolclofos-methyl	Triadimefon
Triadimenol	Tricyclazole	Trifloxystrobin	Triflumizole	
Herbicides				
2,4 - D	Atrazine	Azimsulfuron	Bentazone	Bispyribac-sodium
Chlorimuron-ethyl	Chlorpropham	Ethoxysulfuron	Fluroxypyr	Imazapic
Imazapyr	Imazethapyr	Linuron	Metsulfuron	Monolinuron
Pendimethalin	Picloram	Propanil	Propazine	Pyrazosulfuron-ethyl
Pyridate	Quinclorac	Simazine	Sulfentrazone	
Insecticides				
Azinphos-ethyl	Azinphos-methyl	Buprofezin	Carbaryl	Carbofuran-3-OH
Carbofuran	Chlorpyrifos-ethyl	Chlorpyrifos-methyl	Deltamethrin	Diazinon
Dimethoate	Fenthion	Fipronil	Imidacloprid	Lufenuron
Malathion	Mecarbam	Methiocarb sulfone	Methiocarb methyl	Mevinphos

Monocrotophos	Oxamyl	Paraoxon	Pirimicarb	Pirimiphos-ethyl
Pirimiphos-methyl	Profenofos	Propargite	Propoxur	Pyridaben
Pyridafenthion	Sulfathiazole	Terbufos	Thiacloprid	Thiamethoxam
Thiodicarb	Triazophos	Trichlorfon	Vamidothion	

Sampling locations and procedures

RS state is located in Southern Brazil, as shown in Figure 1. Lies within the south temperate zone and its climate is predominantly humid subtropical (Cfa, according to the Köppen climate classification). There are four relatively well-marked seasons and rainfall is well distributed throughout the year. The annual average rainfall ranges from 1300 and 1800 mm (Table 2).

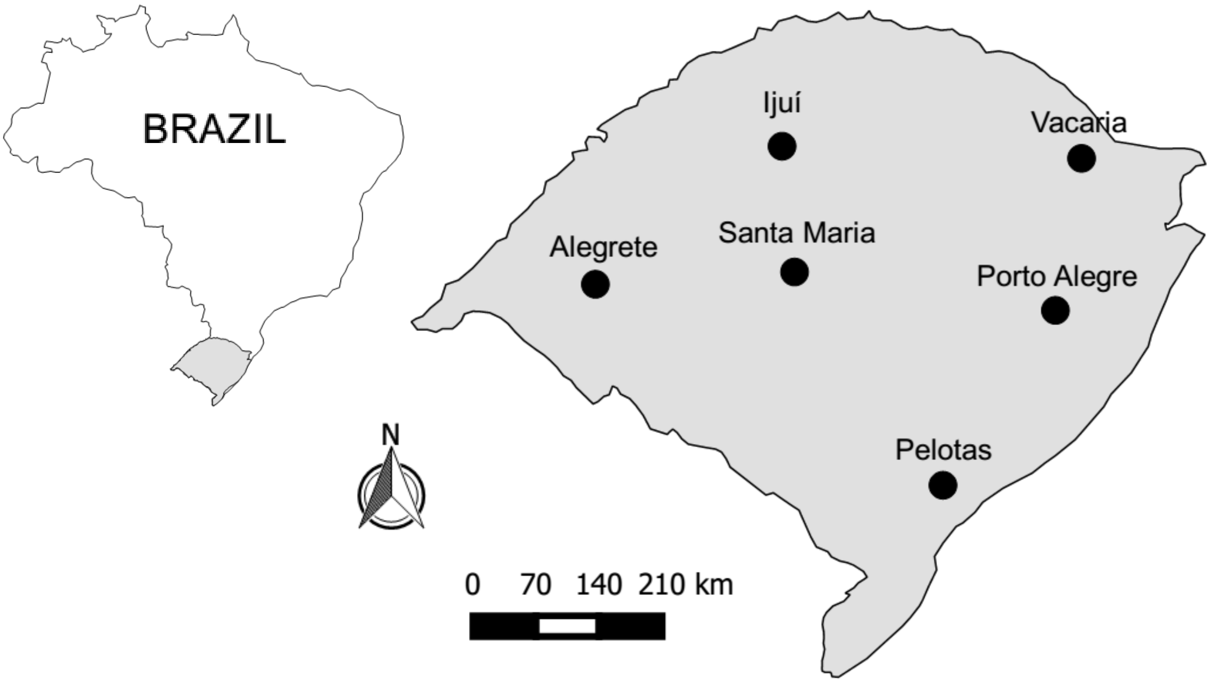

Figure 1. Sampling sites in Rio Grande do Sul.

Samples from municipal drinking water sources were collected in September and December of 2013 and February and June of 2014, which were considered as four sampling seasons (spring, summer, fall and winter). Sampling was performed at six locations across the RS: Porto Alegre, Vacaria, Ijuí, Santa Maria, Alegrete and Pelotas (Figure 1). The sites were selected on the basis of geographic distribution and agricultural influence to cover a wide range of features, which were able to represent the water quality in RS sources, once various pollution levels, different pesticides, regions and crops were considered. Corn, soybean and wheat are the main crops cultivated in Northern RS (Ijuí, Vacaria), while in the South rice, soybean and cattle production cover the majority of the agricultural activities (Alegrete, Santa Maria, Porto Alegre and Pelotas).

Table 2. Geographic coordinate of cities, sampling site of source water, average temperature (AT) and cumulative rainfall from six sampling sites in Rio Grande do Sul State during the studied period.

City	Geographic coordinate		Spring		Summer		Fall		Winter	
	City	Source water	AT (°C)	CR (mm)	AT (°C)	CR (mm)	AT (°C)	CR (mm)	AT (°C)	CR (mm)
Ijuí	28°23'24.94''S 53°55'55.49''W	Potiribú River	20	566	25	559	19	721	15	731
Alegrete	29°47'34.80''S 55°48'04.70''W	Ibirapuitã River	20	433	25	395	19	546	15	319
Santa Maria	29°41'01.37''S 53°48'35.76''W	Rodolfo Costa e Silva and DNOS lakes	19	497	25	487	19	546	15	712
Vacaria	28°30'19.10''S 50°56'22.23''W	Vacaria lake	17	571	22	500	17	552	13	599
Porto Alegre	30°01'42.25''S 51°11'22.92''W	Guaíba River	20	453	26	304	20	284	16	630
Pelotas	31°46'10.72''S 52°20'19.09''W	Santa Bárbara lake	18	456	24	550	19	320	15	419

At least two samples were collect in each locality per season, one from the drinking water source (lakes or rivers) before treatment and other from the tap water after being treated by the municipal water company. In total 52 samples were collected. In Vacaria, Santa Maria and Pelotas the municipal water supply is from lakes, while for the others cities the supply come from rivers. Water samples of 1 L were collected and stored in an amber bottle. After each sampling procedure the bottles were closed and placed in a box with ice to being transported to the laboratory, for further extraction and analysis. The compounds analyzed were some of the frequently used pesticides in the main crops of RS. Furthermore, marked water bottles from 12 different brands were also chosen, which represent the most commonly found in the RS market, to be analyzed for the presence of the same 97 pesticides.

Standard solutions and calibration curves

Stock solutions were prepared by dissolving an exact amount of each pesticide in methanol. A stock mixture of pesticides with the same concentration was obtained from individual stock solutions by measuring and combining the desired volumes. An aliquot from this mixture was then diluted in methanol to obtain concentrations of 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 50.0, 100.0, 200.0 µg L^{-1} used for calibration. Standard solutions were all stored at -18 °C prior be used. Pesticides concentrations (µg L^{-1}) in the samples, mentioned in the following sections, were quantified based on the standard curves. Subsequently the data was adjusted for the final calculations of the compounds in µg L^{-1} of water.

Analytical procedures

Samples (500 mL) were filtered with polytetrafluoroethylene (PTFE) membrane (47 mm and 0.45 µm porosity, from Agilent Technologies, Santa Clara, USA). Considering that the pesticides concentration was low, the samples were concentrated to quantify these compounds. Therefore, SPE (Solid Phase Extraction) cartridges (Oasis®HLB 60 mg) were conditioned in sequence with 3 mL of methanol, 3 mL of ultrapure water and 3 mL of water (pH 2.5). Then, 250 mL of each sample, previously acidified to pH 2.5 with aqueous phosphoric acid (1:1, v/v), was transferred to the SPE cartridges through PTFE tubes in a manifold. The adopted percolation flow rate ranged from 2 to 5 mL min^{-1}. After the sample percolation, 3 mL of purified water was passed through the cartridge. For the elution of the pesticides from the cartridge, 2 mL of the mixture methanol and acetonitrile 1% acetic acid (1:1, v/v) was used. Then, 200 µL of eluate was diluted 5 times with water (800 µL) prior to UHPLC-MS/MS analysis. A concentration factor of 25 times was reached with this procedure. For each time point, aliquots of treatments, controls, and blanks were combined prior to analysis.

LC-MS instrumentation and conditions

To carboxin, chlorimuron, diazinon, epoxiconazole, fenpropimorph, imazalil, mepronil, metalaxyl, pirimicarb, pirimiphos, propargite, propoxur and quinoxyfen, chromatographic analyses were performed using UHPLC-MS/MS system (Waters, Milford, USA) equipped with Acquity UPLC^{TM} liquid chromatography; Xevo TQ^{TM} MS/MS triple quadrupole detector equipped with electrospray source, an autosampler, a binary pump and a column temperature controller (Waters, Milford, USA). The separation was achieved using an Acquity UPLC^{TM} BEH C18 (50 x 2.1 mm i.d., 1.7 µm particle size) analytical column at 40 °C. MassLynx 4.1 software (Waters, Milford, USA) was used for instrument control and data processing. The mobile phase consisted of 98% water, with 2% of methanol (A) and 100% methanol (B), both containing 0.1% formic acid and 5 mmol L^{-1} ammonium formate. The chromatographic method began with an initial mobile phase composition of 5% for solvent B, increased to 100% for 7.5 minute and decreased to 5% for 1 minute, held constant for a further 1.5 minutes. The total run time was 10 min with a flow rate of 0.225 mL min^{-1} and injection volume of 10 µL. Compounds quantification was operated in electrospray ionization positive mode (ESI+) using selected reaction monitoring (SRM). The MS source conditions were as follow: capillary voltage, 2.0 kV; source temperature of 150 °C; desolvation temperature of 500 °C; desolvation gas (N_2) flow, 600 L h^{-1} and cone gas (N_2) flow, 80 L h^{-1}.

The remaining pesticides in this trial were detected using chromatographic analyses according to Donato et al. (2015). The LC-MS/MS system was composed by analytical column UPS Pursuit C18 (50 x 3.0 mm i.d., 2.4 µm particle size). The mobile phase was 5 mmol L^{-1} ammonium formate aqueous solution (A) and methanol (B) at a flow rate of 0.150 mL min^{-1}, resulting in a total run time of 15 min. The chromatographic method began with an initial mobile phase composition of 10% for solvent B, kept constant for 3 minutes, increasing to 50% for 1 minute, to 95% for 4 minutes and to 98% for further 3 minutes, kept constant for a further 2 minutes and returning to the initial condition in 2 minutes. The injection volume was 10 µL. Compounds quantification was operated in electrospray ionization positive mode (ESI+) using SRM. The MS source conditions were as follow: capillary voltage, 2.0 kV; source temperature of 50 °C; desolvation temperature of 250 °C.

Limit of detection (LOD) and limit of quantification (LOQ)

The LOD and LOQ were estimated using the method of signal-to-noise ratio, and the LOD was defined as the lowest concentration at which the analytical signal could be reliably differentiated with a signal-to-noise ratio of 3:1. The LOQ was established as the lowest spiked level concentration, which produced a signal-to-noise ratio of 10:1 with acceptable recovery and precision according to legislation (SANCO, 2013).

Data analysis

In order to evaluate pesticides levels in different water sources and identify their distribution, the water quality dataset was analyzed via descriptive statistics, where the data was transformed to percentage (%) values. The data was presented based on the frequency of pesticides detection in drinking water source and tap water, as well in the different season along the study.

Results and discussion

The selectivity of the method was assured in the LC analyses, as no interference peaks were detected for the blank samples. The analytical curves presented good linearity with R^2 higher than 0.99 for all the compounds studied. The instrumental limit of detection (LOD) and limit of quantification (LOQ) were 0.01 and 0.02 µg L^{-1}, respectively. Good recoveries of the analytes (78.3 – 103.6%; RSD ≤ 15.9) were obtained for all compounds at the 500 ng g^{-1} fortification level.

In total 97 pesticides were analyzed and 33 were detected, where 11 were herbicides, 13 fungicides and 9 insecticides, which are listed in Table 3, with their use and main physico-chemical characteristics. The 12 brands of mineral water analyzed did not show the presence of pesticides. Pesticides were detected in 100% of the samples from drinking water source and tap water, where at least one compound was detected. Considering the total number of samples (52), 83 and 50% of them showed the presence of at least 2 and 5 pesticides, respectively. The frequency of pesticides was higher in the drinking water source than tap water for the majority of them, though the difference between sample source was small (Table 4). The highest difference was observed for carbendazim, where the frequency in drinking water source and tap water were 89.29 and 12.50%, respectively. Probably the low frequency in tap water can be associated with its low water solubility. Other pesticides which demonstrate a significant reduction in tap water were imazethapyr, propoxur, simazine and thiamethoxam. Furthermore, fenpropimorph, imazalil, linuron, mepronil, pirimicarb, pirimiphos and propargite were detected only in tap water in frequencies lower than 10%.

Atrazine, azoxystrobin, carbendazim and imidacloprid had the highest frequency, being detected in more than 50% of the samples, both in drinking water source and tap water. The average concentrations of these pesticides ranged from 0.024 to 0.061 μg L^{-1}. For bentazone, carbofuran, imazapyr, imazethapyr, propoxur, quinclorac, simazine, tebuconazole and thiamethoxan the frequencies ranged from 20 to 50%, while for the other pesticides the frequency was inferior to 20%.

Table 3. Physico-chemical properties of the 33 detected pesticides in this study (IUPAC, 2015).

