

## **RISKS ASSESSMENT OF WATER POLLUTION BY PESTICIDES AT LOCAL SCALE (PESTEAUX PROJECT): STUDY OF POLLUTING PRESSURE**

**Stéphanie NOEL<sup>1</sup> & Boubacar BILLO BAH<sup>2</sup>**

<sup>1</sup> Engineering Department, Agricultural Research Centre of Wallonia (CRA-W)  
Gembloux, Belgium

<sup>2</sup> Biometry, Data management and Agrometeorology Unit  
Agricultural Research Centre of Wallonia (CRA-W), Gembloux, Belgium  
Corresponding author E-mail: noel@cra.wallonie.be

### **SUMMARY**

Pollution of water resources (surface waters and ground waters) by pesticide uses is one of the key point of the European policy with the implementation of the Water Frame Work Directive (2000/60/EC) and the thematic Strategy on the Sustainable use of pesticides. According to this legislation, the Member States must initiate measures to limit environmental and toxicological effects caused by pesticide uses.

The Agricultural Research Centre of Wallonia (CRA-W) emphasized the need of a tool for spatial risk analysis and develop it within the framework of PESTEAUX project. The originality of the approach proposed by the CRA-W is to generate maps to identify the risk of pollution at locale scale (agricultural parcel). The risk will be assessed according to the study of different factors, grouped under 3 data's layers: polluting pressure, vulnerability of the physical environment (soil) and meteorological data.

This approach is directly based on the risk's definition which takes into account the polluting pressure, linked to the human activities, and the vulnerability of the soil, defined by factors of physical environment which characterize the water flow in the parcel. Moreover, meteorological data influence the intensity and likelihood flow of water, and indirectly pesticide by leaching or runoff.

The PESTEAUX's approach to study the pollution is based on the model "source-vector-target". The source is the polluting pressure, in other words, the pesticides which could reach the targets. The main vector is the water which vehicles the pesticide on and trough the soil until the target which are the surface waters or ground waters.

In this paper we introduce the factors contributing to the polluting pressure. These factors are linking to the human activities and more precisely, to the pesticide uses. The factors considered have an influence on pesticide's transport by water (in its solid state or in dissolved state by leaching, run-off, or erosion) but also on a set of process controlling pesticide behavior in the environment such as degradation, sorption, ....

**Key words:** water pollution, pesticide, PESTEAUX project

### **INTRODUCTION**

Pollution water by pesticide is a key issue in the European environmental policy. European directives and strategies, such as the Water Framework Directive (Directive 2000/60/EC) or the Thematic Strategy on the Sustainable Use of Pesticides, impose Member States to take measures to limit environmental hazards caused by the use of plant protection products. The PESTEAUX project, initiated by the Agricultural Research Centre of Wallonia (CRA-W), comes within this framework. This project aims at implementing a decision support system based on a Geographic Information System (GIS) to assess diffuse pollution risks of surface and groundwater resources by pesticides.

Qualitative risk assessment takes into consideration : (i) the polluting pressure linked to the use of pesticide (ii) the vulnerability of the soil defined by factors of physical environment which characterize the water flow in the parcel and (iii) meteorological data which influence state of water soil, the intensity and likelihood flow of water (vector of pesticide), by leaching or runoff. This paper reviews current knowledge regarding factors contributing to pesticide pressure and more precisely, pesticides properties influencing the fate and behaviour of pesticide in soil.

The pesticides applied on the field exert a "polluting pressure" on the environment. Pesticide could reach the water resources, transported by water. Pesticide is transported in its solid state by erosion or in dissolved state by run-off or leaching. The soil compartment has a major influence on the fate and behaviour of pesticide applied. Understanding the fate of a pesticide in soil is a key element to assess his effect on the environment (Kah, 2007). The risk of pollution regarding the "polluting pressure" depends on pesticides uses, period of application (which influences the degradation and the hydric state of soil) and properties of active ingredients.

