Assessment of nitrate contamination risk: the Italian experience

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Abstract

The purpose of this study is to show the results of the Italian research project of national interest (PRIN) launched in 2006 and finished in 2008, concerning the “assessment of groundwater contamination risk by nitrates assessment”. The project verified the IPNOA method for nitrate groundwater contamination risk assessment in four test-sites of Italy. The IPNOA is a parametric index which assesses the potential hazard of nitrate contamination originating from agriculture on a regional scale. The method integrates two categories of parameters: the hazard factors (HF), which represent all farming activities that cause, or might cause, an impact on soil quality in terms of
nitrate (use of fertilisers, application of livestock and poultry manure, food industry wastewater and urban sludge), and the control factors (CF) which adapt the hazard factors to the characteristics of the site (geographical location, climatic conditions and agronomic practices). Finally, the Potential Risk Map is obtained by coupling the potential hazard of nitrate pollution (IPNOA) and the aquifer Contamination Vulnerability Map. The project was carried out by five Research Units (RU) from the Universities of Piacenza, Turin (Polytechnic), Florence, Naples and Palermo. The geochemistry of groundwaters from the four test-sites was studied to determine the distribution of nitrate, and to evaluate groundwater chemical facies. All the study areas are affected by groundwater nitrate contamination and often by hydrogeochemical peculiarities. In some cases isotopic study, $\delta^{18}$O-NO$_3$ $\delta^{15}$N-NO$_3$, allowed to differentiate nitrates of chemical fertilisers from those of biological origin, as well as denitrification processes.

**Keywords:** Groundwater Contamination, Nitrate, Groundwater Vulnerability; Risk Assessment; Italy.

**Introduction**

Most agricultural land uses have provided major sources of diffuse groundwater contamination since the introduction of mechanisation and use of fertilisers, notably nitrogen and manure. Such applications, whilst considerably increasing yields, may cause the leaching of nitrates, potassium and phosphates into underlying groundwater. Furthermore, they may contribute to acidification and the consequent leaching of several heavy metals.

In several countries worldwide and in the north of Italy as well, livestock farming takes place on a huge scale. The growth of animal husbandry (poultry, pigs, calves and so on) has led to serious environmental and groundwater problems due to excessive slurry production. Moreover, in several urban and industrial areas groundwater contamination by nitrates arises from linear sources

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(motorways, leaking sewerage systems) and point sources (surface impoundments, i.e. septic tanks, pits, lakes and landfills).

Much is known on the situation of groundwater contamination by nitrates in several parts of the country. A research project of national interest (PRIN) was launched in 2006 as a logical continuation of the GNDCI – L4\textsuperscript{b} program RIAS (Groundwater Contamination Risk Evaluation). The project was formed from the convergence of five Research Units (RU) from the Universities of Piacenza, Turin (Polytechnic), Florence, Naples and Palermo. The research aim is to assess the contamination risk by nitrates, whether originating from crops and livestock or from municipal and industrial sources, starting from the methodological experience gained within the RIAS program. Since 1990, a new method to assess groundwater vulnerability has been researched by the Turin Polytechnic unit called SINTACS. It is a Point Count System Model (PCSM) based on the assessment and rating of seven factors: depth to water, recharge, unsaturated zone, soil, aquifer, hydraulic conductivity and slope. The method was constantly tested (Civita and De Maio, 2002) and enhanced for the following ten years until the current release 5 (Civita and De Maio, 2000) that allows vulnerability maps to be prepared via Geographical Information Systems (GIS). The GIS allows permanent upgrading and map plotting in real time, which makes the method very important in groundwater protection and planning.

For each factor surveyed, a rating (R) value (usually 1-10) is chosen by appropriate methods referring to a finite element of land. Each assessed rating is then associated to a multiplier (weight - W) which varies according to the hydrogeologic and potential impact situation. Six basic situations (weight strings) are suggested: normal impact, severe impact, drainage (by streams), karst (aquifers), fissured (aquifers), nitrate (impoundments).