Pesticide	Type	Molecular weight (g mol^{-1})	Water solubility (mg L^{-1})	K_{ow}[a]	K_{oc} (mL g^{-1})	Soil half-life (days)	Soil Mobility	GUS[c]
2,4-D	Herbicide	221.04	24300	2.81	39.3	22-38	Mobile	1.69
Atrazine	Herbicide	215.68	35	2.61	100	6-108	Moderately	3.20
Azoxystrobin	Fungicide	403.4	6.7	2.50	589	121-262	Moderately	2.65
Bentazone	Herbicide	240.3	570	2.80	55.3	4-21	Moderately	3.41
Carbendazim	Fungicide	191.21	8.0	1.52	350	11-78	Moderately	2.53
Carbofuran	Insecticide	221.26	322	2.32	22	5.7-60	Moderately	2.28
Carboxin	Fungicide	235.30	134	2.30	99.4	0.27-11	Very mobile	-2.15
Chlorimuron	Herbicide	414.82	1200	2.50	106	14-42	Moderately	3.16
Difenoconazole	Fungicide	406.26	15.0	4.4	3759	53-456	Slightly	0.90
Diazinon	Insecticide	304.35	60	3.81	609	7.5-30	Slightly	1.14
Epoxiconazole	Fungicide	329.76	7.1	-[b]	-	44-124	Slightly	2.28
Fenpropimorph	Fungicide	303.48	4.32	-	-	8-51	Non mobile	0.46
Fipronil	Insecticide	437.15	3.78	4.0	>825	5-135	Slightly	2.45
Imazalil	Fungicide	297.18	184	-	-	5-7	Non mobile	0.61
Imazapic	Herbicide	275.30	2230	0.4	137	31-410	Moderately	3.87
Imazapyr	Herbicide	261.28	9740	0.22	8.81	5-17	Moderately	1.98
Imazethapyr	Herbicide	289.33	1400	1.49	52	14-290	Mobile	6.19
Imidacloprid	Insecticide	255.66	610	0.57	220	77-341	Moderately	3.74
Linuron	Herbicide	249.09	63.8	3.20	739	13-82	Slightly	2.34
Mepronil	Fungicide	269.33	12.7	-	974	50	Slightly	1.72
Metalaxyl	Fungicide	279.33	8400	1.65	162	19-113	Moderately	2.79
Pirimicarb	Insecticide	238.39	3100	1.7	>56	5-13	Moderately	2.73
Pirimiphos	Insecticide	305.33	11	4.12	1100	18-67	Moderately	1.91
Propanil	Herbicide	218.08	95	3.07	152	3	Moderately	-0.72
Propargite	Insecticide	350.47	0.215	5.7	2963	10-240	Non mobile	-1.31
Propoxur	Insecticide	209.24	1800	1.52	30	79	Mobile	3.73
Quinclorac	Herbicide	242.06	0.07	0.266	50	168-913	Mobile	6.29
Quinoxyfen	Fungicide	308.13	0.047	4.66	3600	13-508	Non mobile	-0.93
Simazine	Herbicide	201.66	5	2.18	130	27-102	Slightly	2.00
Tebuconazole	Fungicide	307.82	36	3.7	>470	25-365	Slightly	2.85
Thiamethoxam	Insecticide	291.71	4100	-0.13	70	34-233	Mobile	4.69
Tricyclazole	Fungicide	189.24	596	1.4	169	240-842	Moderately	5.34
Trifloxystrobin	Fungicide	408.37	0.61	4.5	2377	0.3-3.6	Slightly	0.19

[a] http://pubchem.ncbi.nlm.nih.gov/; [b] Not determined; [c] Potential leachers (GUS > 2.8), non-leachers (GUS < 1.8) and transient leachers (1.8 < GUS < 2.8).

Table 4. Frequency (%), maximum (MC) and average (AC) concentrations of the detected pesticides in drinking water source (S) and tap water (T) from six sampling sites in Rio Grande do Sul State during the studied period.

Pesticides	Frequency (%)		MC ($\mu g\ L^{-1}$)		AC ($\mu g\ L^{-1}$)	
	S	T	S	T	S	T
2,4-D	10.71	8.33	1.94	3.78	1.940	2.980
Atrazine	67.85	50.00	0.13	0.09	0.061	0.047
Azoxystrobin	60.71	75.00	14.3	0.12	0.040	0.036
Bentazone	17.85	16.67	0.53	1.45	0.270	0.069
Carbendazim	89.29	4.17	0.07	0.03	0.039	0.024
Carbofuran	17.85	20.83	0.04	0.04	0.030	0.029
Carboxin	3.57	-	0.03	-	0.029	-
Chlorimuron	3.57	-	0.13	-	0.130	-
Difenoconazole	10.71	8.33	0.13	0.07	0.057	0.054
Diazinon	3.57	4.17	0.07	0.03	0.069	0.025
Epoxiconazole	3.57	12.50	0.03	0.04	0.023	0.034
Fenpropimorph	-[a]	4.17	-	0.03	-	0.022
Fipronil	3.57	-	0.04	-	0.043	-
Imazalil	-	4.16	-	0.03	-	0.030
Imazapic	7.14	4.16	0.07	-	0.070	-
Imazapyr	21.43	20.83	0.05	0.03	0.026	0.022
Imazethapyr	42.86	12.50	0.17	0.09	0.069	0.058
Imidacloprid	71.43	66.67	0.29	0.14	0.035	0.034
Linuron	-	4.16	-	0.02	-	0.020
Mepronil	-	4.16	-	0.02	-	0.020
Metalaxyl	7.14	4.16	0.02	0.02	0.020	0.020
Pirimicarb	-	8.33	-	0.02	-	0.020
Pirimiphos	-	4.17	-	0.07	-	0.070
Propanil	3.57	4.17	0.02	4.11	0.020	4.110
Propargite	-	4.17	-	0.02	-	0.020
Propoxur	21.43	8.33	0.04	0.02	0.033	0.020
Quinclorac	17.86	12.50	0.13	2.57	0.096	0.094
Quinoxyfen	3.57	12.50	0.03	0.06	0.023	0.039
Simazine	25.57	16.67	0.08	0.04	0.033	0.031
Tebuconazole	17.85	8.33	0.09	0.03	0.035	0.027
Thiamethoxam	32.14	16.67	0.06	0.06	0.040	0.046
Tricyclazole	10.71	8.33	0.03	0.02	0.024	0.020
Trifloxystrobin	3.57	4.17	0.04	0.02	0.032	0.020

[a] Not detected

Atrazine belongs to the triazines chemical family, which is an herbicide considered as moderately persistent and mobile in soil. It has been constantly detected in water sources in many parts of the word (UNEP, 2014). Based on the inability to keep water contamination in low levels EU banned this pesticide. In RS, this compound has been on the market for many years and rather high amounts are applied over wide areas, mainly in maize and sorghum fields. Therefore, its detection in water samples was expected. Montagner et al. (2014) detected this herbicide in 50% of the tap water samples from São Paulo (Brazil), which is in accordance with the results obtained in this study, where atrazine’s frequency was also 50%. This herbicide is one of the few pesticides with regulated concentrations in surface water in Brazil, with a maximum allowed concentration of 2 μg L^{-1} (CONAMA, 2005). In this study the concentrations detected were below this limit. However, due to high frequency in the tap water samples and some evidence that exposure to atrazine may be associated with cancer and health hazards (Rusiecki et al., 2004), this compound deserves special attention.

Azoxystrobin and carbendazim are broad spectrum fungicides approved for the use on a wide variety of crops in Brazil, including soybean, wheat and maize, which are widely cultivated in RS. Consequently, due to favorable climate to fungal developments, these fungicides are often used in the country. These compounds are often found in water samples, even though they have low water solubility, moderately soil and water mobility. In a study by Battaglin et al. (2010) the authors reported that azoxystrobin was the most frequently detected pesticide in water samples (45%) in US. Another study by Montagner et al. (2014) reports carbendazim as the most frequent pesticide detected in São Paulo (Brazil) rivers and tap water, (85 and 5.6% of the samples, respectively), results that corroborate with the ones obtained in this study.

Imidacloprid is an insecticide traditionally used in RS, mainly in rice, soybean, wheat and maize fields. It was detected in more than 65% of both, drinking water and tap water samples. These results are in accordance with Bortoluzzi et al. (2007) that reported imidacloprid presence in more than 50% of the water samples in RS. Imidacloprid has high solubility, low k_{ow} and is persistent in water, still is one of the most widely used insecticides in the world (Dijk et al., 2013), factors which indicate its high water contamination potential. According with Dijk et al. (2013), imidacloprid concentration in surface water exceeds the water quality regulations in many parts of Netherlands.

The water vulnerability to contamination by compounds can differ seasonally. Atrazine, azoxystrobin, carbendazim and imidacloprid were present in all seasons (Table 5). The high frequency of atrazine corresponded with the spraying time of this herbicide in sorghum and maize fields, between December and February, reaching a frequency of 86% in the samples. Imidacloprid, even though can be used also in winter crops, has higher demand in summer crops, therefore in this period it was detected in 87% of the samples . Azoxystrobin and carbendazim showed high frequency in all seasons, mainly due to their broad spectrum allowing the used during the whole year.

Table 5. Pesticides detection frequency (%) in drinking water source (S) and tap water (T) from six sampling sites in Rio Grande do Sul during the studied period.

Pesticides	Frequency (%)							
	September 2013		December 2013		February 2014		June 2014	
	S	T	S	T	S	T	S	T
2,4-D	-	-	-	-	-	17	43	17
Atrazine	57	17	86	83	86	83	43	13
Azoxystrobin	29	33	57	100	57	67	100	100
Bentazone	-	-	14	17	14	33	43	17
Carbendazim	86	17	100	-	100	-	71	-
Carbofuran	14	17	14	17	14	17	29	33
Carboxin	-	-	-	-	-	-	14	-
Chlorimuron	-	-	-	-	14	-	-	-
Difenoconazole	-	-	-	17	14	-	29	17
Diazinon	-	17	-	-	-	-	14	-
Epoxiconazole	-	33	-	-	14	17	-	-
Fenpropimorph	-	17	-	-	-	-	-	-
Fipronil	-	-	14	-	-	-	-	-
Imazalil	-	17	-	-	-	-	-	-
Imazapic	-	-	14	17	14	-	-	-
Imazapyr	14	17	43	50	29	17	-	-
Imazethapyr	43	-	57	17	43	17	29	17
Imidacloprid	43	33	86	67	87	83	71	83
Linuron	-	-	-	-	-	17	-	-
Mepronil	-	17	-	-	-	-	-	-
Metalaxyl	-	-	29	17	-	-	-	-
Pirimicarb	-	17	-	17	-	-	-	-
Pirimiphos	-	17	-	-	-	-	-	-
Propanil	-	-	-	-	14	17	-	-
Propargite	-	17	-	-	-	-	-	-
Propoxur	14	17	-	-	-	-	71	17
Quinclorac	-	-	29	17	29	33	14	-
Quinoxyfen	-	33	14	17	-	-	-	-
Simazine	29	-	29	33	43	17	14	17
Tebuconazole	-	-	14	-	43	17	14	17
Thiamethoxam	-	-	43	33	29	17	57	17
Tricyclazole	-	-	-	-	29	17	14	17
Trifloxystrobin	-	17	-	-	14	-	-	-

The overall frequencies of the most pesticides were higher during December and February, although the average concentration was higher in February and June for both, drinking water source and tap water (Figure 2). Probably this is due to seasonal patterns (increased diseases and pest infestation) which result in an increased spraying frequency in addition to the great runoff and leaching conditions as a result of more frequent rainfall events. Moreover, rice is one of the main cereals produced in RS being cultivated primarily using flood irrigation, where the flood is kept on the field during the entire crop cycle (IRGA, 2009). This irrigation system method might also increase the occurrence of pesticide runoff from the field during rainfall events, which are frequent in December and February. Runoff can transport pesticides dissolved in solution and/or adsorbed to soil colloids (Watanabe et al., 2007; Chang et al., 2007; Phong et al., 2008). Thereby, the frequency and levels of pesticides detected in water samples in some localities can be strongly associated with leaching and mainly surface runoff from rice fields.

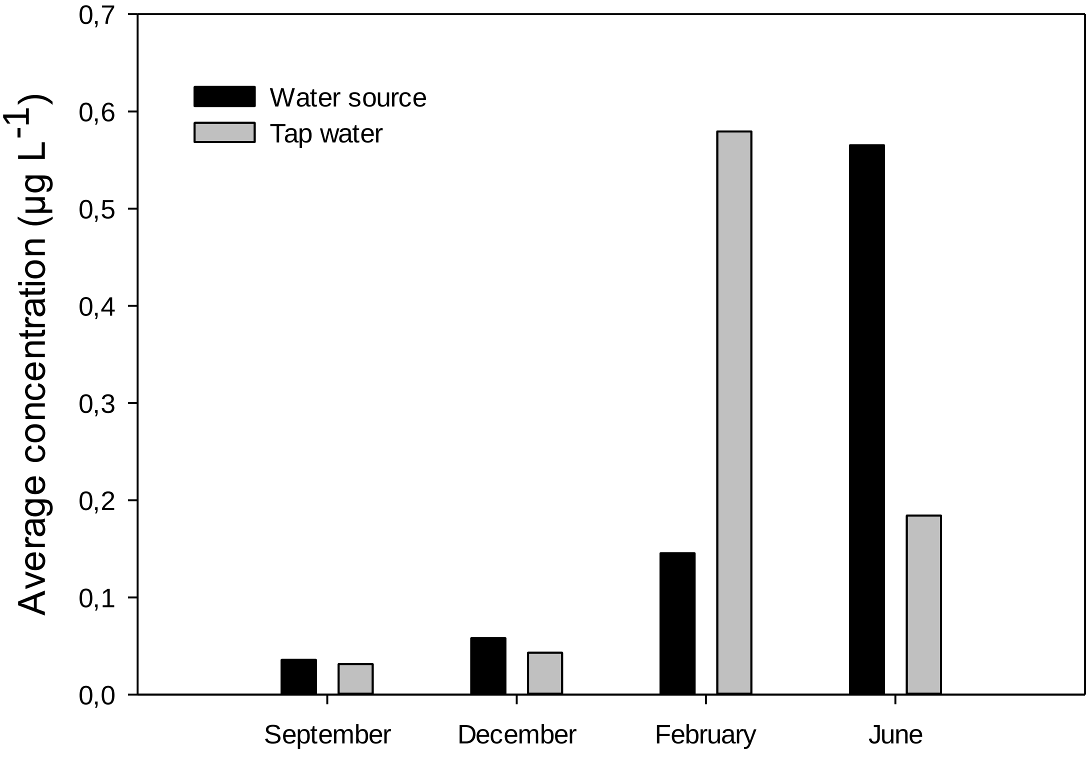

Figure 2. Pesticides concentration average detected in drinking water source and tap water in four different seasons (see the Y axis).

