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Environmental Pollution Due to Veterinary Pharmaceuticals in Treated Veterinary Wastewater

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Abstract: This study comes to summarize the recent bibliography on the detection of veterinary pharmaceuticals (VPs) in water and wastewater, outline the relevant legislation and removal methods, and finally pinpoint the available tools for tracking the evolution of such chemicals in the watercourse. Since the quantity of drugs supplied to animals is unavoidably increasing, measures must be taken to protect the environment and the living organisms, from the cumulative effects of concentrations of chemicals, either by treating livestock wastewater (LWW) more effectively, and/or by constraining the treated LWW from entering sensitive aquifers. The extent of groundwater pollution from VPs is studied by tracking a hypothetical sewage leakage from a LWW treatment plant and the possible infiltration of chemicals in groundwater. The GMS-MT3DMS model is used and evaluated. The model simulates the evolution of a pollutant in terms of advection, dispersion, adsorption and degradation. The study shows that the applied modeling tool can be effectively used to predict the level of the caused environmental pollution, given the soil and water characteristics, as well as the chemical properties of the potential animal drugs contained in LWW. The model can also be used to optimize the location of injection and pumping wells, in order to direct the plume away from sensitive aquifers.

Key words: veterinary pharmaceuticals, water pollution, livestock wastewater, wastewater treatment, GMS-MT3D

1. Introduction

The detection and removal of pharmaceutical substances in the aquatic environment is an emerging research area, especially for veterinary pharmaceuticals (VPs), due to the growing industry of livestock products. The excessive use of certain pharmaceuticals and their insufficient removal from the wastewater treatment plants (WWTPs) requires their prompt detection in the aquifers and ecosystems in general. The environmental pollution due to VPs, especially in groundwater and soil, seems to have a significant impact on human health [1, 2], but it is not yet very well established.

LWW undergoes biological treatment, after separation techniques (primary treatment). Biological treatment is accomplished, usually, under anaerobic conditions with the additional supply of proper microorganisms [3]. However, the pre-existing pharmaceuticals in the wastewater are not removed sufficiently at the WWTP, and flow freely in the environment [4].

The persistence of VPs in the aquatic environment is attributed, mainly, to their physicochemical properties, but also to the applied veterinary and agricultural practices, the climatic conditions and certain characteristics of the catchment areas (e.g., soil, slope, etc.) in the vicinity of the WWTPs [5].

Thus, contamination by VPs varies according to seasonal weather fluctuations and soil morphology, that enables their transport from the soil to surface and/or ground water.

This study has reviewed the recent literature on the environmental pollution caused by VPs and the LWW treatment procedures that are followed globally, in order to assess the level of awareness and preparedness. The existing legislative framework enforced in Greece

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and the European Union is also presented, with respect to the enforcement of limits to various agricultural activities, animal waste and VPs that cause water pollution.

The efficiency of pharmaceuticals' removal with the aid of plants is presented and analysed from a case study in Portugal.

Finally, this report concludes with the presentation of an operational tool which assists the management and containment of a VPs' spill underground. MT3DMS is used to simulate the fate of a pharmaceutical substance in groundwater aquifers and trace and evaluate its dispersion. MT3DMS is an articulate three-dimensional model, which involves two-layer simulation of dispersion and adsorption processes with an additional calculation of the deceleration factor [6].

2. Legislative Framework

Ministerial Order 1420/82031/2015 (FEK 1709B/17.08.2015) is the latest legislation in Greece which addresses the minimization of water pollution from various agricultural activities. The purpose of these guidelines is to provide good guidance for the implementation of good agricultural practices in order to ensure environmental protection. It aims to minimize nitrogen pollution from various agricultural activities. Common guidelines encourage the use of the treated animal wastes as bio-fertilizers, after their aerobic or anaerobic biological treatment. This practice aims to reduce the use of chemical fertilizers and the related nitrogen pollution. Untreated livestock wastes cannot be used as soil improvements.

Council Directive 91/676/EEC, which adopted by Ministerial Order 16190/1335/1997 (FEK B΄ 519). The Directive concerns the protection of waters against pollution caused by nitrates from agricultural sources, and indicates the need to monitor aquifers for the designation of vulnerable zones from nitrogen pollution.

