Developments in Environmental Science, Volume 5
D. Sarkar, R. Datta and R. Hannigan (Editors)

ISSN: 1474-8177/DOI:10.1016/S1474-8177(07)05009-7

Chapter 9

Agriculture-induced contamination of surface water and groundwater in Portugal

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Abstract

From the end of the 1980s, many studies have drawn the attention to the environmental consequences of "industrial agriculture", namely significant soil erosion and a decrease in water quality. European citizens have demonstrated a growing interest in understanding how their tax money is used in efforts to guarantee the safety and quality of consumer goods and to protect the environment. When Portugal joined the EC in 1986, its main agricultural indices contrasted significantly with those of the other member states. Agriculture made up 12% of gross domestic product, and provided employment to roughly 20% of the active population. In Portugal, the adoption of new technologies, namely improved seeds, higher inputs of fertilizers and pesticides, and mechanization, were introduced later than in other European countries. Sparingly used fertilizers and pesticides partially avoided the negative impact in terms of soil and underground water contamination that took place in many European countries. However, maintenance of the traditional pattern of land allocation to crops had negative impacts in some regions. Extensive cattle breeding in silvo-pastoral systems, low intensity of crop rotation, and excessive tilling resulted in erosion and degradation of soil organic matter with consequent loss of fertility.

The adoption of less-polluting farming practices can only be made with the full cooperation of the agriculture community and largely depends on demonstrating both the environmental and economic benefits of such practices to land managers.

9.1. Agriculture, water quality and ecodevelopment

Agricultural research in 20th century was primarily focused on increased production of food ignoring the impact of agrochemicals on ecosystems.

Agriculture worldwide has several positive effects such as open space and landscape amenities as well as habitat preservation for many wildlife species (Vitousek et al., 1997). Contrarily, negative effects associated with agriculture include loss of biodiversity from conversion of forests and wetlands to agricultural land, degradation of soil and water quality, and overuse of surface water and groundwater for irrigation (Abler et al., 2002). Water quality in rivers is generally linked with land-use in the catchment areas that can affect the amount and quality of run-off during and following rainfall (Ngoye and Machiwa, 2004). Forestry, agriculture, industrialization and urbanization modify watershed management and consequently influence run-off quality and quantity. Additionally, with many rivers experiencing severely reduced flow, wetlands diminishing, and major groundwater aquifer depletion at unprecedented rates, we are moving towards significant scarcity of water resources. The projected need to double food production "must largely take place on the same land area and using less water" (Task Force on Building a Science Roadmap for Agriculture, 2001).

In the European Community (EC), between 1960 and 1980, employment in the primary sector fell from 18.2% to 7.8%, while income from agriculture fell from 11% of total income in 1958 to 3.4% in 1980 (Freire and Parkhurst, 2002). When Portugal joined the EC in 1986, its main agricultural indices contrasted significantly with those of the other member states. Agriculture made up 12% of gross domestic product, and provided employment to roughly 20% of the active population (Freire and Parkhurst, 2002). In Portugal, the adoption of new technologies, namely improved seeds, higher inputs of fertilizers and pesticides, and mechanization, were introduced later than in other European countries, mainly after the entry of Portugal into the European Economic Community. Sparingly used fertilizers and pesticides partially avoided the negative impact in terms of soil and underground water contamination that took place in many European countries. Therefore, Portuguese agroecosystems supported an important agro-biodiversity (crop varieties and livestock breeds) and wild biodiversity (non-domesticated animals and plants). On the other hand, maintenance of the traditional pattern of land allocation to crops had negative impacts in some regions. For instance, the soil erosion that occurred in the basin of the Guadiana River resulted from the use of marginal land (with low-quality soils and excessive slopes for tillage) for the production of wheat under the Wheat Campaign of the 1930s, aiming to ensure the country's self-sufficiency in wheat production (Giordano et al., 1992). Extensive cattle breeding in silvo-pastoral systems, low intensity of crop rotation, and excessive tilling resulted in erosion and degradation of soil organic matter with consequent loss of fertility.

Agricultural intensification in certain regions (mainly in Algarve, Ribatejo and Oeste, coastal Alentejo and coastal Beira Litoral), has led to the overexploitation of underground water. Leaches from pesticides and fertilizers not only polluted groundwater but also surface water with farm run-off, particularly phosphorus (INAG, 1997). In Portuguese agro-ecosystems, the run-off is extremely variable due to intra- and inter-annual variations in precipitation. The highest run-off occurs during the winter months followed by prolonged periods of low run-off. Mean annual rainfall is 922 mm, with 577 mm of the water budget in evapo-transpiration and 385 mm in run-off (INAG, 2001). Total annual water consumption in Portugal is 8754 hm^3, with about 45% from surface run-off and the remainder from underground sources (INAG, 2001). About 74% of water consumption is associated with agricultural activity.