Although a wide range and high frequency of pesticides were found in water samples, the concentration was low for the majority of them considering EU settled strict limits for pesticides in drinking water for individual compounds (Council of the European Communities, 1998). Concentration lower than 0.05 µg L^{-1} were quantified for 78% of the pesticides detected in each sample, whereas in 30% of these the concentration was less than 0.01 µg L^{-1}. Concentration between 0.05 and 1 µg L^{-1} were quantified for 20% of the pesticides detected, whilst less than 5% had more than 1 µg L^{-1} (Figure 3). The pesticides with higher concentrations in drinking water source were azoxystrobin and 2,4-D, with maximum concentrations of 14.3 and 1.94 µg L^{-1}, respectively. In tap water propanil, 2,4-D, quinclorac and bentazone showed higher concentrations with maximum concentrations of 4.11, 3.78, 2.57 and 1.45 µg L^{-1}, respectively (Table 4). Considering the sum of compounds in the same sample, the majority of them exceed the regulated drinking water concentration thresholds for pesticides in EU.

Propanil, 2,4-D, quinclorac and bentazone are widely used herbicides in rice fields in RS. Rice fields are generally located in flat areas, with the water table near the soil surface and/or positioned close to streams, creeks or rivers. These factors establish rice fields as potential sources of water pollution and can affect both aquatic ecosystems and drinking water quality. In a study carried out by Marchesan et al. (2010), the authors also detected propanil, 2,4-D and bentazone in maximum concentrations of 5.4, 2.7, 3.6, respectively, similarly with the results obtained in this trial.

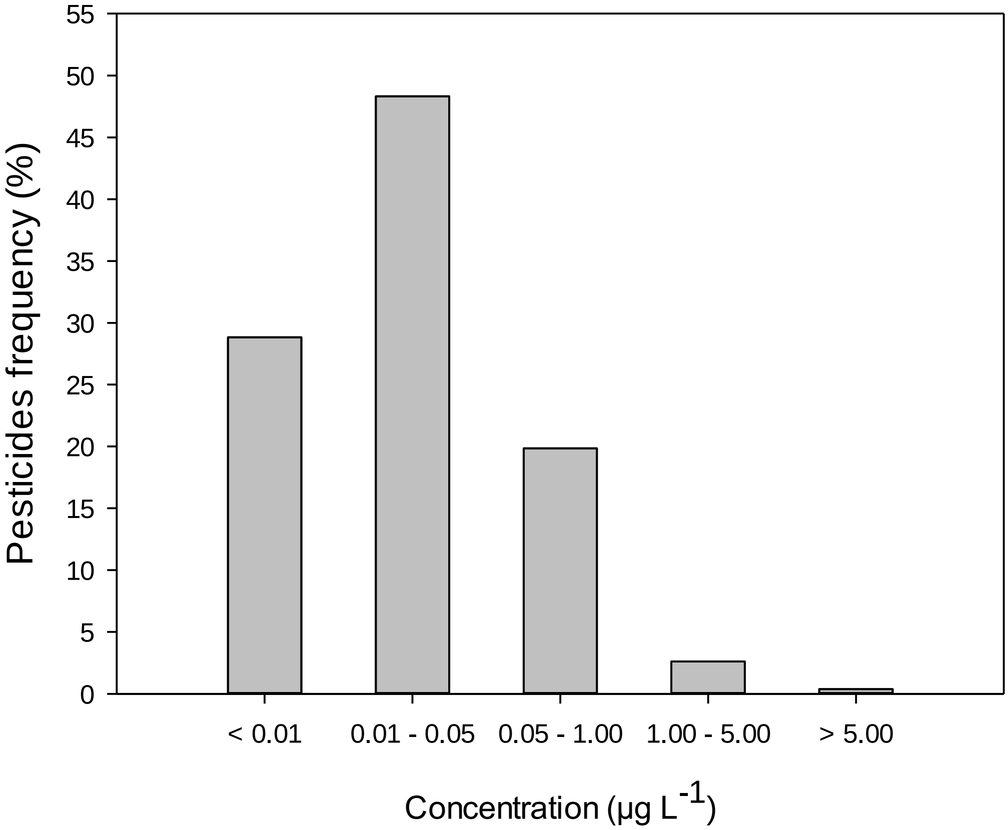

Figure 3. Pesticides frequency and concentrations in all samples during the studied period.

There was not observed significantly differences between the sampling locations (data not shown). In general, the same pesticides were presented in each site in similar concentrations.

In general the results indicated that most of the pesticides were not eliminated during the water treatment processes (such as flocculation, filtration, sedimentation, activated sludge, chlorination and fluoridation) performed by the municipal water company. Previous studies evaluating the occurrence and removal of pesticides by municipal water treatments also indicate a quite poor efficiency and high variability (Bueno et al., 2012; Schulmeyer et al., 2013). This might be explained by sampling variations due to sampling conditions limitations. Drinking sources and tap water samples were collected at the same day, however the water can be under treatment during 25 days depending on the plant.

In general, the drinking water sources are located nearby highly populated areas or intensive agricultural production sites in RS, conditions that are favorable for water contamination and can be exacerbated due to tropical climate. The pesticides found in the water samples, mainly in tap water, demonstrate that there is a contamination issue and consequently they represent a threat to human health. Though, the Brazilian Health Agency established a limit of pollution level for some pesticides, the majority of them are not included in the list. Considering the limits of pesticides and metabolites established by the European Community (Council of the European Communities 1998), the majority of the drinking water and even tap water samples analyzed in this work cannot be consumed.

Conclusions

During the experimental period residues of 33 pesticides were detected in the water samples analyzed. The 12 brands of mineral water analyzed did not show the presence of pesticides. In water source and tap water, at least one pesticide was detected in 100% of the samples. From the total of 97 pesticides evaluated 35% were detected. The most frequently detected pesticides were atrazine, azoxystrobin, carbendazim and imidacloprid. Contamination frequency and levels in tap water and drinking water source are similar, which suggest that the municipal water treatments are not efficient for pesticides removal. The pesticides with higher concentrations in drinking water source were azoxystrobin and 2,4-D, with maximum concentrations of 14.3 and 1.94 μg L^{-1}, respectively. In tap water propanil, 2,4-D, quinclorac and bentazone were the ones with higher concentration detected, being the maximum concentrations of 4.11, 3.78, 2.57 and 1.45 μg L^{-1}, respectively. The observed pesticide residue levels in water samples correlate with current pesticide applications and rates.

Considering the precautionary principle, continuous monitoring and stronger quality control are advised in order to gain a more complete knowledge of the environmental status of the main water sources. This is very important if a representative picture of water sources quality is wanted, mainly because pollutants levels vary both spatially and temporally. Additionally, pollutants monitoring should be complemented with studies dealing with the determination of the effects caused by the contamination.

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Manuscript 3 – Water research*

Residential water treatment as an alternative for pesticides removal from drinking water

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Residential water treatment as an alternative for pesticide removal from drinking water

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Abstract

Water pollution via natural and anthropogenic activities has become a global problem, which led to short and long-term impacts for humans health and the ecosystems. Substantial amount of individual or mixtures of organic pollutants move into the surface water via point and non-point sources. They are known to be toxic and difficult to remove from water sources, thus affecting its quality. Moreover, environmental regulations in developed countries have become very strict for drinking water treatment over the last few years, especially regarding pesticide compounds. The aim of this study was to evaluate the efficiency of different residential water treatments to remove 13 pesticides, with distinct physico-chemical characteristics, from the drinking water. Nine water treatments were applied: four membrane filters, an activated carbon filter, ultraviolet, reverse osmose, ion exchange resins and ozonation. The trial was performed with tap water. According to the results, activated carbon and reverse osmose were 100% efficient for pesticide removal, followed by ion exchange resins and ultraviolet. Membrane filters in general showed low efficiency and should, therefore, not be used for this purpose.

Keywords: removal; membrane filters; activated carbon; ultraviolet; reverse osmose

Introduction

Pesticides applied in agricultural areas are associated with effective control of pests and diseases in order to increase food production (Nasrabadi, et al., 2011). However, because of the large and often incorrect use of these compounds, they are associated with environmental damage, especially as a source of surface and groundwater pollution resources, which is an increasing problem in many parts of the world (Plakas and Karabelas, 2012).

The presence of pesticides in different compartments is often studied, mainly in drinking water sources where a broad range of contaminants have been detected. Loos et al. (2009) report an EU-wide reconnaissance of the occurrence of polar organic persistent pollutants in European river waters. Samples from over 100 rivers from 27 countries were analyzed for 35 compounds and only 10% of them could be classified as “very clean”, in terms of chemical pollution. Another report produced by the UNEP, also showed the presence of one or more pesticides in 90% of the samples in the major United States rivers and streams (Global Environment Outlook 5, United Nations Environment Programme 2014).

The current knowledge about the contamination levels of water resources with anthropogenic organic pollutants alerts for the necessity of developing economically and environmentally sustainable remediation methods. Within the organic contaminants, pesticide active ingredients are a vast class of compounds with enormous impact in the environment, mainly due to their great persistence in aquatic ecosystems. Pesticides can move long distances in the environment reaching regions where they have never been applied. Therefore, they can cause negative effects in non-target organisms, even in low-doses (Tankiewicz et al., 2010).

The presence of pesticides in the drinking water is one of the main sources from where humans are exposed to them. Consequently, different international legislations such as from the European Union (EU), United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) established the maximum concentrations of pesticides which can be accepted in drinking water. The EU has a specially strict legislation, which sets limits for pesticides in drinking water of 0.1 $\mu l\ l^{-1}$ for individual compounds and 0.5 $\mu l\ l^{-1}$ for the sum of pesticides (Council of the European Communities 1998).

During the last decade, researchers have been focusing on strategies to remove organic pollutants from water. The most commonly available and traditionally drinking water treatment processes are flocculation, filtration, sedimentation, activated sludge and chlorination. However, they demonstrated low efficiency to eliminate these compounds (Benner et al., 2013; Rivera-Utrilla et al., 2013). Moreover, advanced water treatment are sometimes expensive to operate and not suitable or feasible for all situations (Benner et al., 2013). Therefore, alternative strategies are needed to efficiently remove pesticides from drinking water resources and limit human exposure.

Thereby, one interesting solution, if the efforts to prevent pollution from entering in water resources are ineffective or insufficient, is to further treat the drinking water at the residential level. Thus, the use of activated carbon sorption, oxidation using ozone, ultraviolet radiation and membrane filtration become an alternative to improve tap water quality.

Activated carbon sorption has been the most common adsorbent used to filter drinking water (Kyriakopoulos and Doulia, 2006; Altmann et al., 2014) due to its versatility and efficiency in removing organic contaminants (Yu et al., 2008; Yu et al., 2009). However, its effectiveness is greatly reduced by the presence of natural organic matter which competes for binding sites, or particulates which block the pore spaces (Bolong et al., 2009; Snyder et al., 2007). Membrane filtration and reverse osmosis also have a great potential to remove a wide range of emerging contaminants from water (Nghiem et al., 2005, 2006; Snyder et al., 2007), though their efficiency is highly dependent on both membrane and pesticide characteristics (Plakas and Karabelas, 2012; Bellona et al. 2004). Ternes et al. (2002) investigated the use of ozonation to remove selected compounds from drinking water, in laboratory, which shown to be quite efficient in eliminating polar compounds.

Ultraviolet radiation is widely used for drinking water disinfection due to its effectiveness against a wide range of waterborne pathogens (Linden et al., 2002). Furthermore, ultraviolet can also promote the degradation of photolabile organic compounds by direct photolysis (Shemer et al., 2005; Pereira et al., 2007a,b), however, some molecules are not able to strongly adsorb the LP/UV radiation reducing the treatment efficacy.

Among the water treatment techniques, filtration processes are apparently efficient in removing organic contaminants in low-doses from water, requiring low economical and operational investments. Still there is limited information regarding to the efficiency of residential water treatments in the removal of pesticides from drinking water. There might be specific responses related to the pesticides physico-chemical characteristics that can influence filters efficiency. These informations could be further used to suggest possible combinations of treatments which assure higher water quality by increasing the process effictiveness.

Thus, the aim of this study was to evaluate the efficiency of different residential water treatments to remove 13 pesticides, with distinct physico-chemical characteristics, from the drinking water.

Material and methods

Reagents and chemicals

Analytical standards of the pesticides were obtained from Dr. Ehrenstorfer (Augsburg, Germany), with purity above 95%. Selected physico-chemical properties are given in Table 1. Full-scan mass spectrometric analysis revealed no contamination. HPLC grade methanol (MeOH), acetonitrile (MeCN), and optima grade acetic acid (HAc) from J. T. Baker (Phillipsburg, USA) were purchased for this study. Ammonium acetate was purchased from Merck (Darmstadt, Germany). Ultrapure water was obtained with a Milli-Q Direct UV3® system from Millipore (Molsheim, France). Vortex mixer model QL-901 was acquired from Microtécnica (Curitiba, Brazil). The polymeric SPE sorbent cartridges Oasis® HLB (60 mg; 3 mL) was from Waters (Wexford, Ireland).

Table 1. Pesticides physico-chemical properties.

