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# Null-space Monte Carlo particle tracking to assess groundwater PCE (Tetrachloroethene) diffuse pollution in north-eastern Milan functional urban area

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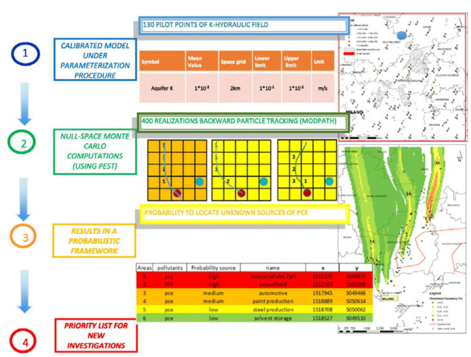
## HIGHLIGHTS

- A new tool useful for groundwater management of PCE diffuse contamination in Functional Urban Areas.
- A new methodology combining Null-Space Monte-Carlo with particle backtracking.
- Aquifers hydraulic conductivity uncertainty and its influence on flow directions are considered.
- Frequency maps of particles crossing each model cells are produced.
- Maps show areas with the highest likelihood to host sources responsible for diffuse contamination.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The Lombardy Region in Italy is one of the most urbanized and industrialized areas in Europe. The presence of countless sources of groundwater pollution is therefore a matter of environmental concern. The sources of groundwater contamination can be classified into two different categories: 1) Point Sources (PS), which correspond to areas releasing plumes of high concentrations (i.e. hot-spots) and 2) Multiple-Point Sources (MPS) consisting in a series of unidentifiable small sources clustered within large areas, generating an anthropogenic diffuse contamination. The latter category frequently predominates in European Functional Urban Areas (FUA) and cannot be managed through standard remediation techniques, mainly because detecting the many different source areas releasing small contaminant mass in groundwater is unfeasible. A specific legislative action has been recently enacted at Regional level (DGR IX/3510-2012), in order to identify areas prone to anthropogenic diffuse pollution and their level of contamination. With a view to defining a management plan, it is necessary to find where MPS are most likely positioned. This paper describes a methodology devised to identify the areas with the highest likelihood to host potential MPS. A groundwater flow model was implemented for a pilot area located in the Milan FUA and through the PEST code, a Null-Space Monte Carlo method was applied in order to generate a suite of several hundred hydraulic conductivity field realizations, each maintaining the model in a calibrated state and each consistent with the modelers' expert-knowledge. Thereafter, the MODPATH code was applied to generate back-traced advective flowpaths for each of the models built using the conductivity field realizations. Maps were then created displaying the number of backtracked particles that crossed each model cell in each stochastic calibrated model. The result is considered to be representative of the FUAs areas with the highest likelihood to host MPS responsible for diffuse contamination.



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## 1. Introduction

Stating that groundwater is the most sensitive and the largest body of freshwater in the European Union and the main source of public drinking water supplies in many regions, the European Community in 2006 (European Union, 2006) established some measures in order to prevent and control groundwater pollution. One of the main aim of the Community (European Environment Agency, 2013) has been to issue rules for groundwater management and to identify point source contaminations as the first step toward remediation. Point sources (PS) can be defined as contamination hot spots releasing plumes with high concentrations. Nevertheless, in many urbanized areas, contaminant plumes originated by single point sources frequently overlap with a widespread contamination caused by multiple-point sources (MPS). These are made up of a series of unidentifiable small sources clustered in a large area, generating a diffuse contamination not ascribable to a unique known source. These areas cannot be remediated by recourse to standard remediation techniques, mainly because: a) the identification of MPS is difficult or impossible by virtue of their small mass release and b) the wide extension of the contaminated areas. Therefore, the design of alternative remediation approaches beforehand requires methods to assess the presence of a diffuse contamination and methods to distinguish point source (PS) and multiple-point source (MPS) contribution.

Kuroda and Fukushi (2008) observed that urban areas are the most important MPS of groundwater contamination due not only to the small number of big industries, but also to the large number of residents, whose collective actions bring about serious consequences. The extension of sewage system networks and the inadequateness of old sewer systems to cope with the increased effluent load represent some major causes (Nolan et al., 2002; Stevenazzi et al., 2015, 2017). Furthermore, other forms of urban MPS pollution include roadways, parkings and other surfaces of improperly managed construction sites from which oil, grease and toxic chemicals can be released (Frumkin, 2002).