According to the European Commission Regulation 142/2011, guidelines are set for the use of animal by-products and products not intended for human consumption. Animal wastes should be in situ incinerated.

Furthermore, the Ministerial Order 166640/13 (FEK 554B/08.03.2013) on "Additional environmental licensing obligations for biogas plants using anaerobic biomass treatment", highlights that detailed nitrogen and phosphorus mass balances must be performed for the effective reuse of the treated veterinary WW, without any environmental damage (e.g., nitrogen or phosphorous pollution). The required area is, thus, calculated for the effective use of the organic liquid digest as a bio-fertilizer.

The safe use of VPs must be accomplished according to EU Regulation 2019/6 of the European Parliament and the Council on Veterinary Medical Products. All EU member states must supply appropriate collection and disposal systems, in order to protect the environment, animals and public health. The concept of pharmaceuticals' environmental risk assessment is also mentioned. The assessment occurs in two stages; the level of environmental risk of a certain substance when exposed to the environment, is examined first, followed by the examination of the risks in certain environmental components (e.g., air, soil, water). However, less attention is given to the safe allowable limits of pharmaceuticals that a water recipient can abide. This situation renders their use harmful to the environment and the ecosystems. All pharmaceutical originated wastes (e.g., containers) fall in the 18th category of the European Catalogue of Wastes (18 02: Wastes from research, diagnosis, treatment or prevention of disease involving) and must be managed as hazardous wastes [7].

3. Livestock Wastewater Treatment and Disposal Practices

3.1 Livestock Wastewater Treatment

The livestock wastewater treatment is achieved in two separate stages:

- Primary Treatment
- Biological Treatment

Primary treatment mainly involves the separation of the suspended solids comprised in wastewater, or the dehydration of the waste. Solids are separated by static or vibrating sieves (Fig. 1).

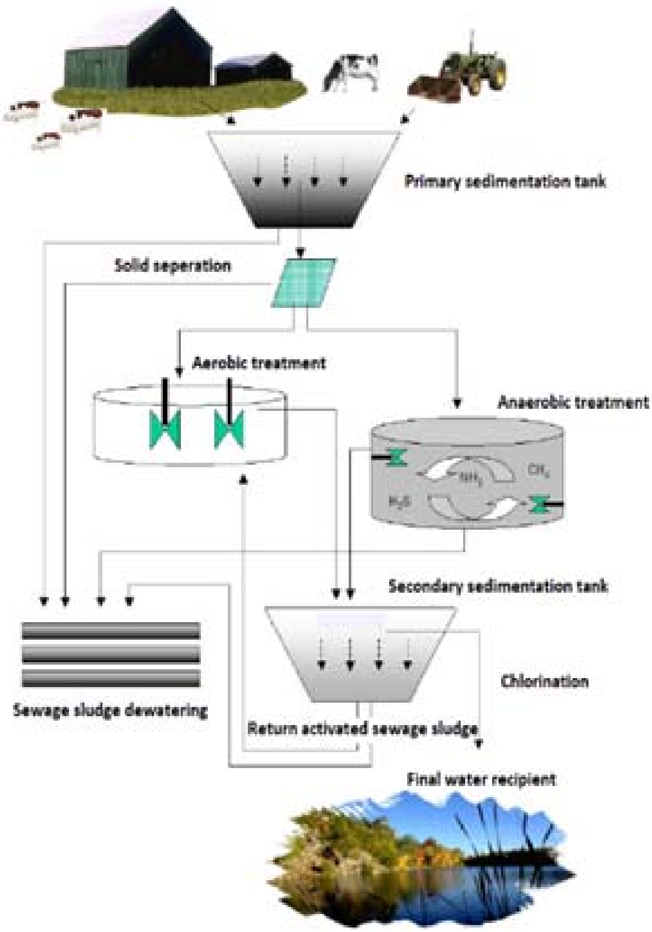

Fig. 1 Flowchart of Livestock WWTP [8]

The biological treatment of animal waste is achieved by the degradation of the complex organic compounds that exist in wastewater, using appropriate micro-organisms. This process can be accomplished either under aerobic or anaerobic conditions [3].