Pesticides	Pesticide Type	Group	CAS N°	Molecular weight[a] (g mol^{-1})	Water solubility[a] (mg L^{-1})	K_{ow}[b]	Soil half-life[a] (days)	Pka[a]	Polar surface area/Å2[b]	Number of H bond acceptors[b]
Azoxystrobin $C_{22}H_{17}N_3O_5$	Fungicide	Strobilurin	131860-33-8	403.4	6.7	2.5	35.2-248	-[c]	104	8
Carbaryl $C_{12}H_{11}NO_2$	Insecticide	Carbamate	63-25-2	201.22	9.1	2.36	2.3-98.7	10.4	38.3	2
Carbofuran $C_{12}H_{15}NO_3$	Insecticide	Carbamate	1563-66-2	221.26	322	2.32	5.7-60	-	47.6	3
Difenoconazole $C_{19}H_{17}Cl_2N_3O_3$	Fungicide	Triazole	119446-68-3	406.26	15.0	4.4	53-456	1.07	58.4	5
Imazapic $C_{14}H_{17}N_3O_3$	Herbicide	Imidazolinone	104098-48-8	275.30	2230	0.4	31-410	2.0, 3.9, and11.1	91.6	5
Imidacloprid $C_9H_{10}ClN_5O_2$	Insecticide	Neonicotinoid	138261-41-3	255.66	610	0.57	77-341	-	86.3	4
Propanil $C_9H_9Cl_2NO$	Herbicide	Anilide	709-98-8	218.08	95	3.07	3	19.1	29.1	1
Propiconazole $C_{15}H_{17}Cl_2N_3O_2$	Fungicide	Triazole	60207-90-1	342.22	150	3.72	29-92	1.09	49.2	4
Quinclorac $C_{10}H_5Cl_2NO_2$	Herbicide	Quinolinecarboxylic acid	84087-01-4	242.06	0.07	0.266	168-913	4.34	50.2	3
Tetraconazole $C_{13}H_{11}Cl_2F_4N_3O$	Fungicide	Triazole	112281-77-3	372.15	156.6	3.56	136-1688	0.65	39.9	7
Thiamethoxam $C_8H_{10}ClN_5O_3S$	Insecticide	Neonicotinoid	153719-23-4	291.71	4100	-0.13	34-233	-	115	6
Tricyclazole $C_9H_7N_3S$	Fungicide	Triazolobenzothiazol	41814-78-2	189.24	596	1.4	240-842	-	58.4	3
Trifloxystrobin $C_{20}H_{19}F_3N_2O_4$	Fungicide	Strobilurin	141517-21-7	408.37	0.61	4.5	0.3-3.6	-	69.5	9

[a] IUPAC (2015); [b] source: http://pubchem.ncbi.nlm.nih.gov/; [c] Not determined;

Laboratory experiments

Thirteen pesticides (Table 1) were chosen based on their occurrence in drinking water and mainly due to their molecular structures and physico-chemical properties differences. Nine water treatments were used in the experiment, which are summarized in Table 2. These are the most common methods used for water treatment in the residential level available in the marked. The four filters used had 10 x 5 inches (height x width, respectively).

Table 2. General information for the different water treatments selected in this study.

Filter type	General information	Brand and model
String Wound (SW)	5 microns; 100% polypropylene cord	HYDRONIX SWC-45-1005
Polypropylene (PO)	5 microns	HYDRONIX SDC-45-1005
Absolute (AB)	0.22 micron; double layer Structur; polypropylene; pleated	HYDRONIX AR0020
Pleated (PL)	5 microns; durable polyester	HYDRONIX SPC-45-1005
Activated carbon (AC)	Granular	HYDRONIX SPD-4510
Mixed bed resin (MB)	mixture for electrical discharge machining; Polymer Structure of Gel polystyrene crosslinked with divinylbenzene;	Purolite®, MB 478
Ultraviolet (UV)	10 watts; wavelength 254 nm	POLARIS™, UVC 1
Reverse osmose (RO)	Membrane type polyamide thin-film composite; low pressure	DOW FILMTEC™, TW30-1812-100
Ozonator (OZ)	Residential ozone generator	Neo life™, Standart

A stock mixture of 13 pesticides with same concentration (10 mg L^{-1} of each pesticide) was obtained from individual stock solutions by measuring and combining the desired volumes. To proceed the experiment, 50 µL aliquot of the stock mixture was applied at an erlenmeyer of 5 L (feed tank) filled with tap water, using an electronic pipette. The final concentration of each pesticide in the water was 0.1 µl L^{-1}. This concentration was chosen accordingly with the EU regulations for individual compounds in drinking water. Moreover, taking 0.1 µl L^{-1} as reference assured sufficient analytical precision to reveal even small differences between the treatments.

The experiment was conducted in laboratory where the water treatment equipment was connected to 5 L feed tank. The water circulation was maintained by a pump at 5.5 bar of pressure and the flow rate at 0.86 L min^{-1}. The presence of the pesticides was assessed after the solutions going through the different equipment once. A representation of the system can be seen in Figure 1. The water temperature for all solutions was set at 25.0 (± 0.2 °C). The tap water used in the experiment was collected from the municipal pipeline at Santa Maria, Rio Grande do Sul State, Brazil.

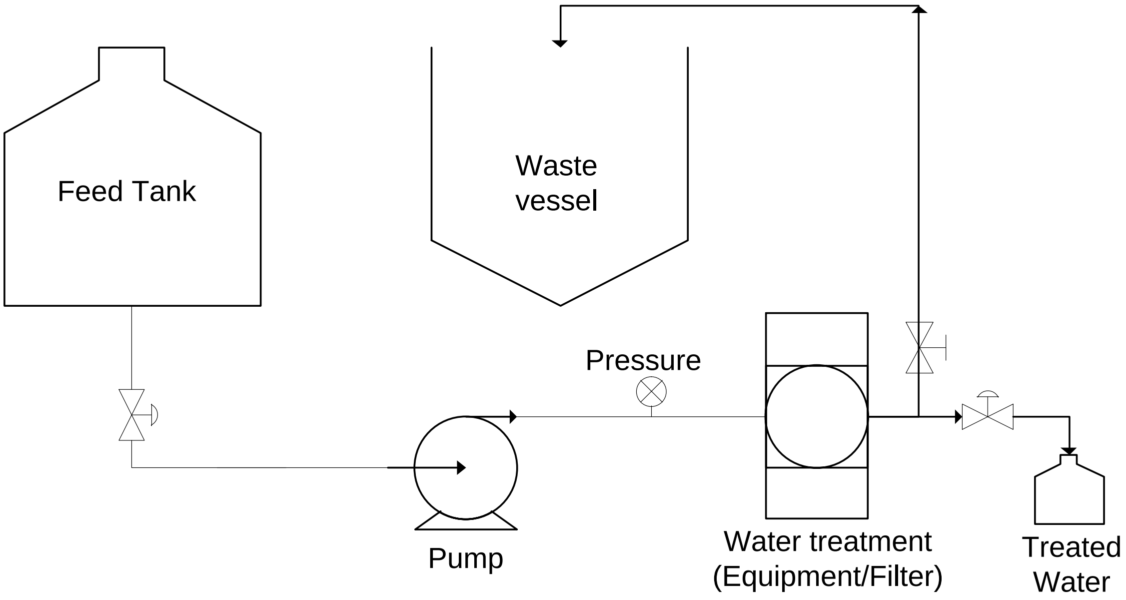

Figure 1. Schematic drawing of the water treatment process.

The filters were washed prior the experiment be performed with 10 L of tap water, to assure the right conditions from them to adsorb the chemical molecules. Six samples (500 mL each) were collected per water treatment: one samples of only tap water, to assure that the water source was not contaminated; one sample from the feed tank, used as reference; and four treated water samples. The feed tank volume was kept constant during the experiment, with fresh solution been added after each sampling.

Standard solutions and calibration curves

Stock solutions were prepared by dissolving an exact amount of each pesticide in methanol. A stock mixture of pesticides with the same concentration was obtained from individual stock solutions by measuring and combining the desired volumes. An aliquot from this mixture was then diluted in methanol to obtain concentrations of 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 50.0, 100.0, 200.0 µg L^{-1} used for calibration. Standard solutions were all stored at -18 °C prior be used. Pesticides concentrations (µg L^{-1}) in the samples, mentioned in the following sections, were quantified based on the standard curves. Subsequently the data was adjusted for the final calculations of the compounds in µg L^{-1} of water.

Analytical procedures

Considering that the pesticides concentration was low, the samples were concentrated to quantify these compounds. Therefore, SPE (Solid Phase Extraction) cartridges (Oasis®HLB 60 mg) were conditioned in sequence with 3 mL of methanol, 3 mL of ultrapure water and 3 mL of water (pH 2.5). Then, 250 mL of each sample, previously acidified to pH 2.5 with aqueous phosphoric acid (1:1, v/v), was transferred to the SPE (Solid Phase Extraction) cartridges (Oasis®HLB 60 mg) through PTFE tubes in a manifold. The adopted percolation flow rate ranged from 2 to 5 mL min^{-1}. After the sample percolation, 3 mL of purified water was passed through the cartridge. For the elution of the pesticides from the cartridge, 2 mL of the mixture methanol and acetonitrile 1% acetic acid (1:1, v/v) was used. Then, 200 µL of eluate was diluted 5 times with water (800 µL) prior to UHPLC-MS/MS analysis. A concentration factor of 25 times was reached with this procedure. For each time point, aliquots of treatments, controls, and blanks were combined prior to analysis.

LC-MS instrumentation and conditions

Chromatographic analyses were performed using UHPLC-MS/MS system (Waters, Milford, USA) equipped with Acquity UPLC^{TM} liquid chromatography; Xevo TQ^{TM} MS/MS triple quadrupole detector equipped with electrospray source, an autosampler, a binary pump and a column temperature controller (Waters, Milford, USA). The separation was achieved using an Acquity UPLC^{TM} BEH C18 (50 x 2.1 mm i.d., 1.7 µm particle size) analytical column at 40 °C. MassLynx 4.1 software (Waters, Milford, USA) was used for instrument control and data processing. The mobile phase consisted of 98% water, with 2% of methanol (A) and 100% methanol (B), both containing 0.1% formic acid and 5 mmol L^{-1} ammonium formate. The chromatographic method began with an initial mobile phase composition of 5% for solvent B, increased to 100% for 7.5 minute and decreased to 5% for 1minute, held constant for a further 1.5 minutes. The total run time was 10 min with a flow rate of 0.225 mL min^{-1} and injection volume of 10 µL. To quantify the compounds was operated in electrospray ionization positive mode (ESI+) using selected reaction monitoring (SRM). The MS source conditions were as follows: capillary voltage, 2.0 kV; source temperature, 150 °C; desolvation temperature, 500 °C; desolvation gas (N_2) flow, 600 L h^{-1} and cone gas (N_2) flow, 80 L h^{-1}.

Limit of detection (LOD) and limit of quantification (LOQ)

The LOD and LOQ were estimated using the method of signal-to-noise ratio, and the LOD was defined as the lowest concentration at which the analytical signal could be reliably differentiated with a signal-to-noise ratio of 3:1. The LOQ was established as the lowest spiked level concentration, which produced a signal-to-noise ratio of 10:1 with acceptable recovery and precision according to legislation (SANCO, 2013)

Data analysis

Initially, the data was tested for normality and homogeneity of variance assumptions. Subsequently, it was subjected to analysis of variance ($P \leq 0.05$). When statistical significance was observed, comparisons between the pesticides concentrations were proceeded by calculated confidence interval of 95% And the filters were compared by the non-parametric test Kruskal-Wallis.

Results and discussion

The selectivity of the method was assured in the LC analyses, as no interference peaks were detected in the blank samples. The analytical curves presented good linearity with R^2 higher than 0.99 for all the compounds studied. The instrumental limit of detection (LOD) and limit of quantification (LOQ) were 0.01 and 0.02 µg L^{-1}, respectively. Good recoveries of the analytes (77.9 – 102.7%; RSD ≤ 16.7) were obtained for all compounds at the 500 ng g^{-1} fortification level.

The remaining pesticides concentration after going through each treatment is shown in Figure 2. Significant differences were observed between the residential water treatments and pesticides concentrations.

Water treatments with PO, SW and AB, membrane filters, resulted in similar final pesticides concentrations. Little concentration reductions were achieved with these filters, which demonstrate their low efficiency in removing these compounds from the water. According with Nghiem et al., (2005 and 2006) and Snyder et al., (2007), membrane filtration has considerable potential on the removal of a wide range of contaminants, mainly by sieving, which is the primary mechanism to retain the pesticides. However, PO and SW membranes have a pore size of approximately 5 µm, and AB of 0.22 µm. Therefore, they are not recommended for pesticide removal, because the molecular weights and size of almost all pesticides range from 200 to 400 g mol^{-1} and 2 to 12 Å (Chen et al., 2004), respectively.