## MATERIALS AND METHODS

The behaviour of pesticide depending on active ingredients properties, we have reviewed the mean properties. According to Barriuso (2004), behaviour of pesticide depends on:

1. Adsorption
2. Degradation and transformation
3. Transport

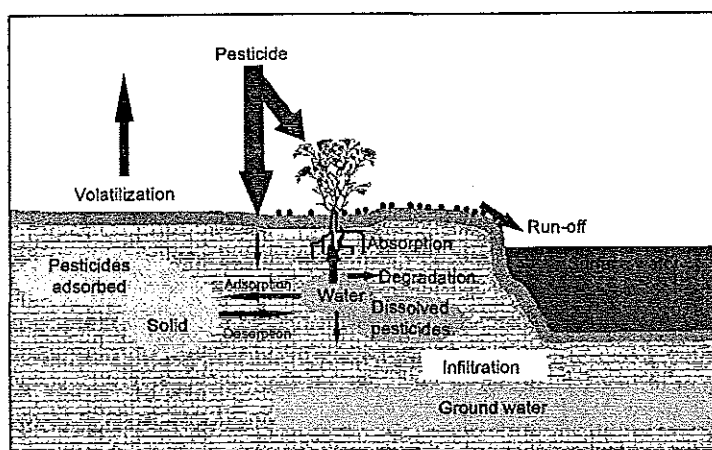


Figure 1. Behaviour of pesticide in soil (Adapted from Barriuso *et al*, 1996).

### Adsorption

Sorption is one the key processes controlling transport, transformation and biological effects of pesticide (Calvet, 1989, quoted from I. Dubus *et al*, 2001). The pesticide sorption, usually summarised by Koc value, has to be considered carefully. Koc is not appropriate for such compounds. For un-ionised pesticides (for example:

isoproturon, diuron, chloridazone, ...) soil organic matter content is the most important soil property for predicting the sorption. The lipophilicity is the most important physicochemical property influencing movement of un-ionised pesticides through soil (hydrophobic adsorption on organic matter). For hydrophobic compounds, sorption to soil organic matter can be described predominantly as a partitioning process between a polar aqueous phase (soil water) and a polar organic phase (soil organic matter). The octanol/water partition coefficient ( $K_{ow}$ ) and the solubility in water ( $S_w$ ) are important parameters used to illustrate the lipophilicity of the pesticide.

Ionisable pesticides (for example: 2-4D, terbutylazine, simazine,...) possess either a basic or an acidic functional group. They can be partially ionised within the range pH of soils (Kah, 2007). So sorption of ionisable pesticides depends on soil pH in relation to the dissociation constant ( $pK_a$ ) of the pesticide (figure 2).

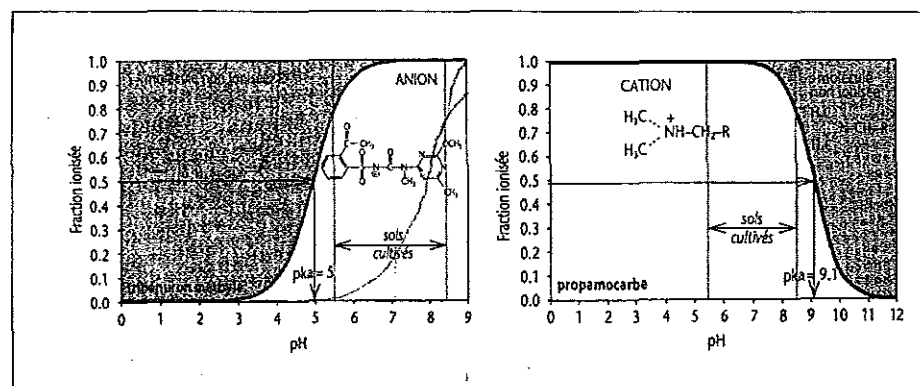


Figure 2. Dependence of neutral or ionic form according to pH (Calvet *et al*, 2005).  
Acidic pesticide: Neutral forms are more strongly sorbed than anionic forms. The anionic forms, due to minus charge, are generally weakly retained in the country.  
Basic pesticide: cationic forms, bonded by cationic exchange, are more adsorbed than neutrals forms.

### Degradation and transformation

The degradation plays an important part in pesticide eliminating from environment. The pesticide degradation are controlled by biotic (biodegradation) and abiotic (hydrolysis, photodegradation, ...) factors and thus depends on chemical and biological properties of the soil.

Rate of pesticide degradation is studied in laboratory and express through *half life time* ( $DT_{50 \text{ labo}}$ ). Soil dissipation studies are carried out in field. The field studies provide  $DT_{50 \text{ field}}$  which takes into account a set of process involved in pesticide eliminating from soil such as degradation but also irreversible adsorption, transport, ... Dissipation rate is determined under defined conditions as Koc so it has to be considered carefully.