Recently, a new statistical methodology has been developed in order to assess anthropogenic diffuse contamination in Functional Urban Areas (Alberti et al., 2016a). However, once the areas prone to diffuse contamination are defined, in order to plan the groundwater resource management it is still necessary to identify the areas most likely to contain the MPS. In the last 20 years, a large amount of methods were tested and developed to identify PS: Integral Pumping Tests (Alberti et al., 2003, 2011; Bauer et al., 2004; Bayer-Raich et al., 2006) and inverse transport modeling (Carrera et al., 2005; Citarella et al., 2015; Zhang et al., 2016). Unfortunately, few methods have been developed to identify anthropogenic diffuse contamination sources. Nevertheless, the identification of areas most likely to host potential MPS and the assessment of their strength is an issue of primary importance, and in this study it has been addressed through the help of groundwater modeling. The approach is that of inverse modeling, by which measurements of system variables provide the information required to identify the system parameters governing the flow equation.

In Functional Urban Areas (FUA), the frequent presence of a diffuse contamination by chlorinated hydrocarbons is the result of a widespread use of these substances in many different production activities since the 1940s (Provincia di Milano, 1992). Transport of these contaminants in groundwater depends on many variables, such as hydraulic conductivity, dispersivity, position and magnitude of sources. The uncertainties inherent in the link between source characteristics (position and magnitude) and concentration measurements make it impossible to unequivocally identify all the sources. Thus, a probabilistic framework allowing to quantify the uncertainties in the position of contaminant sources responsible for a diffuse contamination should be adopted. For this purpose, the present paper focuses on the uncertainty of the hydraulic conductivity distribution and consequently of the groundwater flow direction that conditions the advective component in the transport of contaminants (Pollock, 1994, 2012).

The problem of non-unique groundwater flow solution has been addressed by many authors. Carrera and Neuman (1986) discussed how non-unique inverse problems can be solved in an underdetermined context. In terms of hydrogeological reliability, parameter sets should then be used to estimate model predictions of interest. Therefore, the uncertainty of each model prediction can be characterized by a probability density function with a mean, which is the approximation to the prediction of minimum error variance, and a standard deviation that provides the uncertainty of the model prediction (Herckenrath et al., 2011). Several methods are available for quantifying uncertainty in predictions by use of a calibrated model (Tonkin and Doherty, 2009): linear methods are applied with a variance propagation both in the traditional overdetermined inverse modeling and in the underdetermined context (Bard, 1974; Draper and Smith, 1981; Moore and Doherty, 2005). Nonlinear methods of predictive uncertainty were described by Christensen and Cooley (1996).

The Null-Space Monte Carlo (NSMC) analysis provides a mechanism for the exploration of the uncertainty associated to measurement error, enabling the model to fill the observed data with a suitable stochastic descriptor of parameter variability within the study area. The classical methods such as likelihood uncertainty estimation (Beven and Binley, 1992) are difficult to use in highly parameterized models, especially in solute transport models. There are several examples of constrained Monte Carlo analysis in the groundwater context (Carrera et al., 2005; Guadagnini and Neuman, 1998; Harvey and Gorelick, 1995), but the high computational effort of the model decreases the applicability of these methods. Tonkin and Doherty (2009) presented a new method that achieves efficient production of a multitude of calibration-constrained stochastic parameter fields.

As Northern Italy is one of the most relevant urbanized and industrialized areas in Europe, it hosts a large number of sources of contamination that affect groundwater quality. These facts, together with the availability of a large number of field data and a wide quantity of studies, offer the possibility of finding useful pilot areas for the analysis of diffuse contamination. In this paper, the NSMC methodology is applied and tested in a pilot area in the N-E sector of Milano FUA, where many hydrogeological and chemical data have been collected at different locations over thirty years. The procedure aims at identifying the potential source areas of diffuse contamination taking into account the uncertainties tied to the dynamics of the advective solute transport in groundwater. Therefore, the purpose of this work is not to identify the exact source positions but rather to identify locations with an associated occurrence frequency where MPS may contribute to PCE concentrations measured in groundwater samples that exceed the Italian Decree Law (31/2001) drinking-water standard of 10 μg/l.

### 1.1. Site hydrogeology and groundwater deterministic flow model

The modeled area is located in the Lombardy Region (Fig. 1), within the Po Plain, and it includes the North-Eastern sector of Milan city and some surrounding municipalities. The area is 120 km$^2$ wide, lies at the center of one of the most urbanized and industrialized areas in Europe and is affected by groundwater contamination caused either by some known plumes or by diffuse pollution. The central part is occupied by a former steel plant, which had been active during most of the last century. The area has been subjected to characterization and reclamation since the '90s, hence a significant number of stratigraphic, hydrogeological and concentration data are available covering a period of about thirty years.

Some sectors of the Pilot Area are highly contaminated by chlorinated hydrocarbons (mainly PCE and TCE) and Chromium VI. Thanks to recent investigations funded by Regione Lombardia (ARPA Lombardia, 2016) it has been possible to separate the plumes linked to PS from a diffuse contamination linked to MPS (Alberti et al., 2016a). Through a multivariate statistical approach combined with transport modeling, a diffuse PCE contamination has been identified (Fig. 2 and Fig. S1) with average