The SINTACS index (or contamination potential) is then calculated for each grid element using the formula:

\begin{align*}
\text{SINTACS index} &= \sum R_i \times W_i
\end{align*}

\textsuperscript{b} Research line # 4 of the National Research Group for the Defense against Hydro-geological Disasters (GNDCI), Italian National Research Council (CNR).
Since 1999 (Capri et al., 1999) the research unit of Piacenza University has studied a method to forecast groundwater contamination by phytochemicals. A new parametric agricultural hazard index (IPA) was then proposed, based on two groups of factors: hazard factors, representing all farm activities that cause impact on groundwater and control factors which adapt the first group to the effective scenarios. Combining the IPA index with SINTACS index, a risk assessment is obtained. The method was successfully tested on the whole district of Cremona (northern Italy). Starting from this experience, a new parametric index (IPNOA) was set up to assess the hazard from nitrates of agricultural origin (Padovani and Trevisan, 2002) and was also tested in the Cuneo district of Piedmont (Civita et al., 2003).

The project introduced here started along these methodological lines with the aim of being implemented and tested in different situations of climate and nitrate sources. The task of the Piacenza University Research Unit was to characterise the pedological and chemical attributes of the soils for all the test sites developed by the other project RUs. Moreover, the Piacenza RU implemented the parametric indices from heavy metals and nitrates in the case studies, and set up a computerised data base on the nitrate and heavy metal contents in the groundwater for all the test sites.

The Turin Polytechnic RU applied the methods on a test-site of around 100 km² in a lowland area in the province of Cuneo (NW Italy). The Florence University RU investigated the impact of agricultural and household activities on nitrate content in groundwater in the Cecina Plain (Tuscany, central Italy). The Naples University RU studied the northern part of the Volturno River Plain test-site. This area has peculiar hydrogeochemical features and it is of strategic interest in terms of protecting groundwater resources, having matrix porosity aquifers of different geological age and type. The Palermo University RU conducted research on an area in south-western Sicily yielding high-value agricultural products: the Ribera area which specialises in quality oranges (Washington
Navel). The results gained by the RU and their importance in social and economic terms are described in detail below.

1. Methods

The Directive 91/676/EC concerning the protection of water from pollution caused by nitrates from agricultural sources has been applied in Italy by new national and regional legislation. In Italy, ‘regional’ administrations are responsible for ‘defining vulnerable zones’, for identifying and assessing ‘programmes of measures’ and for drawing up operational monitoring in vulnerable areas. In vulnerable zones it is not possible to use more nitrogen than that required by the crop on the basis of a nutrient balance.

At present, in Italy vulnerability maps are produced by each region on a 1 km$^2$ scale. The maps (Fig. 1) depict vulnerable and non-vulnerable areas (non-vulnerable are where monitoring data show nitrate values below 50 mg/L). The picture is not encouraging: Northern Italy is often affected by severe contamination, and in the more densely inhabited coastal areas of Central and Southern Italy high nitrate contents are recorded.

The Italian scientific community has complained that there are ‘affected areas’ and not ‘vulnerable areas’ and felt that there should be more than two classes of vulnerability. It is possible through parametric models to identify areas with different vulnerability and degrees of risk.

There is a fairly large literature related to assessing groundwater contamination vulnerability and risk (see Zwahlen, 2003 and related bibliography). In this study the parametric methods SINTACS, IPNOA and IPNOC, explained in the next sections, have been applied.

1.1 The model SINTACS R5 for the assessment of aquifer contamination vulnerability

This method is briefly presented herein because it is the method most commonly used in Italy and has many applications in Italy and abroad (Civita and De Maio, 2002 and related bibliography).

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Firstly, the point count system model SINTACS R5 (Civita and De Maio, 2000) provides area discretisation into square cells. The model then applies, to each cell, a point rating system, ranging from 1 to 10, for the following seven parameters: depth to water (S), effective infiltration action (I), unsaturated zone attenuation capacity (N), soil/overburden attenuation capacity (T), hydrogeologic characteristics of the aquifer (A), hydraulic conductivity range of the aquifer (C), topographic surface slope (S). Cell by cell, the selected ratings of each factor must be multiplied by a choice of weight strings, each describing a hydrogeological and impact setting where the cell falls (normal impact, considerable impact, drainage from superficial network, deep karstified terrain and fissured terrain). The addition of the scores gives the SINTACS index. By normalising and splitting into six vulnerability classes, the index provides six vulnerability degrees to groundwater contamination (1 = very low, 6 = extremely high) (Table 1).