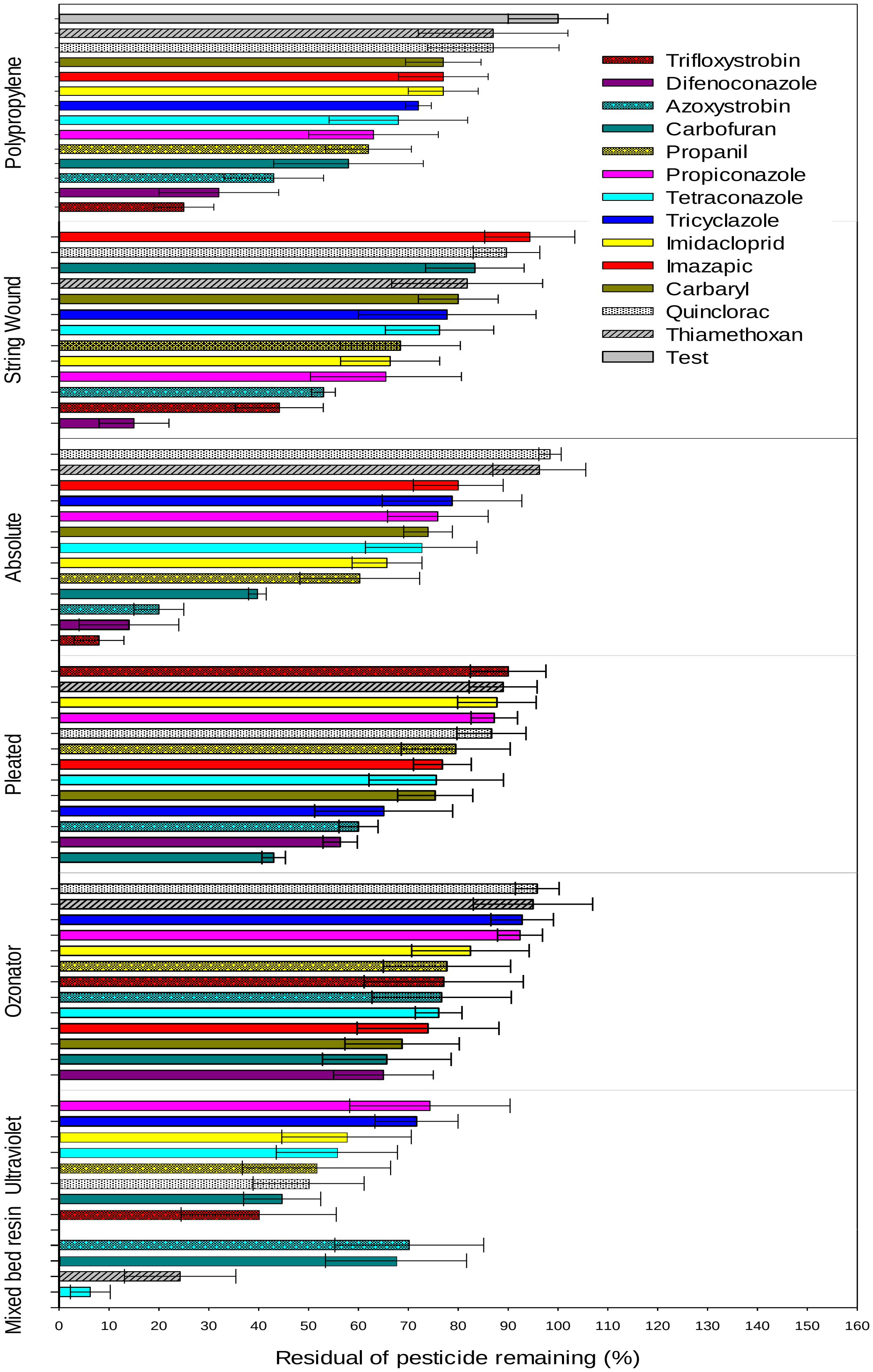

Figure 2. Remaining pesticides concentrations after going through different water treatments. Data is presented in percentage (%) based on the initial concentration of the feed tank solution.

Focusing in the results achieved for individual pesticides, azoxystrobin, difenoconazole and trifloxystrobin, were the most efficiently removed pesticides by PO, SW and AB membranes. These results can be further explored by considering pesticides physico-chemical features which are related to their hydrophobicity (e.g. solubility, molecular weight and log K_{ow}), adsorbate ability to establish H-bonding with water or with carbon surface functional groups and their acid-base ionization (pKa) (Moreno-Castilla, 2004; Vázquez-Santos, 2008; Baccar et al., 2012). However, K_{ow}-values is the parameter which gave the most relevant indication for the final pesticide concentration in water for these treatments, which generally decreased with higher $K_{ow,}$ as shown by their Pearson correlations in Figure 3. These results are supported by Kiso et al., (1999), which reported the adsorption property of many organic compounds, including pesticides, to cellulose acetate and polyethylene as having a great correlation with compounds K_{ow}-values.

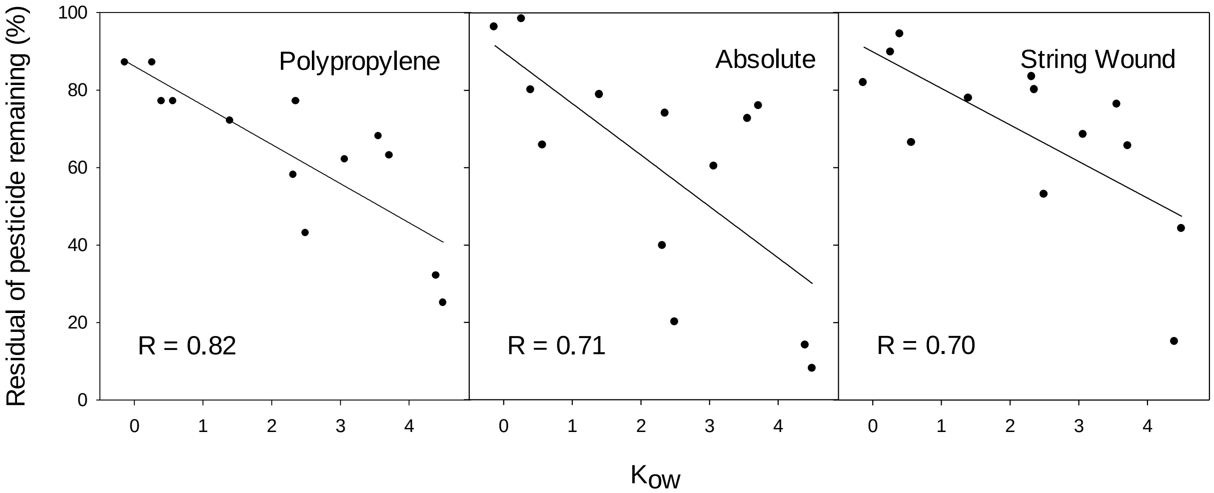

Figure 3. Pearson correlation (R) as a function of final pesticides concentrations and their K_{ow}-values for polypropylene, absolute and string wound filters.

Moreover, PO, SW and AB are made of polypropylene, which is a highly hydrophobic material. The Pearson correlation between the pesticides in these filters ranged from 0.70 to 0.82, indicating that a hydrophobic interaction was the main factor regulating the pesticides adsorption and consequently their reduction post-filtration. However, it must be considered that pesticides adsorption in solid surfaces is a dynamic process affected by several factors related to their structure, as well the solid substrate and physical-chemical variables (Lundstrom, 2007; Nakanishi et al., 2001).

PL filter did not have a great efficiency reducing the pesticides in general, except for carbofuran, difenoconazole and azoxystrobin, significant reductions were observed. These results were already expected, since PL membrane has a pore size of approximately 5 microns and is made of polyester, a material less hydrophobic than polypropylene, leading to less pesticides adsorption.

Pesticides physico-chemical features are normally related with their deportment, however, limit the membranes efficiency to pesticide features is not always possible. Adsorption is a complex and spontaneous phenomenon which is mostly governed by interactions dictated by the adsorbent's and adsorbate's characteristics. This process contributes to an initial retention of the molecules, however an increased surface concentration can favor their diffusion through the membrane and consequently reduce the adsorption efficiency to some extent (Nghiem and Schäfer, 2006). Therefore, even though pesticides features indicate adsorption tendencies, this process is not always straight forward.

Reverse Osmosis is also a size-exclusion filter, offering in general good prospects for pesticide removal as shown in this trial with 100% rejection efficiency. Similar results were reported by Hancock et al. (2011), Plakas and Karabelas (2012), Xie et al. (2012) and Yangali-Quintanilla et al. (2010) where this filter showed great efficiency to remove micropollutants from the feed water. One of the main features of this filter is related to its porosity (Kyriakopoulos and Doulia, 2007), since RO has quite small pores (< 1 nm), which are able to rejected many pesticides by their molecular size. Moreover, sorption-diffusion mechanism can also contribute to pesticides removal in RO filters, attributed to hydrophobic interactions or hydrogen bonding between the pesticides and the membrane surfaces (Nghiem and Schäfer, 2005).

Pesticides acid-base ionization is also an important feature to be considered once the majority of the commercial membranes filters are negatively charged. Therefore, electrostatic repulsion of negatively charged pesticides at the membrane surface is expected to enhance the overall rejection performance. This is in agreement with results obtained by Berg et al. (1997), where the rejection of the negatively charged herbicides (at neutral pH) was greater than for non-charged of the same size. The feed water pH in this trial was 6.5, except to carbaryl and propanil, once all pesticides have pKa-values lower than the water pH this feature is not correlated to their rejection.

AC filter was also 100% efficient, rejecting all pesticides, even the more hydrophilic and with higher pKa. Generally, ACs are very efficient in the adsorption pesticides from surface waters, therefore it is applied where it was not possible to find new unpolluted aquifers (Søgaard and Madsenm, 2013). The results here presented correspond with the ones by Ioannidou et al. (2010), where the pesticide removal efficiency of AC was from 90–100%. ACs are extremely porous adsorbents, with mostly micropores (diameter around 5–6 Å) and a minor percentage of mesopores (Ioannidou et al., 2010), which results in a quite large surface area available for adsorption or chemical reactions. Thus, primarily the contaminant adheres to the exterior surface of the AC particle, moving along the wall to larger pores located deeper inside the particle. Then, the contaminant will move to a final resting place on the inner surface of the AC grain. This process is continuous until no more contaminants can be adsorbed by the activated carbon (Baup et al., 2000).

Another important adsorption mechanism for AC filters is associated with the presence of oxygen and nitrogen functional groups on the carbon surface. These functionalities determine the surface charge, hydrophobicity, and the electron density of the graphene layers (Moreno-Castilla et al. 2001). Daiem et al. (2015) showed that molecules which have aromatic rings, like the majority of the pesticides, can be activated by phenolic groups presents in AC increasing its electronic density and theoretically favoring their adsorption. Furthermore, AC is generally an efficient water treatment on the removal of organic micropollutants, however, its polymer membranes also suffer with saturation decreasing filtration efficiency (Plakas and Karabelas, 2012). Therefore, when the concentration of the filter exceeds a certain level (breakthrough filter limit) it must be replaced or regenerated.

For the majority of the pesticides used in this study, non-significant differences were found when comparing their reduction after feed water ozonation. Major reductions were observed for carbaryl, carbofuran, and difenoconazole, with remaining concentrations of 68, 65 and 65%, respectively. Some studies on carbaryl and carbofuran indicated relatively high reactivity toward ozonation (Reynolds et al., 1989; Ohashi et al., 1993; Benítez et al., 2002). Ohashi et al., (1993) reported that for most carbamate pesticides, radical reactions are more important. Furthermore, Rashidi et al., (2011) reported that depending on the ozone concentration, difenoconazole degradation ranged between 30 and 50%, which is consistent with the results obtained in this study.

The understanding of the actual mechanisms of ozonation is complex and not complete. Ozone is a highly reactive unstable molecule, therefore, it rapidly degrades in O_2 by releasing a free oxygen radical. This free oxygen radical can bind to another free oxygen radical forming a new molecule of O_2 or oxidize other chemicals (Guzel-Seydim et al., 2004). It is known that radical reactions are the key processes of the OZ degradation. Experimental results indicate that hydroxyl radical (HO•) binds pesticides at two preferably positions: aromatic rings and the position occupied by chlorine, leading to the formation of oxygenated organic products and low molecular weight acids that are more biodegradable (Beltran et al., 1998; Beltran et al., 1999). Moreover, high rates of removal by ozonation are usually observed for compounds with double bonds, aromatic structure or heteroatoms, and functional groups bearing sulfur, phosphorous, nitrogen and oxygen atoms (Zwiener, 2007).

In this trial, the low range of pesticide degradation is possibly associated with the short exposure time to ozonation. However, many researchers believe that the complete pesticides destruction is likely impossible with ozonation alone or even in ozone-based (Ikehata and El-Di, 2005). It is also worth mentioning that a careful analysis of the degradation products must be performed to evaluate the overall gain of the process, with respect to degradation of original compounds and the formation of potentially harmful products.

A complete removal of azoxystrobin, carbaryl, difenoconazole, imazapic and thiamethoxam was observed when using UV radiation. Water treatments based on UV radiation usage, with monochromatic light at 254 nm, are widely used for cleaning drinking water, since these promote the degradation of photolabile organic compounds by direct photolysis due to their potential to absorb light (Shemer et al., 2005; Pereira et al., 2007a,b). Several studies have mentioned high pesticide degradation (Bianchi et al., 2006; Djebbar et al., 2008; Acero et al., 2008, Giri et al., 2011; Sanches et al., 2010; Kim and Tanaka, 2009; Canonica et al., 2008) through an electronic excitation of the organic substrate which leads to the transference of an electron from the excited state of the substrate to ground state molecular oxygen, or the homolysis to form organic radicals which can then react with oxygen (Legrini et al., 1993).

The majority of the pesticides in this study were not sufficiently removed during the treatment with UV. The remaining amount ranged from 40 to 74%. However, some molecules are not able to strongly absorb the UV radiation. This characteristic and the existence of a large number of organic compounds combined with the presence of complex organic constituents in waters, complicates the understanding of the UV mechanisms. (Giri et al., 2014). Studies have shown that pollutants degradation by direct UV photolysis depends largely on the target compound being studied (Kim and Tanaka, 2009).

For MB, only azoxystrobin, carbofuran, thiamethoxan and tetraconazole, remained after the filtration, with final concentrations of 70, 67, 24 and 6%, respectively. MB is a special ion exchange resin based on polystyrene crosslinked with divinylbenzene with sulfonic acid and quaternary ammonium functional group. Anion exchange is well known as an alternative water treatment, and its effectiveness in removing organic substances has been reported (Neale et al. 2010; Kim and Dempsey 2010; Boyer et al. 2008; Singer et al. 2009). Drikas et al. (2009) have shown that during the ion exchange process, both hydrophobic and hydrophilic organic substances are removed, in agreement with the data presented in this study. Previous studies have also shown its usefulness in removing aromatic substances (Xue et al. 2009; Zhi-gang et al. 2010), with a simultaneous increase in process effectiveness and in molecular mass (Graf et al. 2014). However, there is a lack of information on pesticide removal by ion exchange resins.