Additional studies to determine fate and behaviour in surface water and groundwater are carried out. Hydrolytic degradation studies carried out at pH 7 without light illustrate pesticide behaviour in groundwater. Water/sediment studies supply pesticide degradation into surface water. These studies carried out for the pesticide agreement provide information on pesticide persistent into water.

Some risk assessment methods consider high risk of pesticide pollution if the  $DT_{50}$  field is upper than 21 days (slow dissipation) and  $K_{oc}$  value below 500 L/kg (high mobility) (Barriuso, 2004).

This method doesn't take into account the pesticide persistent inside groundwater. By this way, pesticides with high degradation are considered as low risk pollution. In vulnerable areas (karstic constraints, underground water), where preferential flows lead to rapid transport through groundwater, the pesticide persistent into groundwater has to be taken into account.

### Transport

The major factors influencing pesticide movement in the soil are: sorption coefficient, the transformation rate, the excess of rainfall and the evaporation, the season of application and the uniformity of water flow in soil (Boesten, 1987; Calvet, 2005). The table 1 summarizes the main way of pesticide transport.

Table 1. Pesticide movement into the environment

| Main type of flow                          | Transport in the liquid phase                        |  | Transport in the gaseous phase |
|--|--|--|--------------------------------|
|  | Movement in the soil and to the groundwater          | Movement on the soil and towards surface water | Towards atmosphere             |
| Transport of pesticide in gaseous state    | Diffusion  |  | Volatilization                 |
| Transport of pesticide in dissolved state  | Diffusion (In interstitial water)<br>Convective flow | Leaching                                       | Runoff                         |
| Transport of pesticide in solid state      | Particle transport<br>Massive transport              | Tillage  | Erosion<br>Runoff              |
| Transport of pesticide by living organisms | Biological transport                                 | Earthworm                                      |                                |

Pesticide movement in the soil takes place in solid, liquid or gaseous state. Pesticide properties influencing transport in gaseous state are vapour pressure and Henry coefficient ( $K_h$ ). Volatile pesticides, with a vapour pressure upper than  $10^{-4}$  Pa and a high  $K_h$  (upper than  $2.10 \text{ atm}\cdot\text{m}^3\cdot\text{mole}^{-1}$ ), reach atmosphere by volatilization. The transport by volatilization can decrease 90 % of the dose applied (Bedos *et al*, 2002).

Pesticides are carried by water, to groundwater or surface water, in dissolved state or linked with particle. The transport in liquid state depends on pesticide properties, among other things, as mostly solubility and adsorption (Lecomte, 1999). Solubility increases pesticide transport, in dissolved state, by leaching. Adsorption decreases leaching but increases risk of particle transport and thus pesticide movement through surface water (IUPAC, 1995).

## RESULTS AND CONCLUSION

The main pesticide properties taken into consideration to study pesticide movement in soil and to assess risk of water pollution by pesticide are: adsorption coefficient, half life time in soil and in water, hydrophobicity of the molecule. The hydrophobicity properties are deduced from solubility and octanol/water partition coefficient ( $K_{ow}$ ).

As we have seen, the properties can change according to the pH for ionised pesticide. We have to be conscious of pH playing an important part of pesticide fate in soil. Pesticide properties are taken into consideration to assess polluting pressure according to ionised or un-ionised pesticide (Figure 3).

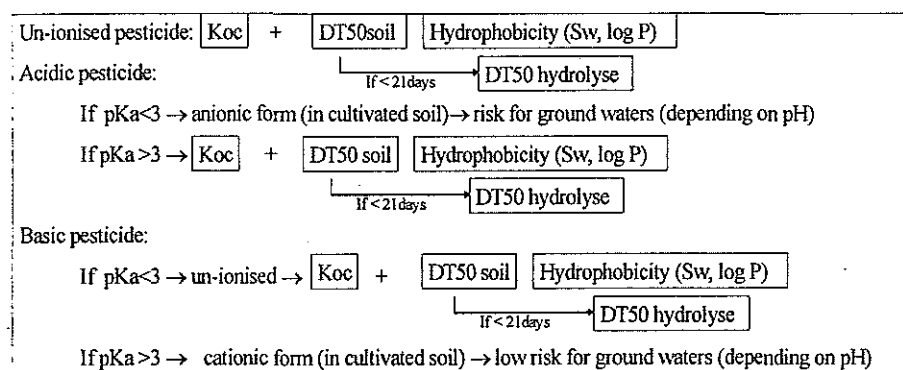


Figure 3. Main pesticides properties considered for risk assessment, according to pesticide type. Log P = Log  $K_{ow}$

The risk assessment based only on pesticide properties is a first step; other parameters must be taken into consideration as meteorological data and vulnerability of the soil.