1.2 The agricultural nitrate hazard index: IPNOA

Worldwide, nitrogen is the most critical plant nutrient for food and fibre production. Humans have always added nitrogen to crops through animal manure, legume crops or fertilisers. The most common forms of nitrogen in fertilisers are ammonium, nitrate, urea and natural organics. However, while nitrate is essential for the growth and development of healthy crops, it is also very soluble in water and hence very mobile within soil solution.

In 1991 the European Community adopted the Nitrates Directive (91/676/EC), which aims to reduce water pollution caused or induced by nitrates from agricultural sources and prevent further such pollution by requiring Member States to place mandatory restrictions on agricultural practices where these contribute to the nitrate pollution of waters.

Several hydrogeology models have been developed in recent years to simulate nitrate transport in the aquifer (Padovani and Trevisan, 2002). Furthermore, some models for assessing nitrate fluxes at basin scale are available. Usually, such models use complex mechanistic approaches, physical and

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hydrological parameters that are difficult to monitor and if they are applied at basin scale, they require a large amount of data. Therefore risk assessment becomes quite difficult to carry out. Hence, despite the availability of mathematical models, parametric indices are often used because they are characterised by low and easily available input data.

Following the EU Nitrates Directive (676/91/EC), the Italian Law Decree 152/99 and the subsequent Law Decree 258/2000 concerning water protection established the criteria and methodological approaches to identify areas vulnerable to the leaching of nitrates from agricultural activities. In these laws different tiers of evaluation are indicated; the second tier indicates that the nitrogen load and environmental factors which may contribute to pollution should be important issues to be included in the assessment. When contamination sources are diffuse, it is more difficult to quantify the contamination events. Hence the use of parametric approaches, which are less precise but easier to apply, can be helpful.

In 2002, the agricultural nitrate hazard index (IPNOA) was developed to assess the potential hazard of groundwater contamination by nitrates from agricultural sources at regional and provincial scale, using a parametric approach which entails first the selection of all the parameters involved in the potential hazard of groundwater contamination, and then assigning a progressive score to each parameter depending on its importance as determined during the final evaluation (Padovani and Trevisan, 2002). The method took into account the nitrogen load from different agricultural activities, which gives the quantity of nitrogen available in the soil and which can potentially leach to groundwater, and summary indicators related to environmental factors. IPNOA integrates two categories of parameters: the hazard factors, which represent all farming practices that cause, or might cause, an impact on groundwater in terms of nitrate, and the control factors, which modify the hazard factors according to the site characteristics and agricultural practices. Through the hazard factors the nitrogen quantity applied to arable land can be estimated; this quantity may represent a hazard for groundwater quality, depending on the natural nitrogen content of the soil, the climatic characteristics of the site and the agricultural practices used. All variables are inter-related after
being classified, assigning to them an index that characterises the nitrogen load or incidence of the factors involved in nitrate leaching. This parameterisation minimises the possible errors from the assessment and subjectivity of the measurements, and allows graphical representation of the results.

### 1.2.1 IPNOA calculation

IPNOA gives a potential hazard classification and only the nitrogen load from farming was taken into account. Thus only farmed areas, which are the main sources of potential nitrate contamination, were considered. All the data refer to the nitrogen quantity applied per hectare to the arable land.

In IPNOA the hazard factors include organic (manure and sewage) and inorganic fertilisers, and sludge. In determining the nitrate supply to the soil it was assumed that the farmers followed good agricultural practices and that the supply did not exceed actual plant requirements. Five hazard classes were assigned to the different hazard factors, according to the varying amounts of nitrogen supplied through the different types of fertilisations (Table 2).

The behaviour of nitrates in soil is determined by the combination of climatic, pedologic and agronomic factors that regulate the hydrologic balance. In the IPNOA calculation these factors are called control factors and are: the natural nitrogen content in soil, the climate, agronomic practices and the irrigation system used. The different control classes assigned to the different control factors are shown in Tables 3, 4, 5 and 6.