Treatment usually takes place at WWTPs, although, in recent years, it is common, for small wastewater facilities, to use artificial wetlands for the biological removal of pathogens and microorganisms [9-11]. The most commonly used species are cattails (Typha spp.), bulrush (Scirpus spp.) and common reed (Phragmite Australis) [12].

3.2 Disposal of Treatment Products

Products derived from livestock wastewater treatment consist of a liquid effluent, sludge and, in the case of anaerobic biological treatment, biogas. The effluents extracted from the LWWTPs are disposed to water recipients, if they comply to the following limits, provided by the Council Directive 91/676/EEC:

- COD: 125 mg/l
- BOD5: 25 mg/l

With regards to the sludge, produced during the treatment process, it is disposed primarily in agricultural lands as a fertilizer, as it contains high concentration of nitrogen, phosphorus and potassium, as mentioned in the Ministerial Order 1420/82031/2015.

4. Veterinary Pharmaceutical Substances

The active substances of the veterinary drugs provide the best treatment and prevention for animal diseases. Although the benefits of VPs for the target species are significant, the remaining substances leaching into the environment are harmful, as they can adversely affect many non-targeted species. Veterinary practices mainly use antibiotics, antiparasitic drugs and steroid hormones [1]. The most commonly detected VPs and their environmental impacts are described in the following Table 1.

In 25 European Union countries, the yearly use of VPs is estimated to 5393 tons of antibiotics, 194 tons of antiparasitics and 4.6 tons of steroid hormones, as shown in Table 1 [13].

Table 1 Environmental impact and quantity of commonly detected veterinary pharmaceuticals [1, 2].

Veterinary Pharmaceuticals	Environmental Impact	Use of VPs in EU (tn/yr)
Antibiotics	Increase of antimicrobial resistance	5393
Antiparasitics	Increase of antimicrobial resistance	194
Steroid hormones	Development of intersex species	4.6

Veterinary pharmaceutical substances enter the environment through the following routes [14]:

- Wastewater drainage from livestock farms
- Use of treated manure as a fertilizer in agricultural crops
- Aquaculture units

In addition, VPs given to free-range animals, such as cattle, are excreted directly in the fields by animal waste, producing high concentrations and causing negative effects on microbial populations that exist in soil. On the other hand, pharmaceuticals used in aquaculture enter directly water ecosystems, since the most common procedure is the addition to the food. Thus, a respectable amount of food that is not consumed by fish and remains in the water is responsible for extensive pollution of the aquatic environment [15].

Fig. 2 Phragmites Australis species.

Fig. 3 Region of North Portugal under study [16].

5. A Simple Removal Method of VPs from LWWs

Extracting from the literature review one case study, it concerns the fate and removal of VPs in LWWs with the use of plants; more specifically the *Phragmites Australis* (PA) species (Fig. 2).

The experiment took place in a region of northern Portugal (Norte), as shown in Fig. 3. The potential removal of three types of VPs, namely enrofloxacin (ENR), ceftiofur (CEF) and tetracycline (TET) using PA species was studied [16].

The study showed that PA species, informally called *common reed*, are large perennial grasses found in wetlands throughout temperate and tropical regions of the world; they belong to the *Poacea* and the *Molinieae* family and were chosen for their great ability to survive against the toxicity of the LWW [16, 17].

The species were harvested at the mouth of Rio Lima river in Norte region, at four different time periods, July 2010 for ENR, November 2010 for CEF, February 2011 for TET and May 2011, for wastewater testing for each drug substance.

A simple analytical method was used to detect VPs in treated wastewater samples.

The samples were pretreated with solid phase extraction (SPE) technique. The separation of the substances was performed by applying High Performance Liquid Chromatography (HPLC) technique. The recovery rates of the method were 86% for TET, 87% for ENR and 80% for CEF. The total variability of the method was below 14% [16].

