



# Ecological risk assessment of pesticide mixtures in the alluvial aquifers of central Italy: Toward more realistic scenarios for risk mitigation

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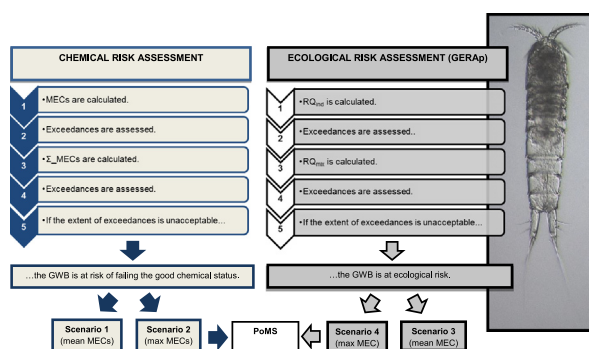
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## HIGHLIGHTS

- Four risk scenarios were analyzed in 11 alluvial aquifers in Italy.
- A procedure for groundwater ecological risk assessment (GERAp) is presented.
- GERAp is based on the stygobiotic species sensitivity to pesticides.
- GERAp's scenarios support risk managers in developing mitigation measures.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study we used the data of an extensive pesticide monitoring survey that took place in 11 alluvial aquifers of central Italy from 2010 to 2015 to explore 4 different scenarios of risk. The Scenarios 1 and 2 were used to depict the risk of failing to meet the good groundwater chemical status as defined by the Water Framework Directive. The Scenarios 3 and 4 were used to assess for the first time the ecological risk in groundwater bodies, defined as the likelihood of hazard to the groundwater communities stably residing in the 11 alluvial aquifers that may be affected by pesticide contamination. The ecological risk was assessed through a new procedure called GERAp (Groundwater Ecological Risk Assessment due to pesticides). The main results of this study highlighted that: 1) the Scenario 1 provided information of little use for risk managers; 2) more realistic information was provided by using the highest concentrations measured in the six-year monitoring period and considering the ecological risk in a combined scenario (Scenarios 2 and 4); 3) the achievement of the good chemical status by 2027 in 3 aquifers will be likely much more difficult than in the others because the ecosystem services, such as pesticide biodegradation, are likely less efficient in the 3 groundwater bodies; 4) some pesticides that were banned in Europe in 2009 should be kept monitored in the next surveys because they showed a persistent occurrence in the 11 aquifers; 5) DDT forms, Dieldrin and Heptachlor are expected to damage groundwater communities at concentrations that are lower than the present legal limits.

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## 1. Introduction

In most European states the consumption of pesticides by weight is slightly but constantly decreasing since 2011 (EUROSTAT, 2016).

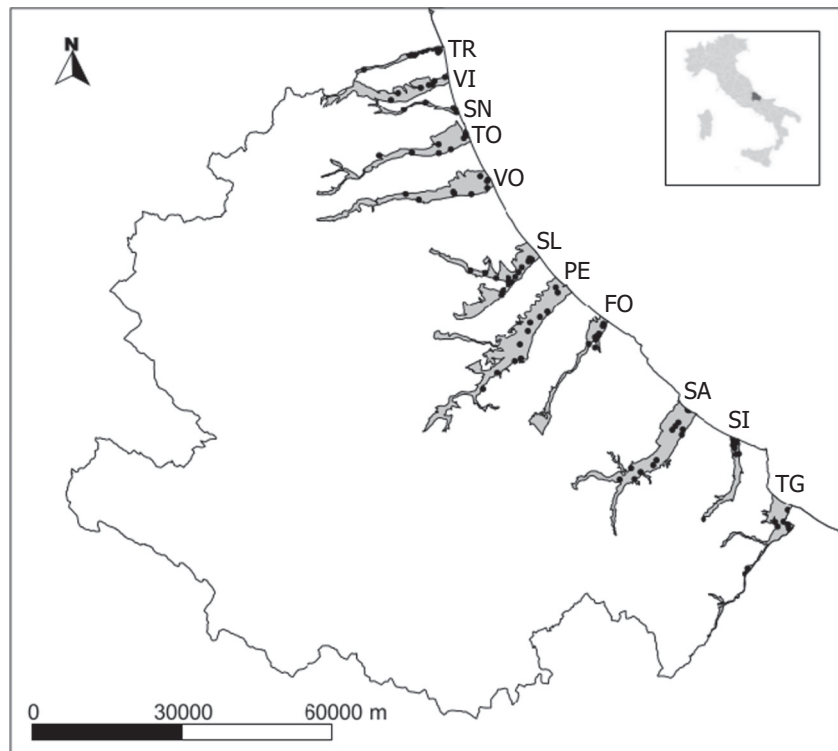
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However, the environmental potential damage determined by these substances is not related to the amount used. Given their undisputed role in limiting, inhibiting and preventing the growth of harmful bacteria, fungi, weeds, invasive plants and animals, pesticides have been massively used in agriculture since the agrarian revolution after the World War II. Pesticide pollution in aquatic ecosystems worldwide has become a large-scale environmental problem since that time (Meffe and de Bustamante, 2014; Silva et al., 2015). Groundwater protection against pesticide contamination is a priority in the global environmental policy because pesticide contamination in groundwater (1) can last for decades, (2) damages the sources of potable water, (3) affects the quality of groundwater associated ecosystems such as most rivers whose base flow relies on groundwater and (4) poses a risk to groundwater ecosystems, despite this key-point is still not ruled by any Directive. Pesticide contamination affecting groundwater bodies has been reported by all EU Member State but Sweden (Meffe and de Bustamante, 2014). Particularly problematic is the contamination in the Mediterranean area, where groundwater ecosystems are under continuous water stress in the dry season when water demand exceeds the available amount. In addition, groundwater bodies are usually exposed to a cocktail of pesticides rather than to one individual compound (EUROSTAT, 2016). Despite the common occurrence of pesticide mixtures, modern EU regulations focus almost exclusively on the risk assessment of individual chemicals. However, the toxicity of a pesticide mixture is usually higher than the toxicity of the individual components (Verbruggen and van den Brink, 2010). This implies that all the compounds may contribute to the overall mixture toxicity, even if they occur individually at concentrations that are not harmful to the freshwater biota (Carvalho et al., 2014).