The assessment of the potential hazard index (HI) for nitrate contamination from agricultural sources (Fig. 2) is obtained by multiplying the different hazard classes (HF) by the control classes (CF) as shown in the following equation:

\[ HI = (HF_f + HF_m + HF_s) \times CF_n \times CF_c \times CF_{ap} \times CF_i \]

where the subscripts indicate: \( f \)= fertilisers, \( m \)= manure, \( s \)= sludge, \( n \)= nitrogen content, \( c \)=climate, \( ap \)=agronomic practices, \( i \)=irrigation. The total incidence of the control factors is determined by multiplying the single factors in order to limit the weight of these parameters with respect to the real impact of the nitrogen load evaluated by the hazard factors. The HF values range between 0 to 5.
and CF values between 0.94 to 1.10. Finally IPNOA is obtained from HI, by classifying the resulting values on the basis of the percentile of the 135,125 possible combinations, on a scale ranging from 1 to 6 representing the different scores (Table 7).

1.2.2 Considerations about the IPNOA method

Since the IPNOA index does not consider the soil characteristics or hydrological structure of the subsoil, it gives no indications of the real risk of contamination. The original aim was to develop a method which gives a hazard classification of nitrate contamination from agricultural sources. However, as a parametric index, IPNOA can be easily overlapped with an aquifer intrinsic vulnerability evaluation, to give an evaluation of potential risk of groundwater contamination. For this reason, SINTACS (Civita and De Maio, 2000), a point count system model for assessing intrinsic vulnerability, was linked to IPNOA to assess the potential risk of groundwater contamination. This correlation was obtained by the mean values of both classifications (Tables 1, 7 and 8).

The method developed, even though it could be improved in terms of factor and control classes ratings, provides a mechanism for comparing different areas according to the potential for contamination by agricultural sources of nitrate and could be a useful tool for management and policy goals.

1.3 The Index of Hazard from Nitrates of Household Origin: IPNOC

Most of the nitrates in groundwater come from agriculture, but in many areas a non-negligible contribution comes from sewage leaks and from household discharges not connected to sewerage systems. The IPNOC method of assessing the Hazard Index by Nitrates of Household Origin (Frullini and Pranzini, 2008) is described briefly here.

Starting from the volume of waste water reaching the treatment plants, the load of nitrogen coming from each town is proportionally distributed to the diameter of the sewer pipes, according to the criterion that the greater the diameter of the pipe, the greater the discharge. In this way the average annual load of nitrogen in transit per metre of conduit NI (hazard factor) is calculated.

Frullini R., Pranzini G.
Leakage from sewer pipes is the control factor. Table 9 shows the average life-time of sewer pipes of different materials and the average percentage leakage as reported in the literature (see Frullini and Pranzini, 2008). These leakage percentages are to be attributed to the average life-time of pipes. Leakages are caused by wear and accidental breakage, and depend on pipe material and age. We can consider the relationship between age and wear linear, and that between age and accidental breaking exponential. For each pipe a leakage percentage based on its material and age is then assigned with the formula: \( L_c = L \times \text{age/average life}^{1.2} \), where \( L_c \) = adjusted leakage and \( L \) = leakage related to the average life-time of that type of pipe.

For each mesh of the grid in which the study area has been divided, the annual value of nitrogen leaking from the sewer pipes is calculated with \( N_c = \sum L_c \times N_i \), where \( L \) is the length of each type of pipe in the mesh, \( L_c \) its leakage %, and \( N_i \) its average annual nitrogen load in transit.

The scattered houses not connected to sewerage systems dispose of sewage through sub-irrigation, phytodepuration, and underground dispersion. A number of equivalent people is assigned to each house. Every inhabitant equivalent produces 5.5 kilograms of nitrogen a year. It was estimated that 15% of the load is removed and that the remaining 85% infiltrates underground. Multiplying the 4.67 kg of N per year by the number of inhabitants in each unit area, the amount of nitrogen infiltrating underground is calculated. This figure is added to that obtained for the leakage of the sewer pipes, resulting in a total of N annually infiltrating each mesh. This nitrogen represents the potential pollution load for groundwater.

The limits of the IPNOC classes, on the amounts of nitrogen infiltrating underground, are the same as those used for the IPNOA classes for organic fertilisers.

### 2 Potential nitrate risk of contamination of a plain in the province of Cuneo (NW Italy)\(^f\)

The point count system model SINTACS R5 (Civita and De Maio, 2000) for the assessment of aquifer vulnerability, and IPNOA (Padovani and Trevisan, 2002) for hazard index, have been applied synergistically to unconfined aquifers, geographically belonging to the Piedmontese Plain (NW Italy), whose waters are used for drinking water supply (Fig. 3).