Diffuse pollution is recognized as the main cause of pollution in Portuguese surface water and groundwater, where most of the detected compounds (pesticides and chlorophenols) are present at concentration levels $<1\,\mu g\,l^{-1}$. Higher values (up to $12\,\mu g\,l^{-1}$) are due to specific and punctual pollution episodes, local treatments or accidental spills (Lacorte et al., 2001).

The socio-economic development of Portugal is characterized by a concentration of the population and economic activities near the coast, causing an imbalance in managing water resources. Over the last few years, water resource management has been implemented through the EU Water Framework Directive (2000/60/EC). It requires all inland and coastal waters to reach “good status” by 2015. It will do this by establishing a river basin district structure within which demanding environmental objectives will be set, including ecological targets for surface waters.

9.2. Nitrate pollution

Increased agricultural production over the last 50 years has resulted in increased nitrate (NO_3^-) concentrations in rivers, lakes and underground aquifers. This loss of nitrogen from agriculture represents an economic shortfall, in that the applied nitrogen is not being utilized for food production (Merrington et al., 2002). Nitrate pollution has major impacts on the quality of drinking water and public health, and the eutrophication of surface waters.

The European Community maximum admissible content of nitrate in water for human consumption is $50\,mg\,l^{-1}$. The Alentejo region, in the South of Portugal, is subjected to periods of acute water shortages, as it is common in a Mediterranean climate. This region is extremely dependent on groundwater resources for public supply and agriculture. Beja is a major town of the Alentejo region (*ca.* 20,000 inhabitants) and its public water supply depends partially on groundwater resources of the gabbro-dioritic aquifer surrounding the city and surface reservoir of the Roxo dam (Paralta and Ribeiro, 2001). Increasing concentrations of nitrate in groundwater supplies in Beja were recognized as early as the 1940s. Nitrate monitoring of Beja Aquifer System, performed between 1997 and 2000, revealed median values between 53 and 86 $\mathrm{mg\,l^{-1}}$, and maximum nitrate content between 126 to 225 $\mathrm{mg\,l^{-1}}$ (Paralta and Ribeiro, 2001).

According to a report of the Portuguese Ministry of Environment and Ministry of Agriculture (MAOT, 2000), three vulnerable areas of nitrate pollution were recognized, based on groundwater analysis: Esposende/Vila do Conde (North), Aveiro (North) and Campina de Faro (Algarve, South). To reduce nitrate pollution of groundwater, some agricultural measurements were implemented in these three areas, namely reduction of organic fertilizers applied per hectare. The simulation model Root Zone Water Quality Model (RZWQM), developed by the USDA-ARS (Ma et al., 2001), was used to simulate/evaluate the effectiveness of the agricultural measurements to reduce nitrate leachates. According to the model, the three vulnerable areas would reduce by 50% the nitrate leachates within a nine-year period (MAOT, 2000).

9.3. Pesticides contamination and pollution

Pesticides have become an integral part of modern farming, with most crops receiving several applications per year. Pesticides reduce attack by pests, diseases and weeds and contribute to higher yields and higher economic return. An ideal pesticide would only affect its target organism, be non-persistent and have no harmful environmental effects. However, most pesticides do not have these traits. Pesticides may cause pollution by direct contamination of ground and surface waters, by soil contamination and subsequent leaching into ground and surface waters, and by contamination of non-target organisms (Merrington et al., 2002). In a review work, Pimentel (1995) concluded that less than 0.1% of pesticides reach their target organism.

The amount of plant protection products sold in Portugal, during 2003 was 17,030,910 kg, expressed as active ingredients (Table 9.1). The evaluation of exposure of Portuguese groundwater to pesticides started in the early 1990s (Batista et al., 2002). In 2000, the pesticides and/or metabolites most frequently found in the groundwater of "Beira Litoral"

Table 9.1. Sales of plant protection products in Portugal in 2003 (kg of active ingredients)

Total	17,030,910
Fungicides	12,954,391
Inorganic	11,084,776
Based on dithiocarbamates	1,110,567
Based on benzimidazoles	27,513
Based on diazoles or triazoles	23,396
Others	708,139
Herbicides	2,381,549
Based on phenoxy-phytohormones	84,407
Based on triazines	361,558
Based on amides	11,572
Based on carbamates	114,711
Based on dinitroaniline derivatives	18,924
Based on derivatives of urea, of uracil and sulphonylurea	113,751
Others	1,676,626
Insecticides and acaricides	505,458
Based on pyrethroids	7032
Based on chlorinated hydrocarbons	46,814
Based on carbamates	35,283
Based on organophosphorus products	315,670
Biopesticides	1236
Others	99,423
Molluscicides	27,467
Plant growth regulators	2766
Physiological regulating products	2276
Antisprouting products	490
Rodenticides	29
Mineral oil	582,325
Soil sterilants	549,185
Others	27,740