The study showed that PA species could effectively remove VPs from LWWs as shown in Table 2 [16]. This solution could be the beginning of a low-cost additional wastewater treatment system for livestock farms and slaughterhouses, in order to remove the substances and protect the environment. Of course, further studies should be carried out to evaluate its efficiency in pharmaceuticals' removal, especially considering the reuse of wastewater, in order to safeguard environmental ecosystems.

Table 2 Efficiency of PA species on pharmaceuticals' removal from LWW [16].

Variable	Concentration (P[b]) (TCC ml^{-1})	Concentration (C[c]) (TCC ml^{-1})
TET	60.26×10^6	77.62×10^6
CEF	50.7×10^6	87.1×10^6
ENR	45.7×10^6	51.29×10^6
WW[a]	112.2×10^6	

[a]: Initial LWW, [b]: Presence of PA species, [c]: Absence of PA species.

6. The MT3DMS Tool

The extent of groundwater pollution from VPs is studied by tracking a hypothetical sewage leakage from a LWW treatment plant and the possible infiltration of chemicals in groundwater. In order to study the fate of a VP, MT3DMS model of US Army Corps of Engineers is used, which is based on the original MT3D [6]. The improved mass transport model that is referred to as MT3DMS, combines the Modular 3-Dimensional Transport model (MT3D) with the Multi-Species (MS) structure for accommodating add-on reaction packages [6]. MT3DMS has a comprehensive set of options and capabilities for simulating in two-layers advection, dispersion/diffusion, and chemical reactions of contaminants in groundwater flow systems under general hydrogeologic conditions.

The model has been used in the past as an optimization tool to remove efficiently a contamination plume from groundwater. This algorithm used MODFLOW to simulate underground aquifer flow, and MT3D to simulate the plume's evolution. The containment of the plume can be achieved by choosing the optimum pumping and injection wells' locations in combination with the optimum pumping rates for plume removal [18, 19].

6.1 Case Study

The MT3DMS — Conceptual Model simulation was applied in this study. The hypothetical VPs spill is in the vicinity of a LWWTP. There are two rivers and two pumping wells, in the area, which need to be protected from the contaminated plume, as shown in Fig. 4.

A transport simulation scenario was studied in order to visualize the long-term potential effect of a pollutant that may leak from the WWTP, in case of an accidental wastewater leakage, and enter into the aquifer. The initial conditions are given in Table 3.

In order to run the chemical reaction package of MT3DMS, which includes the sorption and decay processes, sorption and biodegradation input data were considered in the model for each ground layer. The data are shown in Tables 4a and 4b.