\(^f\)Civita M., De Maio M., Fiorucci A., Offi M.
Choice of the location was determined by the presence of many arable and livestock farms, with relative on-ground nitrogen loading. Operationally, the study area was split into grid cells (50 m x 50 m). The SINTACS index and IPNOA were then computed cell by cell; on the basis of these indexes, the potential risk of groundwater contamination from nitrates of agricultural origin was assessed.

It was therefore possible to determine the impact of the nitrates and, in general, of land use on groundwater. IPNOA gives an evaluation of how arable and livestock farming influence the presence of nitrates at the soil level, while SINTACS evaluates whether such nitrates from the soil manage to leach to the piezometric level of the underlying aquifer. The results were validated by monitoring water chemical concentrations at about 60 wells; the results of the analyses were then used for geochemical characterisation of the aquifers. The relative thematic maps were compiled by GIS.

The potential risk of contamination is the product of two factors: contamination vulnerability, a specific characteristic of the aquifer system, here evaluated through the SINTACS R5 method (Civita and De Maio, 2000), and hazard. The latter is, however, an element anything other than easy to appraise, in the groundwater resources field (RIS), because it brings with it a statistical content, being the probability that a specific polluting event occurs in a specific time period (Civita, 1999). Clearly, therefore, valid assessment of hazard is difficult, given the many sources of contamination, point and diffuse, that could be present in an area. Fewer problems are associated with defining a danger index related to the various types of impact. In such a case, however, one can only speak of potential risk, which could become real only by accepting the hypothesis that, over very long time periods, the hazard and the danger index coincide.

In this case study, or rather the contamination study linked to the nitrates of agricultural origin, the danger index of contamination was determined through the use of the IPNOA parametric model (Padovani and Trevisan, 2002).
2.1 The Fossano area

The potential risk of contamination from nitrates of agricultural origin was studied on a plain of around 100 km$^2$ in the province of Cuneo (NW Italy). This is an area extremely suited to arable and livestock farming, with several farms scattered throughout the area. The crops mostly present are maize and wheat, while mostly pigs and cattle are raised (see Table 10). From a hydrogeologic point of view (Civita et al., 2000), only the Main Alluvial Complex outcrops in the study area, belonging to the hydrogeological Quaternary system; it is characterised by gravels with slightly silty matrix, between 20 and 40 metres thick, and permeability linked to the percentage of silt in the matrix, but generally medium-high. Underlying this complex is that of the altered gravels, formed in the Plio-Pleistocene, with altered gravels in an abundant fine silty-clayey matrix, with rather low permeability. This complex acts as an impervious layer to the overlying complex. The main alluvial complex encompasses an unconfined aquifer showing a rather constant flow pattern (Fig. 4), with SW-NE direction and a hydraulic gradient of 0.5%. The depth to water is maximum (12 m) at S and it decreases moving toward N, to go to zero in the NE sector of the Fossano area.

2.2 Considerations on the Potential Nitrate Risk Map of the Fossano area

Application of the most modern GIS software (e.g. ArcGis) to the working method illustrated above allows, amongst other things, the construction of thematic maps, as shown in Figs. 5, 6 and 7, which report, respectively, the aquifer contamination vulnerability map, the nitrate contamination hazard map and the potential nitrate risk contamination map.

As noted, the potential risk is generally extremely high or high, due to aquifer vulnerability, where the “extremely high” rate appears, but also the contamination hazard, where the rates very high, high and moderate are frequent. The risk map is compared with the chemical analyses, related to two subsequent sampling times (December '04 and April '05, Fig. 8).
The concentration of 50 mg/l (drinking water limit as regards NO$_3^-$) is exceeded to the north and west of Fossano. Additionally the 40 mg/l limit is exceeded across a region that includes almost the entire E-W central zone, and the southern part, of the study area. This area agrees with those characterised by “high” and “very high” potential risk, considering the aquifer values of hydraulic conductivity and of the flow motion pattern. These first good results, together with other positive findings reported in the literature, like that conducted by our working group in another area of the Cuneo plain (Civita et al. 2003), show that the joint application of the SINTACS and IPNOA parametric models can represent a valid method for assessing the potential risk of contamination by nitrates of agricultural origin. Besides, it must be remembered that the ease of retrieving data required for calculating the SINTACS and IPNOA index, and hence the risk index, together with the good results that can be yielded by applying GIS tools, makes it a valid tool for public administrations to use in their own Water Resources Management and Protection policies, concerning nitrate contamination and agricultural planning, as required under current European law (91/676/EC).