Source: MADRP (2005).

and "Ribatejo e Oeste", important agricultural regions of Portugal, were atrazine, used in maize, and its metabolites desethylatrazine and desisopropylatrazine; simazine used in vineyards and orchards; alachlor and metolachlor used in maize and metribuzin used in tomato and potato (Batista et al., 2002). The detection of pesticides in groundwater was relatively frequent, although their occurrence at levels above 0.1 $\mu g\,l^{-1}$ was rare. The highest detected values were for metolachlor (17.0 $\mu g\,l^{-1}$), molinate (16.3 $\mu g\,l^{-1}$), atrazine (11.2 $\mu g\,l^{-1}$), alachlor (8.0 $\mu g\,l^{-1}$), 3,4-dichloroaniline (3.8 $\mu g\,l^{-1}$), α-endosulfan (1.4 $\mu g\,l^{-1}$), dimethoate (1.2 $\mu g\,l^{-1}$) and lindane (1.1 $\mu g\,l^{-1}$). Most peak pesticide levels were detected after a period of pesticide application and during the irrigation period, i.e., from March to May (Batista et al., 2002). Leaching losses of pesticides from soil occur when rainfall (or irrigation) exceeds evapotranspiration losses and the soil water content rises above field capacity. The susceptibility of a pesticide to leaching depends upon the interaction of the chemical properties of the pesticide with the chemical and physical properties of the soil (Merrington et al., 2002).

The solubility in water and partition coefficient (K_{ow}) of pesticides varies considerably and has an important influence on their environmental persistence (Munz and Bachmann, 1993). The partition coefficient (K_{ow}) is calculated has the ratio between the distribution of the pesticide between the liquid layers of 1-octanol and water. As the value of $\log K_{ow}$ increases a pesticide tends to become more hydrophobic and it is more likely to bind to organic molecules. Pesticides with partition coefficients values greater than 7 do not generally move far in the agro-ecosystem, but tend to bind strongly to the organic matter in soils and sediments (Merrington et al., 2002). However, $\log K_{ow}$ between 4 and 7 indicate that the chemical is lipophilic and can accumulate in fatty tissues, with potential bioaccumulation effects.

Atrazine and simazine are two herbicides commonly used to control broadleaf and grassy weeds in agricultural lands and on non-cropped industrial lands. They are both significantly water soluble, have relatively low-soil adsorption coefficients and are persistent in both soil and groundwater (Wauchope et al., 1992). Like other organic pesticides, the fate of atrazine and simazine in soil and groundwater systems is controlled to a great extent by its physicochemical interactions with soil and aquifer material. Capriel et al. (1985) reported that nine years after application of atrazine to a field soil, as much as 90% of the herbicide residue was associated with soil organic matter. Systematic studies of the impact of contact time on sorption, desorption and extractability of agrochemicals to surface soils remain scarce. Such studies have the potential to contribute significantly to a better understanding of post-application herbicide dynamics in agricultural fields (Lesan and Bhandari, 2004).

9.4. Phenolic compounds in two dams of Alentejo region (south Portugal)

Water quality monitoring in dams used for human water consumption, carried out by the Alentejo Regional Authorities of the Environment (south Portugal), revealed seasonal peaks of phenolic compounds above the water-quality legislation. Owing to their toxicity and persistence in the environment, phenolic compounds are listed as priority pollutants (Pocurull et al., 1996). Such compounds originate from industrial applications or from the degradation of agricultural pesticides (Daví and Gnudi, 1999).

To identify the main phenolic compounds present in water and soil leachates, and to determine the sources of the seasonal concentrations of phenolic compounds, two catchments in Alentejo were selected, with different land-use patterns: Roxo dam, mainly dry land agricultural area, and Santa-Clara dam, mainly surrounded by shrubs and trees. Surface water and soil samples were collected in several points in the catchments basins of Santa-Clara and Roxo (Fig. 9.1) (Barrico, 2004).