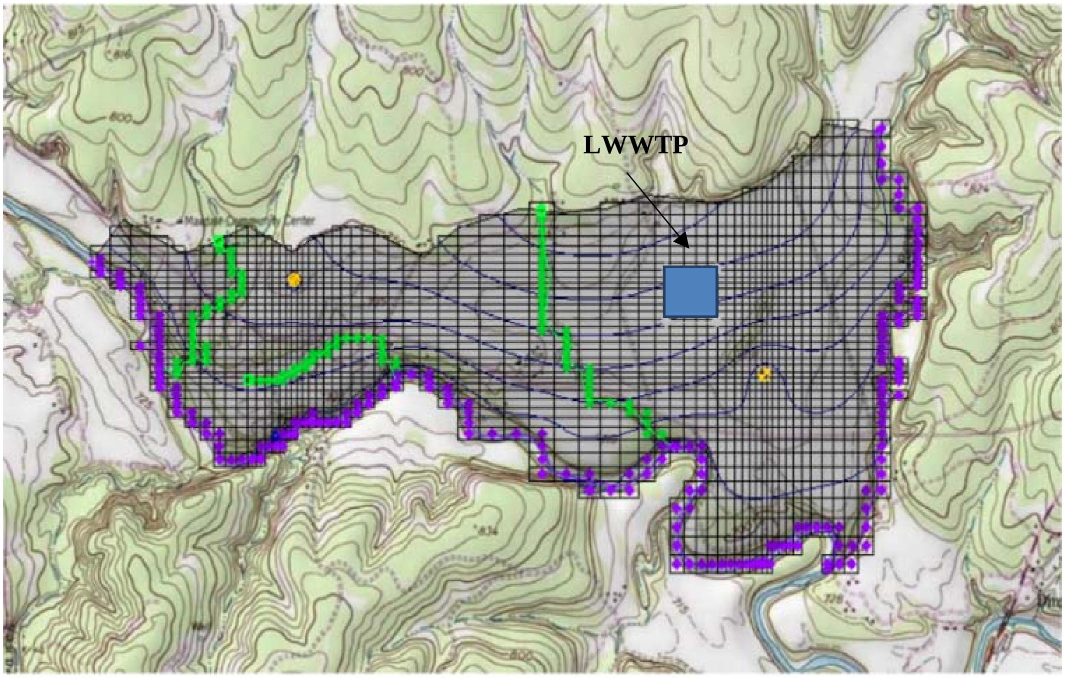

Fig. 4 Study area (LWWTP in blue, wells in yellow, rivers in green).

Table 3 Initial conditions for the simulation.

Variable	Value
Simulation time (d)	3000
Porosity	Layer 1: 0.3 Layer 2: 0.2
Long. Dispersion	20
Pollutant's Concentration (ppm)	20000 ppm
Ratio of horizontal transverse dispersion to longitudinal dispersion	0.2
Ratio of vertical transverse dispersion to longitudinal dispersion	0.1

Tables 4 (a) Sorption and biodegradation data for Layer 1 (4a) and (b) Layer 2.

(a)	
Bulk Density	51500
1st sorption constant	0.00000585
Rate const. (dissolved)	0.00005
Rate const. (sorbed)	0.00005

(b)	
Bulk Density	53500
1st sorption constant	0.00000585
Rate const. (dissolved)	0.0001
Rate const. (sorbed)	0.0001

6.2 Simulation Results

The simulation results, illustrated in Fig. 5, show the fate of the substance due to advection, dispersion, sorption and decay. It is clearly shown that the pollutant does not reach the wells or the rivers after 3000 days, given these initial conditions. Consequently, the plume does not contaminate the drinking water and does not pose any threat to human life.

Fig. 6 shows the pollutant's concentration, expressed in ppm, versus time. The concentration can be measured at any selected point, which could be significantly important in terms of the water quality (pumping well, water supply source etc). In the simulation, cell ID 1310, SE of the LWWTP has been selected to portray the concentration. It is clear that it doesn't reach the predefined threshold of 1ppm after 3000 days.

6.3 Discussion

Even though this is a simple example, it clearly demonstrates however that MT3DMS is a useful tool in the assessment of a pollutant's transport. It provides, through its graphical results, the evolution of the plume and its concentration variation through time. Given initial data and a prespecified concentration threshold, the results can depict whether the contamination will reach a sensitive aquifer or a restricted value. Depending on the initial amount and concentration of the pharmaceutical substance, its fate and evolution can be predicted in order to safeguard the sensitive aquifers and take the necessary measures, in order to remove the substance and contain the pollution. This operational tool can help to manage the dispersion of VPs in the aquatic environment.

One way to achieve that is by installing injection and pumping wells at carefully selected points inside the area under study [18, 19].