## LITERATURE

- ATTEIA O. (2005). Chimie et pollutions des eaux souterraines. Edition LAVOISIER. 398p.
- BEDOS C., P. CELLIER, R. CALVET & E. BARRIUSSO (2002). Occurrence of pesticides in the atmosphere in France. *Agronomie* 22:35-49.
- BARRIUSSO E., P. AUROUSSEAU, C. BOCKSTALLER, R. CALVET, I. DUBUS, F. MALTERRE & B. REAL (2004). *Estimation des risques environnementaux des pesticides*. Paris, France, Institut National de la Recherche Agronomique (INRA), 123 p.
- BOESTEN J.J.T.I. (1987). Leaching of herbicides to ground water: a review of important factors and available measurements. *Proceeding: British crop protection conference-weeds*. 559-565.
- BRGM (2005). Cartographie de la vulnérabilité intrinsèque des eaux souterraines en région Nord-Pas-de-Calais. 113p.
- DUBUS I.G., E. BARRIUSSO & R. CALVET (2001). Sorption of weak organic acids in soils: clofencet, 2,4-D and salicylic acid. *Chemosphere*, 45:767-774.
- CALVET R. (2005). Les pesticides dans le sol. Conséquences agronomiques et environnementales. Edition France Agricole. 637p.
- CALVET R., E. BARRIUSSO & I.G. DUBUS (2007). Application of two surface complexation models to the adsorption of weak organic acids by soil: an additive approach. *European Journal of Soil Science*, 58:609-624.

- DE BRUYN B. (2004). Etude de la vulnérabilité des eaux aux produits phytosanitaires : indicateur environnemental et modèle mécaniste, en vue d'une meilleure gestion du bassin versant de la Leysse (Savoie). Thèse de doctorat préparée au Laboratoire d'étude des Transferts en Hydrologie et Environnement et du SOGREAH - Grenoble. 256p.
- HALLET V. (2008). Cours d'hydrogéologie. FUNDP. 147p.
- IUPAC (1995). Offsite transport of pesticides in water : Mathematical models of pesticide leaching and runoff (technical report). Pure and applied chemical, vol. 67, 12. 2109-2148.
- KOLLER R., J. SAUTER, S. PIERRILLAS & M. VIROT (2004). Classification des bassins versants alsaciens en fonction de leur sensibilité aux produits phytosanitaires. Etude et gestion des sols, volume 11(3):219-234.
- LECOMTE P. (1998). Les sites pollués: traitement des sols et des eaux souterraines. 2<sup>ème</sup> édition. LAVOISIER. 204p.
- NOVAK S., JM PORTAL, JM MOREL & M SCHIAVON (1998). Mouvement de produits phytosanitaires dans le sol et dynamique de transfert par l'eau, Comptes-rendus à l'Académie d'Agriculture. 119-132.
- NICHOLLS P.H. (1988). Factors influencing entry of pesticides into soil water. Pesticide Science, 22:123-137.
- SCHIAVON M., C. PERRIN-GANIER & JM PORTAL (1995). La pollution de l'eau par les produits phytosanitaires : état et origine. Agronomie, 15:157-170.
- SCHIAVON M. (1998). L'eau et les produits phytosanitaires. Mécanismes de dispersion et de transfert selon les conditions climatiques et selon le produit. Phytoma, 511:16-19.
- SURDYK N., I.G. DUBUS, C. CROUZET, A. GAUTIER, C. FLEHOC & BT NOLAN (2008). Estimation de la mobilité dans les sols de molécules ioniques à caractère acide faible : application à l'évaluation des risques environnementaux dans le cadre de l'homologation de produits phytosanitaires. Rapport final du projet BRGM PDR04EAU19, mai 2008. 111pp.