In a study by Humbert et al. (2005), the removal of atrazine and isoproturon, was reported as ranging from 5-7%. This low removal range was attributed to the non-ionic nature of the pesticides in the experimental conditions. Despite this, specific and non-specific interactions, such as hydrophobically assisted ion exchange and hydrogen bonding, can occur between neutral acidic species such as phenolic groups (at pH 7) and the polymer (Yang et al., 2003; Tan and Kilduff, 2007). The porous nature of the resin can assist with the removal of neutrally charged contaminants (Shorrock and Drage, 2006). It is also likely that non-ionic micropollutants can interact with the resin polymer through hydrogen bonding (Bolto et al., 2002).

AB, OZ, PL, PO and SW did not show high efficiency on the removal of pesticides from the water (Table 3). UV was an intermediate method for pesticide removal, however the best results were achieved with AC, RO and MB.

Table 3. Average pesticides concentrations after water treatments.

Treatments	Pesticides concentrations (%)
Absolute	60.5 d
Activated carbon	0.00 a
Mixed bed resin	13.1 b
Reverse osmose	0.00 a
Ozonator	79.6 d
Pleated	71.9 d
Polypropylene	66.1 d
String wound	68.9 d
Ultraviolet	33.3 c

* Treatments average was done with the reaming percentage of all pesticides for each replication. Kruskal-Wallis test (non-parametric) was used.

When designing a drinking water treatment plant, one of the most crucial issues to be addressed is the generally organics contaminant present in the water, due to the effectiveness of each method used being dependent on the contaminants. Furthermore, some treatments using UV and RO, although efficient in removing organic micropollutants, can lead to newly-formed (toxic) by-products (Rossner et al., 2009; Snyder et al., 2007).

One way to increase the total removal of pesticides is to integrate the membrane filters as part of a system, where the filtration step is combined with a second treatment technique, mainly via adsorption. In order to remove possible pesticides and formed by-products, these techniques often are followed by an AC extraction (Bonné et al., 2002). Although there are few studies with MB, this filter also could be a good alternative.

Conclusions

According to the preceding results, the selection of an appropriate membrane is primarily made on the basis of key pesticide parameters, like the molecular dimensions (length and width) and the hydrophobicity/hydrophilicity (K_{ow}). Size exclusion is the most important mechanism of pesticide retention for membranes.

Porosity, degree of ionic species rejection, surface charge and membrane type (polymer composition) are also significant.

Reverse osmosis and activated carbon are the best options for organics contaminants removal from water sources, both treatments achieved 100% of pesticide removal in a continuous water flow. Mixed bed resin and ultraviolet have shown an intermediate removal potential. Absolute, ozonator, pleated, polypropylene and string wound showed low efficiency and should, therefore, not be used on the removal of pesticides. The combination of different water treatment methods, even in a residential level, is highly recommended to increase drinking water purity. This study provides a platform where future researches can stand to deepen the knowledge focusing on pesticides that are locally found on drinking water sources.

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Manuscript 4 - Journal of Environmental Pollution*

Degradation of fluazifop-P-butyl and formation of metabolites in Danish soils

*Manuscript formatted according to the Journal's guidelines.

Degradation of fluazifop-P-butyl and formation of metabolites in Danish soils

SCHREIBER, F.; LAURSEN, B.; OLSEN, P.; FOMSGAARD, I. S.

Abstract

Degradation is a key process affecting fate and transport of pesticides in the environment. The use of fluazifop-P-butyl in Denmark has been quite significant particularly in potato, oilseed rape, and sugar beet cropping fields. There is still limited information in the litetature about fluazifop-P-butyl degradation rate and metabolite formation. Thus, the aim of this study was to clarify the degradation rate of the herbicide fluazifop-P-butyl and the formation and degradation rate of its major metabolites in three Danish soils. Soil samples from three locations in Denmark were collected at the 10-20 cm soil layer to conduct a laboratory trial. The results showed that in incubated soil and under aerobic conditions fluazifop-P-butyl exhibits very low persistence. In the degradation pathway sequence, fluzifop-P-butyl is followed by fluazifop-p acid, 2-(4-hydroxyphenyl)-5-trifluoromethylpyridine (compound IV) and 5-trifluoromethyl-2- pyridine (compound X). Fluazifop-p acid is the major degradation product, while, 2-(4-hydroxyphenyl)-5-trifluoromethylpyridine is observed in minor concentrations. The most persistent metabolite in soil is 5-trifluoromethyl-2- pyridine.

Keywords: herbicide; LC-MS/MS; Denmark; half-life; incubation

Introduction

The extensive use of pesticides in agriculture and the transport (via leaching and runoff*)* from fields is threatening water quality of aquatic systems in large parts of the world (Schwarzenbach, 2006; Drewry et al., 2006; Ippolito et al., 2015). Thereby, water resources protection regarding pesticide contamination is a major concern (Younes and Galal-Gorchev, 2000). Mitigation measures have mainly concentrated on pesticide parent compounds (PCs) (Reichenberger et al., 2007). Recently, the focus was extended to products of the incomplete degradation of pesticides, transformation products (TPs) (metabolites), which were also found in the aquatic environment (Olsson et al., 2013) and may be equally or more mobile, persistent and toxic than their PCs (Boxall et al., 2004). According to the E.U. Regulation No. 1107/2009, TPs are deemed environmentally relevant if they have unacceptable toxicological properties.

Degradation is a key process in the fate of these compounds in the environment (Linn et al., 1993; Rudel et al., 1993). The degradation process can be biotic (catalyzed by soil microorganisms) or abiotic, and is influenced by several factors, such as pH, organic matter content, moisture content, texture and microbial activity (Dolaptsoglou et al., 2007; Mueller et al., 2010; Wang et al., 2010; Lourencetti et al., 2012.). The degradation process however primarily depends on the molecular structure of the specific pesticide involved (Boivin et al., 2005; Mamy et al., 2005). Several transformation products can be formed and/or complete degradation (mineralization) can take place (Fomsgaard, 1997; Helweg, et al., 1998)

Fluazifop-P-butyl [butyl (2R)-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoate], is a post-emergence systemic herbicide belonging to aryloxyphenoxypropionates group. It has been used mainly to control grass weeds in broad-leaved crops by the suppression of Acetyl-coenzyme A carboxylase (ACCase), which is a biotin-containing enzyme that catalyzes the ATP-dependent carboxylation of acetyl-CoA to form malonyl-CoA. This reaction is the first step in the synthesis of fatty acids (Harwood, 1996, Nikolskaya et al., 1999, Yu et al., 2004). Thereby, this herbicide inhibits development and function of membranes (Harwood, 1988). In the environment it shows relatively low toxicity to birds and mammals, however, it can be highly toxic to fish and aquatic invertebrates.

Fluazifop-P-butyl has low mobility in soil, since it is strongly bound to soil colloids, and is not reported as a contaminant in ground or surface water. In a study by Gessa et al. (1987), the authors reported that this herbicide can bind irreversibly in clay soils through several different mechanisms. In the soil, hydrolysis or microbial degradation are responsible for its degradation, with no other mechanisms been reported. This herbicide is rapidly hydrolyzed to fluazifop-p acid in both soil and water (Smith, 1987). In soil, fluazifop-P-butyl half-life varies between one and two weeks (WSSA, 2014). However, when environmental conditions favor microbial metabolism, with warm weather and high soil moist, degradation rates can be higher (Negre et al., 1993), reducing its half-life to less than one week (EXTOXNET, 1996). On the other hand, the metabolite fluazifop-p acid shows to be more persistent, with half-life values reported in two different Danish soils of more than two months (BADAWI et al., 2015).

Like for many other organic contaminants, there is still limited information in the literature about fluazifop-P-butyl degradation rate and metabolite formation. The supposed degradation scheme in soil, according to EFSA (European Food Safety Authority, 2012), is fluazifop-P-butyl followed by fluazifop-p acid, 2-(4-hydroxyphenyl)-5-trifluoromethylpyridine (named compound IV in EFSA (2012) and in Badawi et al. (2015)) and 5-trifluoromethyl-2- pyridine (named compound X in EFSA (2012) and in Badawi et al. (2015)). However, there is still a lack of information on the degradation kinetics of these metabolites, which will help to determine formation fraction values and more reliable soil DT_{50}-values to be used in fate modeling.

The mechanisms involved in these processes are essential to understand the fate of pesticides in the environmental allowing the development of strategies to improve environmental protection (Peruzzo et al., 2008). Thus, the investigation of fluazifop-P-butyl degradation pathways and its interaction with different soils become mandatory to access the herbicide environmental impact. The aim of this study was to determine the degradation rate of the herbicide fluazifop-P-butyl and the formation and degradation rate of its major metabolites in three different Danish soils.

Material and methods

Reagents and chemicals

Analytical standards (purity 99%) of fluazifop-P-butyl, fluazifop-p acid, 2-(4-hydroxyphenyl)-5-trifluoromethylpyridine (compound IV) and 5-trifluoromethyl-2-pyridine (compound X) (Figure 1) were obtained from Sigma-Aldrich. Selected physico-chemical properties are given in Table 1. Deionized water was prepared using a Millipore Milli-Q purification system (Millipore, USA). Full-scan mass spectrometric analysis revealed no contamination of the Milli-Q water. HPLC grade methanol from Rathburn (Walkerburn, Scotland) and optima grade acetic acid (Fisher, Canada) were purchased for this study. Ammonium acetate was purchased from Merck (Darmstadt, Germany).

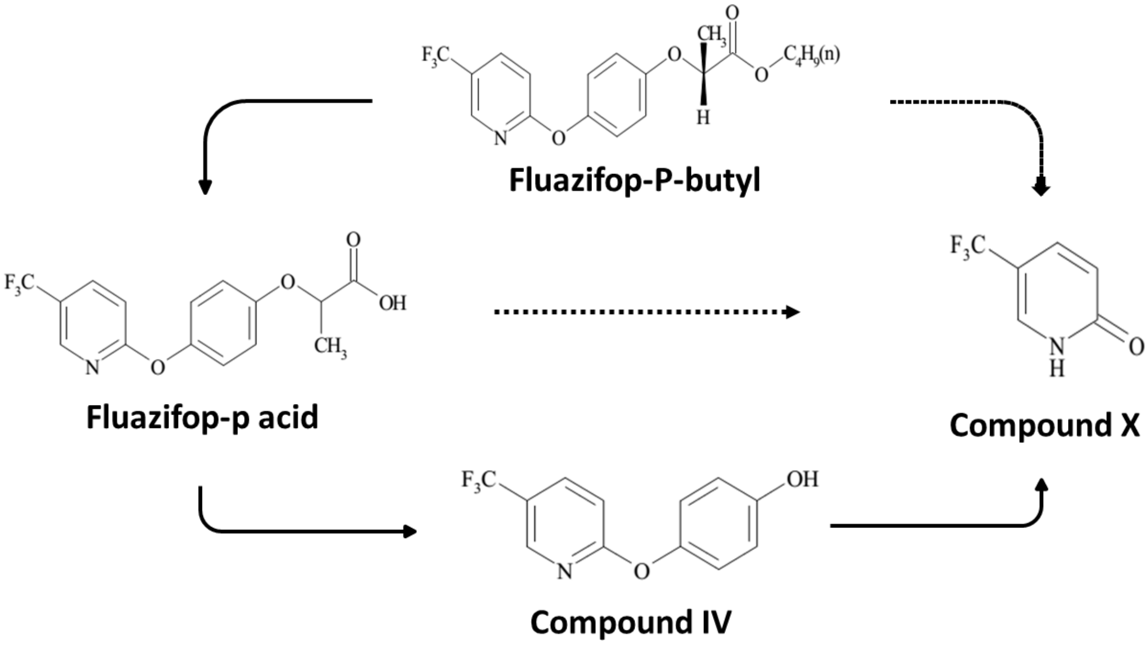

Figure 1. Supposed degradation pathway of fluazifop-P-butyl and selected metabolites in soil according to EFSA (2012). Solid lines represent observed microbial degradation steps in soil. Doted lines represent theoretical degradation steps not confirmed in this study

Table 1. Molecular formula, physico-chemical properties and surface water contamination probability (GUS) for fluazifop-P-butyl, fluazifop-p acid, compound X and compound IV.

	Fluazifop-P-butyl[a]	Fluazifop-p acid[a]	Compound X[a]	Compound IV[b]
CAS N°	79241-46-6	83066-88-0	33252-63-0	69045-85-8
Molecular Formula	$C_{19}H_{20}F_3NO_4$	$C_{15}H_{12}F_3NO_4$	C_6H_4NO	$C_{12}H_8F_3NO_2$
Molecular weight (g mol^{-1})	383.36	327.26	163.09	255.19
Water solubility (mg L^{-1})	0.93	40.5	6000	-
Log K_{ow}[c]	5.3	3.18	-[e]	-
K_{oc}[d] (mL g^{-1})	3394	205	36	-
Soil half-life (days)	0.3-3.3	25	28-58	-
Soil Mobility	Slightly	High	High	Medium
GUS leaching potential	Low	High	High	Medium

[a] IUPAC (2015).
[b] European Food Safety Authority (2012)
[c] Partition coefficient between n-octanol and water (Harper, 1994).
[d] Partition coefficient between soil organic matter and soil solution (Harper, 1994).
[e] Not determined.

Standard solutions and calibration curves

Stock solutions were prepared by dissolving an exact amount of each compound in methanol. A stock mixture of each compound of same concentration was obtained from individual stock solutions by measuring and combining the desired volumes. An aliquot of this mixture was then diluted in methanol to obtain concentrations of 0.19, 0.39, 0.78, 1.56, 3.125, 6.25, 12.50, 25, 50, 100, 200, 400 and 800 µg L^{-1} used for calibration. Standard solutions were all stored at 4 °C prior to use. Concentrations of fluazifop-P-butyl and metabolites (µg L^{-1}) in all sample extracts, mentioned in the subsequent sections, were quantified based on the standard curves. Subsequently the data was adjusted for the final calculations of the compounds in ng g^{-1} of soil.