The main phenolic compound detected was 2,4-dinitrophenol (2,4-DNP), both in stream water and soil leachates, with higher concentrations in Roxo catchments (Fig. 9.2). Roxo catchments presents a larger agricultural area than Santa Clara, and it is likely that the origin of the

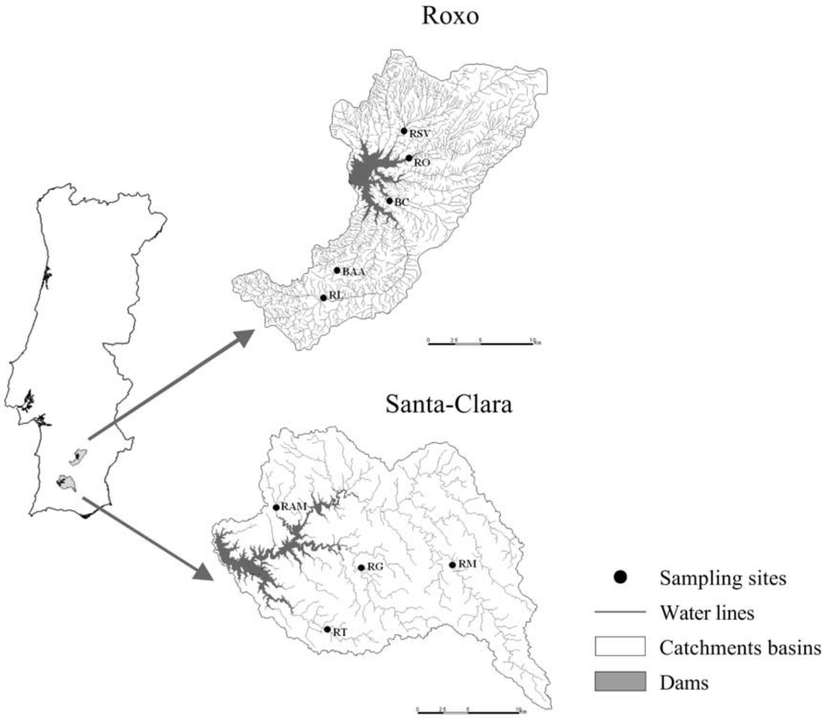

Figure 9.1. Location of the sampling sites in the catchments basins of Santa-Clara and Roxo (Alentejo, south Portugal). Santa Clara: Ribeira das Águas Muitas (RAM), Ribeira de Guilherme (RG), Rio Mira (RM), Rio Torto (RT); Roxo: Barranco da Água Azeda (BAA), Barranco dos Castelhanos (BC), Ribeira dos Louriçais (RL), Ribeira do Outeiro (RO), Ribeira de Santa Vitória (RSV).

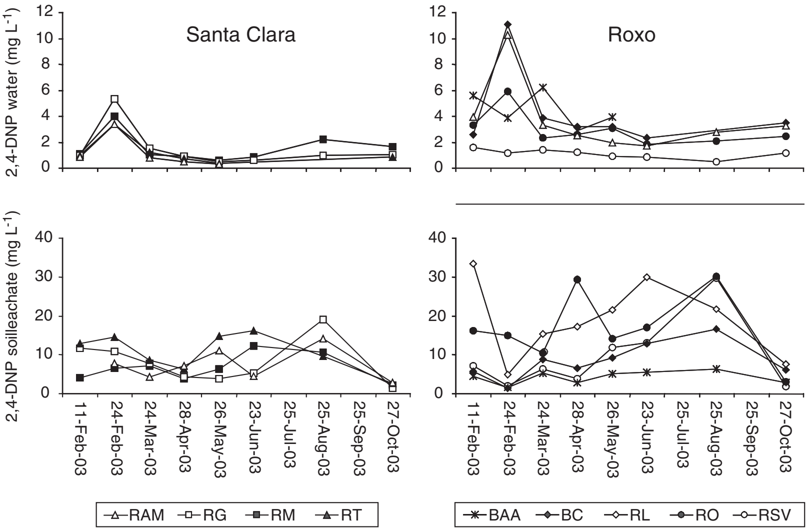

Figure 9.2. Seasonal concentrations of 2,4-dinitrophenol (2,4-DNP) in the water and soil leachate of Santa-Clara and Roxo catchments basins (for legend explanation, see caption of Fig. 9.1).

2,4-DNP is associated with the use of pesticides. According to the National Authorities for Crop Protection of the Portuguese Agricultural Ministry, approximately 20,000 kg fungicides with the active ingredient Dinocape (containing dinitrophenolic substances) were sold in Portugal during 2002.

A peak of 2,4-DNP concentration in stream water, both in Roxo and Santa-Clara catchments, was detected in February, when farmers plough their fields and apply pesticides before planting new crops (Fig. 9.2). The 2,4-DNP peak was probably caused by a precipitation event shortly after application of pesticides, increasing the loss of pesticides from agricultural lands into the adjacent streams.