3 Pollution Risk for groundwater from nitrates of agricultural and household origin in the Cecina Plain (Tuscany, central Italy)$^9$

The area of study (Fig. 3) is the coastal strip between Rosignano and San Vincenzo (central-western Tuscany, hereafter named Cecina Plain), which includes the terminal paths of the Cecina and Fine rivers. It is made up of marine and continental sediments, aged between the Lower Pleistocene and Holocene, that form some terraces inclined towards the sea. The subsoil consists of a succession of (lithologic) bodies with medium to high permeability (gravel, sand, sandy limestone), interbedded with low permeable or impermeable units (silt and clay). These units form the “multi-layered

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$^9$ Pranzini G., Capecchiacci F., Delgado Huertas A., Frullini R., Menichetti S., Nisi B., Vaselli O.
a aquifer system", which is affected by several natural and anthropogenic contaminants that contribute to spoil the water quality of the area, also due to intense tourism activity in summer time. Overall, the main processes affecting groundwater can be summarised as follows: i) sea water intrusion due to the over-exploitation of the water resource (Pranzini, 2004); ii) boron contamination (not studied in the present work) of the Cecina River, due to the geothermal power generation at Larderello and boron-rich mineral processing (Pennisi et al., 2006); iii) nitrate pollution whose sources can mainly be related to agricultural and municipal activity (Grassi et al., 2007; Nisi et al., 2007). Despite the increased efforts to reduce NO₃ inputs from intensive agriculture at national and European (EC Directive 91/676) levels, nitrate is still one of the main contaminants, with about 35% of well waters being characterised by values higher than 50 mg/L (maximum admissible concentrations according to EC Directive 98/83 on drinking water quality). Thus, according to a recent European Community Directive the local administration of Tuscany has declared the Cecina Plain a nitrate vulnerable zone.

In this area the purpose of the study was to assess the risk of pollution from nitrates by combining the aquifer vulnerability with two indices of nitrate hazard, the IPNOA, for the agro-livestock source, and the IPNOC (Frullini and Pranzini, 2008), for that of household origin. Moreover, in order to highlight the origin of nitrate pollution, a geochemical investigation of 88 groundwater samples (analysed by volumetric titration, molecular and atomic absorption spectrophotometry and ion chromatography) was carried out in June and October 2006. Seventeen samples were selected to determine nitrogen and oxygen isotopes in dissolved nitrates with values higher than 20 mg/L by using a slightly modified version of the method proposed by Silva et al. (2000).

3.1 Evaluation of the groundwater Pollution Risk in the Cecina Plain

The aquifer Vulnerability Map was drawn up with the SINTACS parametric method (Civita and De Maio, 2000), with only one change: the soil attenuation capacity parameter was evaluated by the method proposed by Frullini et al. (2007), which takes into account the soil hydrological
characteristics: superficial infiltration, hydraulic conductivity of the soil up to 150 cm of deepness, Available Water Capacity, and internal drainage.

For the risk assessment of nitrate pollution from sewers and domestic discharges it was necessary to implement a separate aquifer Vulnerability Map, because spill of pollutants is not on the surface, as for fertilisers, but at an average depth of 2 m (sewer pipes), and of 1 m (discharges not connected to the sewage system). The vulnerability values of this map are higher than those of the classic one (Fig. 9) mainly because the soil attenuation capacity is lacking.

Using the index IPNOA, only the presence of two hazard factors was detected within the study area: mineral fertilisers and organic fertilisers. Regarding the control factors, the nitrogen content in the soil was measured by analysis of 25 soil samples in two surveys (May and October 2006); the climate is defined as “peninsular Tyrrhenian”; the kind of farming is "traditional" and "minimal" with the distribution of fertiliser across the whole cultivated area; irrigation, where present, is usually made through spraying.