Soils

Soil samples from three Danish locations were collected at the 10-20 cm layer in the soil profile to conduct the laboratory trial. The three soil types used in this study were: Estrup (mixture of equal parts of Abruptic Argiudoll, Aquic Argiudoll and Fragiaquic Glossudalf); Faardrup (mixture of equal parts of Oxyaquic Hapludoll and Oxyaquic Argiudoll); and Silstrup (mixture of equal parts of Alfic Argiudoll and Typic Hapludoll), classified according to United States Department of Agriculture (USDA) classification system (Soil Survey Staff, 1999). Selected physico-chemical properties of the three soils are given in Table 2. The fields where these soils were collected are farmlands since 1942 at least, and the soils had no record of fluazifop-P-butyl use in the last fifteen years.

Table 2. Physico-chemical characteristics from the 10-20 cm soil layer of Estrup, Faadrup and Silstrup soils (The Danish Pesticide Leaching Assessment Programme, 2015).

	Estrup	Faardrup	Silstrup
Total organic carbon (%)	2.38	1.45	1.8
Organic matter content (%)	4.1	2.5	3.1
pH[a]	7.10	6.5	6.84
Sand (%)	69.8	69	59.6
Silt (%)	11.6	13.3	15.9
Clay (%)	14.6	15.3	22.5
C/N[b]	14.3	9	10
C.E.C. (cmol kg^{-1})[c]	15.9	10.4	20.6
W.H.C. (%)[d]	29	24	32

[a] pH determined in $CaCl_2$ solution.
[b] Organic carbon/nitrogen ratio.
[c] Cation exchange capacity.
[d] Water holding capacity.

Laboratory experiments

The soil samples were thoroughly mixed, air-dried and sieved to 2 mm to ensure their homogeneity. Stones and plant residues were removed from the samples. Sub-samples of 10 g were used to conduct the trial. Soil sub-samples were mixed with 5 g of sand in 100 ml Erlenmeyer flasks. Milli-Q water was added to each sample to assure a water content of approximately water holding capacity. Subsequently, an aqueous solution containing 500 ng of fluazifop-P-butyl per g^{-1} of soil was applied with electronic pipette, which is equivalent to a conventional field treatment dose of 750 g i.a. ha^{-1}. Then the Erlenmeyer flasks were wrapped with rubber lid.

Soil samples without herbicide and with water content adjusted were used as blank treatments. Samples were then incubated at 15 °C in darkness for different periods of time.

Extraction procedure

Fluazifop-P-butyl and its metabolites were extracted from the soil immediately after application 0 h (hours), and after 4 h, 8 h, 12 h, 16 h, 24 h, 2 d, 4 d, 5 d, 6 d, 7 d, 8 d, 9 d, 13 d, 16 d, 20 d, 23 d, 30 d, 41 d, 50 d, 89 d, 106 d, 201 d and 876 days (d) of incubation. The soil samples were transferred to 50 ml falcon tubes where 10 ml of 100 % methanol was added to them. The samples were then placed in ultra sound for 10 min and thereafter placed in the Intelli Mixer to rotate at 40 rpm for 1 hour. After this, samples were centrifuged at 4000 rpm for 10 min at 20 °C and the clear supernatant was recovered. To completely extract any remaining residues, the same samples were subsequently extracted again with the same procedure. The clear supernatant from the two extraction cycles was combined and placed in brown flask (100 mL), which were previously weighed to record the extracted volume. Extracts were stored at -18 °C until analysis.

For each soil, the extraction accuracy and precision was evaluated by estimating percentage recoveries and relative standard deviations (RSDs) at two fortification levels (5 and 500 ng g^{-1}) and six replicates, for all analytes.

Analytical procedures

Aliquots of 500 µL from each of the extracts were filtered (PTFE filters, 0.22 µm, Titan Filtration Systems; Sun SRi, Wilmington, NC) directly into high performance liquid chromatography (HPLC) vials, using a syringe and diluted 1:1 with Milli-Q water. For each time point, aliquots of treatments, controls, and blanks were combined prior to analysis.

LC-MS instrumentation

Chromatographic separation of analytes was performed on an Agilent 1200 HPLC system (Santa Clara, CA, USA) coupled with a Sciex (Forest City, CA) 3200 QTRAP triple quadrupole mass spectrometer (MSMS). The MS was equipped with electrospray ionization (ESI). Multiple reaction monitoring (MRM) data were acquired and processed for fluazifop-P-butyl and compound IV in positive ion mode and for fluazifop-p acid and compound X in negative mode. Optimized values of declustering potential (DP), exit potential (EP), collision energy (CE) and collision cell entrance potential (CEP) are listed in Table 3. The selection and optimization of precursor ion and product ions for each analyte were carried out by direct injection of standards prepared in methanol: water (50:50 v/v) at a flow rate of 200 µL min^{-1}. Optimal values of instrumental parameters were selected and applied to obtain the best MRM transition with the highest intensities possible. The two most intense precursor to product ion transitions were chosen for each compound: the most intense being used for quantification and the other used for confirmation. Data obtained was processed using the Analyst software (version 1.5.2).

Table 3. Instrument conditions and MRM transitions of precursor/product ions of analytes.

Analyte	Ion transition (m/z)	DP (V)	EP (V)	CEP (V)	CE (V)
Fluazifop-P-butyl	384.08 → 281.89[a]	66.0	5.0	46.0	27.0
	384.08 → 327.82	66.0	5.0	46.0	21.0
Fluazifop-p acid	325.85 → 253.87[a]	-35.0	-4.5	-22.0	-20.0
	325.85 → 107.99	-35.0	-4.5	-22.0	-54.0
Compound X	161.82 → 114.97[a]	-45.0	-10.5	-18.0	-32.0
	161.82 → 67.00	-45.0	-10.5	-18.0	-52.0
Compound IV	256.08 → 65.04[a]	51.0	3.0	20.0	47.0
	256.08 → 93.05	51.0	3.0	20.0	31.0

[a] Transitions used in quantitation.

The LC system was equipped with a BDS Hypersil reversed-phase C-18 column (250 mm × 2.1 mm; 5 μm) (Thermo Electron Co., UK), at a temperature of 20 °C. In positive ion mode the mobile phase A and B consisted of 99% 10 nM ammonium acetate, with 1% methanol and 90% methanol with 10% 10 nM ammonium acetate, respectively. The chromatographic method began with an initial mobile phase composed of 10% for solvent B, increasing gradually to 100% in 10 minutes, held constant for a further 16 minutes and decreased to 10% for 1 min, held constant for a further 7 minutes. The total run time was 34 minutes.

In negative ion mode the mobile phase A and B consisted of 90% 20 nM acetic acid with 10% methanol and 100% methanol with 20 nM acetic acid (pH: 3.24), respectively. The chromatographic method began with an initial mobile phase composition of 26% for solvent B, increased to 93% over 3 minutes, held constant for a further 12 minutes and decreased to 26% for 1 min, held constant for a further 9 minutes. The total run time was 25 minutes. For both ion modes, positive and negative, the injection volume of sample extracts or standards was 10 μL. The flow rate was 200 μL min^{-1}. Optimization of chromatographic conditions involved the use of different eluents, varying gradients and injection volumes in order to obtain good chromatograms in the shortest time possible.

Data analysis

Initially, the data was tested for normality and homogeneity of variance assumptions, then three different kinetic models were tested: Single First-order (SFO); First-order Multi-compartment (FOMC); and a Dual First-order in Parallel (DFOP) models (Etzerodt et al., 2008). In the model the flow to the sink compartment was considered, according to FOCUS (2011), to describe herbicides degradation pattern and to obtain the correct end points for the metabolites.

Single first-order kinetics (SFO) is a simple exponential equation with two parameters. In this model the time for a decrease in the concentration is constant throughout the experiment and independent of the initial concentration of the pesticide. Until recently this has been the preferred model.

However, results from degradation studies may not be always well described by first-order kinetics, as in cases that the decrease in the concentration is not constant. This is usually referred to as a bi-phasic pattern of pesticide degradation, for which models like FOMC and DFOP can be better fitted. FOMC divide the soil into a large number of sub-compartments, each with a different first-order degradation rate constant, then this result in a simple analytical equation with three parameters. The integrated form of the bi-exponential model (DFOP) is a sum of two exponential equations with four parameters. Because of these two exponentials, an autonomous constituting differential equation does not exist (FOCUS, 2011).

Based on data fit to the curve (dg-adj R^2), errors distribution, the SFO model was chosen, and is represented by Eq. (1):

$$C = C_0 e^{-kt} \qquad \text{(Eq.1)}$$

where “C” is the herbicide concentration at time “t”, “C_0” is initial herbicide concentration and “*k*” is dissipation rate.

The *Chi-square* (x^2) test *with* $\alpha = 0.05$ was used to estimate whether the model is probably appropriate or not and to assess the goodness of models fit. This test considers the deviations between observed and estimated values (numerator) for each model in relation to the measurements uncertainty (denominator) (FOCUS, 2011). The model that produces the smallest error percentage is considered the best, because it would still be valid at an error level at which the other models would have to be rejected. Subsequently, assuming the reaction kinetics to be first-order, their half-lives (DT_{50}) were calculated by Eq.(2):

$$DT_{50} = \frac{ln2}{k} \qquad \text{(Eq.2)}$$

where DT_{50} is the required time to 50% herbicide dissipation, and *ln2* is natural logarithm of two.

Data analysis were performed with R software (R, 2012), where confidence intervals (95%) for estimated parameters were generated, allowing comparisons between soils.

Results and discussion

Good recoveries of analytes (79.5–114.1%; RSD ≤ 3.1) were obtained for all compounds at the 5 and 500 ng g^{-1} fortification level. The observed degradation of the parent and the onset of metabolites formation are shown in Figure 2. The SFO model described the observed degradation data (fluazifop-P-butyl, fluazifop-p acid and compound IV) well across the soils. In general, R^2_{adj} were high and the errors were < 15%, a threshold value in FOCUS (2011). The estimated parameters from the model fits (SFO model), the corresponding degradation end-points (DT_{50}, DT_{90}), and the statistical indicators to evaluate the goodness-of-fit are presented in Table 4.

The fluazifop-P-butyl degradation among the soils happened rapidly and without a lag phase. Eight hours after herbicide application 79, 77, and 61% of fluazifop-p acid were formed in Estrup, Faardrup and Silstrup soils, respectively. These results indicate a direct degradation of the parent to the corresponding free acid fluazifop. The quick degradation of fluazifop-P-butyl can be partly explained by the high water content and pH-values of the soils (Table 2). These features can favor the degradation of the parent via hydrolysis to fluazifop-p acid (Negre et al., 1988), since this process occurs in faster rate than via microbe metabolism.

The degradation pattern of fluazifop-P-butyl showed slight differences among the soils: in Estrup the degradation was slower (DT_{50} = 10 h) than in Faardrup and Silstrup (approximately DT_{50} = 6 h for both soils). These degradation rates exhibited the same pattern reported by EFSA (2012), Negre et al. (1988) and Badawi et al. (2015). Furthermore, Smith (1987) reported that in moist soils only 8% of the fluazifop-P-butyl remained after 48 hours, which agrees with the DT_{90}-values (< 48 hours) in this study.

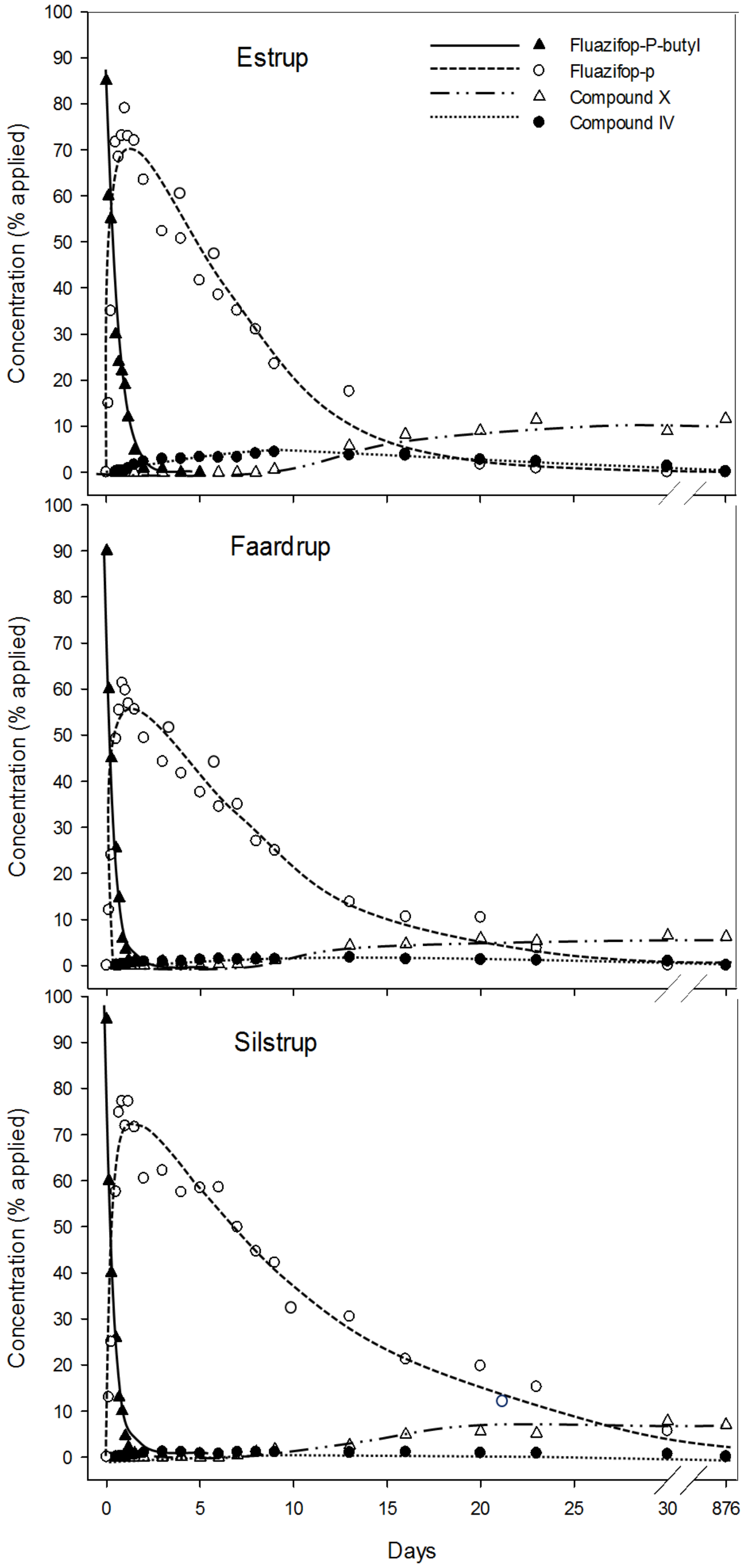

Figure 2. First-order kinetics (SFO) curves describing the degradation of fluazifop-P-butyl and formation and dissipation of metabolites (fluazifop-p acid, compound X and compound IV) in Estrup, Faardrup and Silstrup soils. Data was expressed as relative values considering the fluazifop-P-butyl dose applied as 100%.