The concentrations of 2,4-DNP in soil leachates were lower from February to April, and showed a general increase from April to August, somehow opposite to the seasonal trend of 2,4-DNP concentrations in water (Fig. 9.2). The lowest concentrations of 2,4-DNP from February to April could be explained by the precipitation events that “cleaned” the soil, as reflected by the increasing concentrations of 2,4-DNP in surface water (Fig. 9.2). The general increase from April to August could be attributed to: (1) fungicide application during the plant growing season, (2) the absence of precipitation, (3) the decrease on the rate of 2,4-DNP degradation due to lower activity of micro organisms in dry soils (contracted soils) and (4) facility to lixiviate the 2,4-DNP from contracted soils because its pore space does not contain water.

Although there were seasonal fluctuations of 2,4-DNP in soil leachates, it persisted in the soil during the whole sampling period (Fig. 9.2). The 2,4-DNP behaviour is highly pH-dependent due to its weak acid character ($pK_a = 4.09$) (Shea et al., 1983). Adsorption of 2,4-DNP in the soil increases with a decrease in pH when the concentration of non-ionized 2,4-DNP is higher (Shea et al., 1983; O'Connor et al., 1990). All soil samples showed acidic pH values and the leaching process is expected to be difficult, thus more 2,4-DNP remains in soil. Additionally, the microbial degradation (biodegradation), the most important process for the degradation/transformation of 2,4-DNP is not favoured by acidic pH values (Blasco et al., 1999).

The occurrence of 2,4-DNP, besides being related to agricultural activity, also depends on soil type. In Santa-Clara catchments, the highest concentrations of 2,4-DNP in soil leachates were observed in Rio Mira (RM) and Ribeiro do Guilherme (RG) (Fig. 9.2). These sub-basins also show the highest areas of agriculture. In Roxo catchments, Barranco dos Castelhanos (BC) and Ribeira dos Louriçais (RL) showed higher concentrations of 2,4-DNP compared to Ribeira do Outeiro (RO) (Fig. 9.2). These sub-basins showed similar percentages of agricultural area. The observed differences can be explained by the fact that the sub-basin of RO has soils with high-clay content (pellic vertisols) and, as 2,4-DNP is easily adsorbed to clay particles, its run-off from the soil to adjacent streams is probably lower (Shea et al., 1983; O'Connor et al., 1990). Ribeira de Santa Vitória (RSV) showed the lowest concentrations of 2,4-DNP in surface water (Fig. 9.2). Assuming that the agricultural practice is similar among the sub-basins, a likely explanation for the low concentrations of 2,4-DNP in the stream water of RSV, besides the fact that the soils have high-clay content (adsorbing 2,4-DNP), this stream has a high abundance of vegetation, mainly *Scirpus* spp. and *Typha* spp., that may play an important role in the removal of the 2,4-DNP from the water. Plant roots can produce peroxidases that are capable of oxidizing phenolic compounds to free radicals. The oxidation products can form water-insoluble oligomers, with no toxic effect (Agostini et al., 2003). Phytoremediation can constitute an important method to remove specific organic pollutants from contaminated waters.

9.5. Good agricultural practice for the protection of water resources

The production-oriented objectives of agricultural policy in the last 40 years have brought significant costs to the natural environment.

Diffuse pollution can be considered as the most relevant threat for the quality of surface and groundwater, as the majority of point source pollution has been intercepted in Europe and put under control (Lacorte et al., 2001). Diffuse pollution may result from the use of chemicals that are, after application, spread from the point of application to the environment by means of run-off, dispersion and diffusion. Poorly managed agriculture can lead to pollution of surface and groundwater by nitrates/nutrients and pesticides. The political agenda of most developed countries is therefore now shifting towards the integration of agricultural and environmental policy (Merrington et al., 2002). Best agricultural practices for water protection should be promoted and an appropriate network to monitor trends in the quality of groundwater concerning diffuse pollution (Paralta and Ribeiro, 2001). Current forestry research has demonstrated that planting or maintaining buffer strips of land near streams will trap excess agricultural chemicals in addition to providing timber and wildlife habitat (Task Force on Building a Science Roadmap for Agriculture, 2001).

The presence of pesticides residues in groundwater call for a need to improve plant protection and irrigation practices. It may be necessary to select carefully the pesticides to be used, in each agricultural area, according to its hydro-geological vulnerability (Batista et al., 2002). The adoption of less-polluting farming practices can only be made with the full cooperation of the agriculture community and largely depends on demonstrating both the environmental and economic benefits of such practices to land managers (Vandermeer et al., 2005).

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