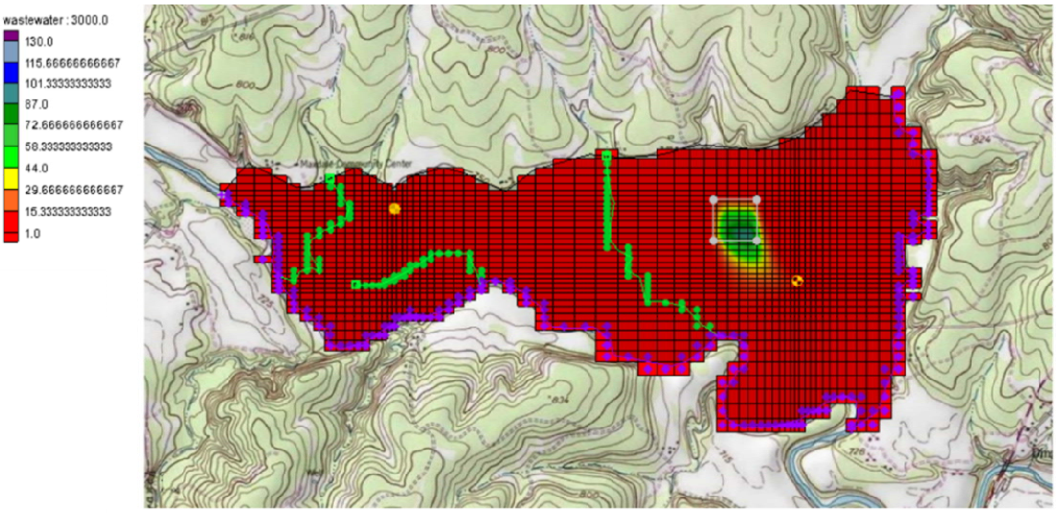

Fig. 5 Graphical results of the simulation.

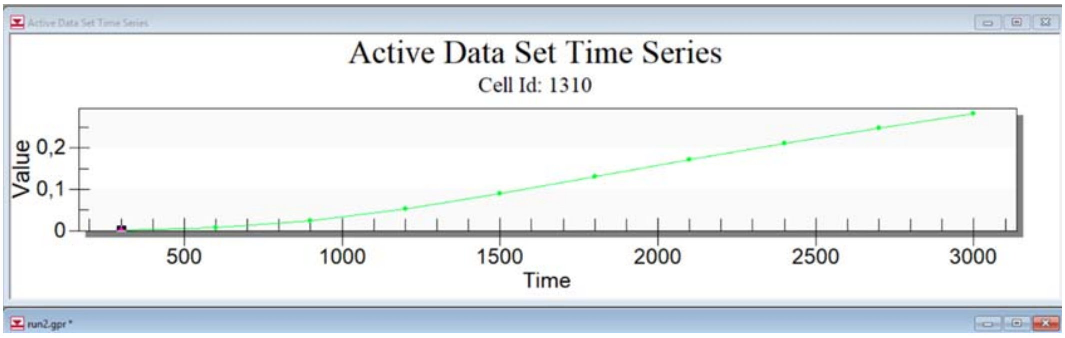

Fig. 6 Concentration of a contaminant vs time for cell ID 1310 (green spot next to WWTP).

7. Conclusions

Pharmaceuticals comprise an important source of environmental pollution, which has only recently started to draw our attention. VPs are excreted by animals directly in the environment, traced in drainage of livestock farms and their immediate disposal to aquaculture units, and recently detected in WWTPs effluents.

This study focuses on the detection of VPs, the applied treatment technologies and their efficiency, the legislative measures in the European Union and Greece, and the application of an operational tool, which can simulate the evolution of the physicochemical properties of a VP substance in groundwater, in order to safeguard sensitive areas, such as rivers and wells.

The legislative framework concerning LWW treatment includes guidelines for the management and disposal of the treatment products, for the effective reuse of the treated veterinary WW, without any environmental damage. Additionally, the legislative framework for VPs contains guidelines for certain preliminary procedures, to safeguard the target species before the authoritative release in the market. However, there are no safe allowable limits set for the pharmaceutical substances released in the water recipients after a WWTP. Even though detection techniques are developed, there is a shortage in VPs removal methods. As a result, pharmaceutical substances remain in treated wastewater and end up in the water recipients.

In order to track a substance's transport in groundwater aquifers, MT3DMS can serve as a managerial tool to predict the path of the pollutant by simulating its physico-chemical characteristics (advection, dispersion, adsorption and decay). In the hypothetical scenario of a malfunction at a WWTP, the model can predict the spreading of the plume, the concentration evolution and the time it will reach a sensitive aquifer or well.

The massive use of VPs and the predicted increase demand the attention of the scientific community on taking preventive measures, such as new technologies directed in removing pharmaceuticals from wastewater. Particularly nowadays, with more intense rainfall and augmented runoff and infiltration due to climate change, monitoring and preventing measures are needed to protect the environment and safeguard public health.

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