The DT_{50}-values for fluazifop-p acid varied between 6 and 10 days among the soils (Table 4). Similar results were reported by Smith et al. (1987), Negre et al., (1993) and Kah et al. (2007), with DT_{50}-values ranging from 6 to 23 days. Fluazifop-P-butyl is formulated as a butyl ester, in this form it is rapidly absorbed into the leaf cuticle. However, once inside the plant the ester linkage is cleaved, producing the free acid which is the active form of the herbicide. This herbicide formulation has advantages by the fact that lipophilic herbicides are rapidly absorbed by plants (WSSA, 2014). In this case fluazifop-p acid is the compound which has the herbicide activity, being generally more persistent than the parent.

Table 4. Parameters of a single first-order models (SFO) for fluazifop-P-butyl, fluazifop-p acid, compound X and compound IV degradation in three different soils.

Herbicide	Soil	C_0[1]	k[2]	CI[3]	DT_{50}[4]	DT_{90}[5]	R^2_{adj}	x^2-*test*
Fluazifop-P-butyl	Estrup	80.97	1.71	1.49-1.96	0.41	1.35	0.99	9.50
	Faardrup	91.83	2.82	2.57-3.09	0.24	0.82	0.99	7.65
	Silstrup	88.82	2.99	2.66-3.36	0.23	0.77	0.99	9.57
Fluazifop-p acid	Estrup	76.60	0.12	0.10-0.13	5.95	19.8	0.98	5.68
	Faardrup	77.20	0.07	0.06-0.08	10.5	33.1	0.98	5.04
	Silstrup	60.20	0.10	0.08-0.11	7.00	23.1	0.98	4.45
Compound IV	Estrup	4.60	0.05	0.04-0.06	13.9	46.0	0.99	8.46
	Faardrup	1.10	0.02	0.01-0.03	30.6	101.6	0.97	8.82
	Silstrup	1.56	0.02	0.01-0.03	35.5	117.8	0.95	11.42
Compound X		Was not possible to measure						

[1] Initial herbicide concentration; [2] dissipation rate; [3] 95% confidence intervals; [4] Required time in days to degrade 50% of the herbicide; [5] Required time in days to degradation 90% of the herbicide; .

The Compound IV maximum concentrations were 4.5, 1.7 and 1.1% formed between 9 and 12 days after initiating the incubation in the three soils (Fig. 3). Maximum concentration of 9.9% for this compound was reported by EFSA (2012) in laboratory conditions, being higher than the observed in this study, since the values can differ depending on the soil physico-chemical characteristics and temperature. The estimated DT_{50}-values for Compound IV were 13.9, 30.6 and 35.5 days in Estrup, Faardrup and Silstrup soils, respectively. This metabolite exhibited a great persistence (DT_{90}-values) in Faardrup and Silstrup soils, being detected up to 100 days after the herbicide application. To our knowledge, this is the first study that reports Compound IV rate of formation and degradation in agricultural soils. Therefore comparisons between our and other soils studies are limited.

As shown in Fig. 3 the maximum concentrations of Compound X were detected approximately at 50 days after incubation. However, it should be noted that Compound X started to be detected around 9 days after parent application, which matches with the days where the maximum concentrations of Compound IV were detected. The presence of Compound X was detected up to 876 days, when the incubation periods were finalized, not allowing the end-point estimations for it. The great persistence of this metabolite in this study can be partly explained by the reduced microbial activity toward the end of a long incubation period (FOCUS, 2011).

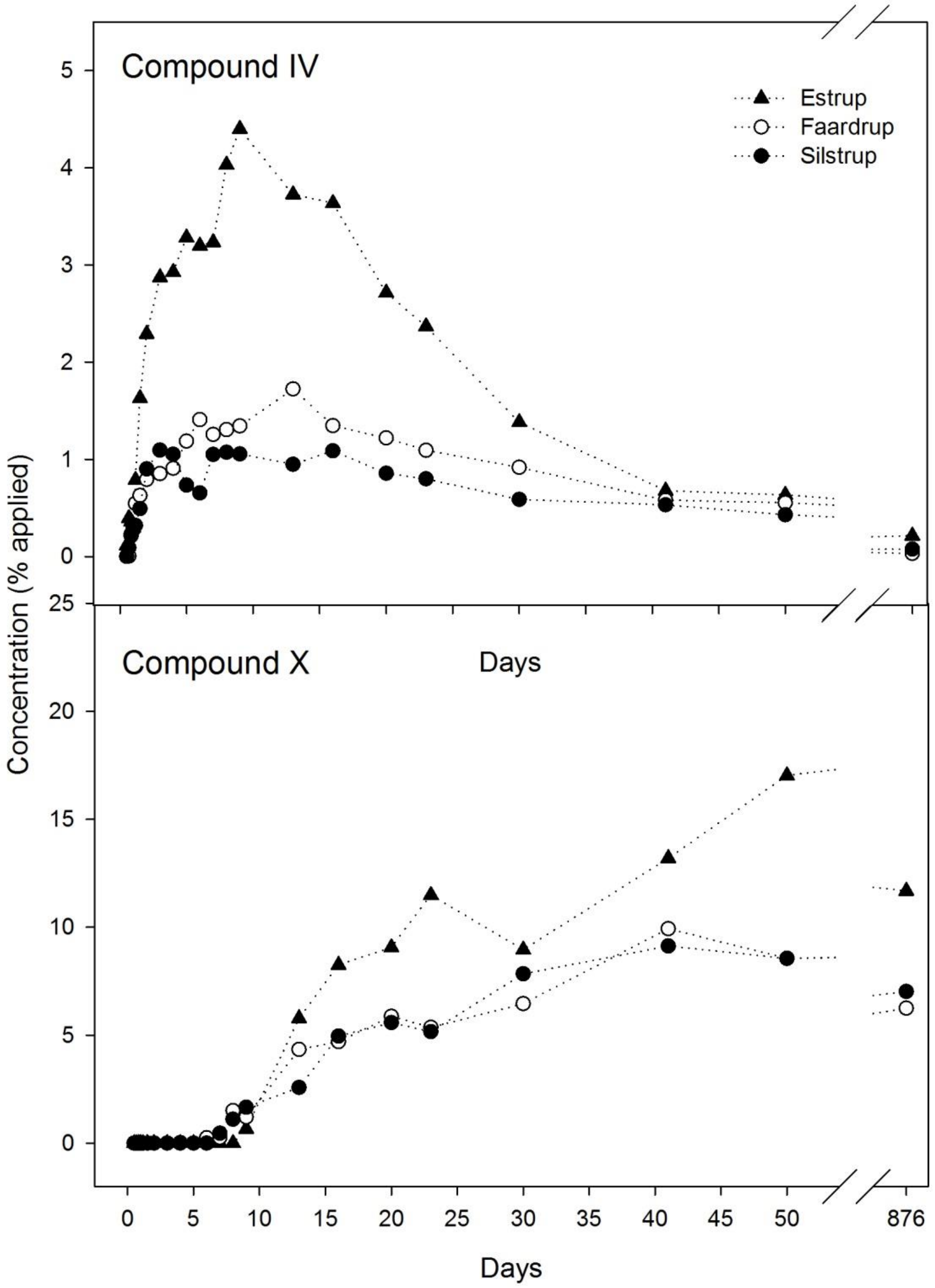

Figure 3. Compound IV and Compound X concentrations in Estrup, Faardrup and Silstrup soils. Data was expressed as relative values considering the fluazifop-P-butyl dose applied as 100%.

The main degradation product of fluazifop-P-butyl was fluazifop-p acid. The sequence of degradation products after the first metabolite suggested the appearance of Compound IV and then Compound X. This pathway matches with the suggested by the EFSA (2012), which also mentioned Compound IV as a major degradation product in soil at 10 °C. However at 15 °C, as in our study, the presence of this metabolite in soil was minor.

A fourth degradation product, (*RS*)-2-(4-hydroxyphenoxy)propanoic acid (designated Compound III in EFSA (2012) and in Badawi et al. (2015)), is also mentioned by the EFSA (2012), but this compound was only observed in plant material at low concentrations after spraying with fluazifop-P-butyl. Future studies in soil should take into account Compound III, which might contribute to the clarification of the complete pathway.

Fluazifop-P-butyl degradation rate was slightly slower in Estrup soil than in the other two soils. However, the fluazifop-p acid and compound IV degradation rate in this soil was faster in comparison to the other two. The greatest detected difference was with Compound IV, where the DT_{50} and DT_{90}-values for Estrup were half of the observed for the other soils (Table 4).

The different soils considered in this study did not have large differences, in regard to their physico-chemical properties. However, there were some minor differences between soils which could influence the herbicide degradation. For the majority of the pesticides, soil organic matter and clay contents are the key properties affecting their sorption and transformation (Durovic et al., 2009; Osborn et al., 2009; Villaverde et al., 2008). There is often a positive correlation between organic matter content and degradation rate, generally seen as an enhanced bioactivity in soils with higher contents.

Estrup soil has a higher amount of organic matter (Table 2), this could relate to the higher degradation rate of fluazifop-p acid and compound IV. Since they are moderately soluble and adhere quite poorly to the soil these compounds are more bioavailable to the microorganisms. Fluazifop-P-butyl is not very soluble in water and has a log octanol-water partition coefficient of 5.3 (at pH 7 and 20 ºC) (Table 1). Hence it is expected to sorb strongly to the organic matter. In this way, the organic matter content has a positive influence on fluazifop-P-butyl sorption processes, inhibiting or reducing its availability to microorganisms and consequently the degradation rate. The slower fluazifop-P-butyl degradation in the Estrup soil, which has higher organic matter content could be explained by the fact that, sorption to humic substances could facilitate the abiotic transformation of the molecule (for example hydrolyses), reinforcing the positive effect of organic matter content on degradation rate (Kah et al., 2007).

The degradation of fluazifop-P-butyl and metabolites could also be related to the size of the microorganism populations originally present in the soils or the microbial diversity, which may cooperate so as to cover different steps in the biodegradation process. Thus, physico-chemical properties of the soil alone are not sufficient to reach accurate conclusions about the differences found among the soils. The degradation process is the result of a complex interaction between different processes and rates of degradation, which are also influenced by biological properties (activity and distribution of microorganisms), environmental conditions, soil temperature, moisture content and the pesticide properties (Kah et al., 2007, Sukul, 2006; Tariq et al., 2006). However, the aim of this study was not to determinate the interaction of these parameters in the degradation process.

According to EFSA (2012), fluazifop-P-butyl is considered to be slightly mobile in soil (Table 1). Fluazifop-p acid exhibits very high to high mobility, while Compound X and Compound IV are very high mobile and medium mobile in soil, respectively. These features explain the slower degradation to Compound IV and Compound X. Taking this into consideration with the results achieved in our trial, field application of fluazifop-P-butyl can give rise to leaching of degradation products to groundwater.

Conclusions

The results show that in soil laboratory incubations under aerobic conditions fluazifop-P-butyl exhibits very low persistence. In the degradation pathway sequence, fluzifop-P-butyl is followed by fluazifop-p acid, Compound IV and Compound X. Fluazifop-p acid is the major degradation product, while Compound IV is observed in minor concentrations. The most persistent metabolite in soil is Compound X. The herbicide degradation pathway has no difference among the soils, even though soil physico-chemical properties are not equal. Thus the degradation pathway is determined by the compounds features, which dictates their fate in the soil.

These results underline the importance of including all products of the fluazifop-P-butyl degradation process in groundwater monitoring programs in areas where this herbicide is used, since they generally show higher persistence in the environment than the parent. Certainly more investigations are required to support these findings under realistic field conditions, which can be explored in future researches related to this herbicide.

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Conclusões Gerais

1 – Pelo menos um agrotóxico foi detectado em 60% das amostras de ar. Os mais frequentes foram chlorpyrifos, fenpropathrin, atrazine e azoxystrobin. Os agrotóxicos com maiores concentrações nas áreas rurais foram chlorpyrifos, fenpropathrin, malathion e atrazine, com uma máxima de 75.8, 73.4, 27.8 e 20.2 ng m^{-3}, respectivamente. Na área urbana chlorpyrifos e fenpropathrin foram os mais frequentemente detectados com concentrações máxima de 16.9 e 15.6 ng m^{-3}, respectivamente.

2 – Pelo menos um agrotóxico foi detectado em 100% das amostras de água. Os mais frequentemente detectados foram atrazine, azoxystrobin, carbendazim e imidacloprid. Os agrotóxicos com maiores concentrações nos rios e lagos foram azoxystrobin e 2,4-D, com uma máxima de 14.3 and 1.94 µg L^{-1}, respectivamente. Em amostras de água residencial propanil, 2,4-D, quinclorac e bentazone foram detectados com a máxima concentrações de 4.11, 3.78, 2.57 e 1.45 µg L^{-1}, respectivamente.

3 – Carbono ativado e osmose reversa foram 100% eficiente na remoção de agrotóxicos, seguido por resina de troca iônica e ultravioleta. Filtros de membrana, em geral, mostraram baixa eficiência, portanto, não são recomendadas para esse propósito.

4 – Em laboratório e sobre condições aeróbicas fluazifop-P-butyl tem baixa persistência no solo. A sequência de degradação é: fluzifop-P-butyl, fluazifop-p, Composto IV e Composto X. Fluazifop-p é o maior produto da degradação, enquanto Composto IV é o com menor concentração e Composto X o mais persistente.

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