In Europe, the Water Framework Directive 2000/60/EC (WFD; EC, 2000) has been developed to protect water resources. The main goal is to achieve the objective of at least good water status within 4 management cycles, each lasting six years. While the good status of a surface water body is reached when the ecological, quantitative and chemical status are at least good (art. 2/18 of the WFD), the objective of good

status for a groundwater body is met when its quantitative and chemical status are at least good (art. 2/20 of the WFD). The ecological status of groundwater bodies is thus neglected by the WFD. However, groundwater bodies are also ecosystems. They house a biodiversity of high conservation value (Maurice and Bloomfield, 2012). Fifteen percent of the European freshwater animal species is represented by obligate groundwater-dwelling (stygobiotic) taxa, most of which are crustaceans (Gibert and Culver, 2009), showing a rate of endemism over 90% (Deharveng et al., 2009). Some stygobiotic taxa are unique, being the only remnants of ancient evolutionary lineages disappeared from surface water environments during their evolutionary history (Galassi, 2001). Beyond the intrinsic conservation value of groundwater species, stygobiotic communities provide a range of ecosystem services (Boulton et al., 2008; Griebler and Avramov, 2014). Groundwater micro-organisms make a major turnover of carbon and energy in groundwater (Danielopol et al., 2003 and references therein; Griebler and Lueders, 2009). Pesticide biodegradation by groundwater micro-organisms often represents the only feasible way to reduce pesticide contamination in groundwater (Singh, 2008; Fenner et al., 2013; Pan et al., 2016). Stygobiotic invertebrates (i.e. groundwater-dwelling species that complete the whole life-cycle in groundwater) provide ecosystem services in support of biodegradation through their interaction with micro-organisms (Kota et al., 1999; Marshall and Hall, 2004). Stygobiotic invertebrates feed on groundwater micro-organisms thus stimulating the production of new microbial colonies and renewing microbial biofilms where biodegradation occurs (Boulton et al., 2008; Maurice and Bloomfield, 2012 and references therein). In addition, burrowing invertebrates positively affect sediment permeability (Griebler and Avramov, 2014) easing groundwater flow and pesticides' dilution. Finally, micro-organisms have been recently found "hitch-hiking", i.e. using stygobiotic crustaceans as vectors to be transported up to 34 folds faster than by the groundwater flow (Smith et al., 2016), thus colonizing other contaminated aquifer sectors where they can provide their services. The general prediction is that an ongoing loss of groundwater biodiversity (i.e. a poor groundwater community status) feeds



**Fig. 1.** Map showing the 11 alluvial aquifers (grey areas) and the 120 sampling sites (dots). TR: Piana del Tronto; VI: Piana del Vibrata; SN: Piana del Salinello; TO: Piana del Tordino; VO: Piana del Vomano; SL: Piana del Saline; PE: Piana del Pescara; FO: Piana del Foro; SA: Piana del Sangro; SI: Piana del Sinello; TG: Piana del Trigno.

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