The hazard which may arise by leakage from sewer pipes or from scattered houses not connected to the sewerage system, was evaluated by the IPNOC index (Hazard Index by Nitrates of Household Origin, Frullini and Pranzini, 2008). By combining the IPNOA and the IPNOC indexes with their vulnerability values, two pollution risk maps were obtained (Fig. 10). As may be seen, the values of risk from nitrate of household origin are higher than the others. This stems mainly from the difference between a vulnerability calculated starting from the surface and from a depth of 1 or 2 m. Nevertheless, in the study area the risk of pollution from nitrates of agricultural origin is about five times that of household origin due to the larger area involved.

3.2 Water geochemistry and isotopic composition of nitrate in the Cecina Plain

The geochemical facies of the groundwater samples is dominated by Ca(Mg)-HCO₃ and Ca(Mg)-SO₄(Cl) and subordinate Na(Ca)-Cl(SO₄) (Fig. 11), likely resulting from water-rock interaction processes between meteoric-derived ground and sea waters with the sedimentary formations of the
plain and the recharge areas, the latter also characterised by Triassic anhydritic formations (Pranzini, 2004; Nisi et al., 2007). The pH values are slightly alkaline (<8), whereas those of TDS (Total Dissolved Solids) are between 1000 and 4,500 mg/L. Setting aside the mixing processes between ground and sea waters, it is worth pointing out relative high concentrations of nitrates in the waters that range from 0.06 to 354 mg/L. Almost 30 water samples from June and October 2006 were above the maximum admissible concentrations (50 mg/L) according to European Legislation. The NO₃/Na vs. Cl/Na molar diagram (Fig. 12) shows that the Cecina Plain groundwaters tend to be distributed along two main trends. The first is characterised by an increase in the Cl/Na molar ratio possibly due to ion exchange processes between clay sediments and seawater-affected ground waters that favour the absorption of Na and the release of Ca, as also supported by the Ca-Cl component in most waters. The second trend is likely to be regarded as a mixing process between the groundwater system and contributions to different degrees from municipal and agricultural sources.

In order to better define the anthropogenic sources of the dissolved nitrates, the isotopic composition of 17 selected waters is reported in the δ¹⁸O-NO₃ vs. δ¹⁵N-NO₃ binary diagram of Fig. 13. The results suggest that chemical fertilisers, which are transported to groundwater via irrigation and rainfall, seem to be the main factors causing the nitrate contents observed. However, denitrification processes, at least for those samples with δ¹⁸O/δ¹⁵N is 2:1, and/or residual effluent from arable-livestock farming and/or urban origin cannot be ruled out. Due to the complexity of the Cecina Plain where the presence of a multi-aquifer system does not allow proper identification of the depth from which the water samples are to be referred to, it is clear that more detailed studies are necessary to further constrain the potential nitrogen sources. Nevertheless, this isotopic investigation illustrates the utility of δ¹⁵N and δ¹⁸O analysis in dissolved nitrates. In addition, a limited number of samples may be useful to plan a focused investigation and assess nitrate sources and cycling.
4. Nitrate Contamination Risk Mapping and Influence of the Hydrogeochemical Pattern in the northern part of the Volturno River Plain (southern Italy)

With the purpose of verifying the IPNOA method for nitrate groundwater contamination risk assessment in an area with hydrogeochemical peculiarities the northern part of the Volturno River Plain was selected (Fig. 3). The choice was suggested by the following considerations:

- the medium-low human pressure;
- the absence of nitrate contribution from the upstream areas of the groundwater flow; in fact, the area is located at the foot of almost uninhabited limestone mountains.

4.1 Hydrogeology and hydrogeochemistry of the northern part of the Volturno River Plain

The northern part of the Volturno River Plain is surrounded by the Mesozoic limestone mountains of the Southern Apennines: Mt. Massico and Mt. Maggiore (N and E) and by the extinct Roccamonfina volcano (N). Based upon more than 450 borehole stratigraphies in the area, the main aquifer has been recognised in the alluvial, pyroclastic and marine porous sediments. These sediments outcrop occasionally; more often they underlie tufaceous rocks of the Campanian Ignimbrite unit (Romano et al., 1994; De Vivo et al., 2001) or older tuffs, with low permeability and thickness increasing toward the mountains (Fig. 14). The groundwater moves in the levels with coarse granulometry, discontinuous and located at different depths from the top surface. Notwithstanding this, the levels with different granulometry constitute a single groundwater body. The piezometric surface of the aquifer was mapped by using more than 120 monitoring wells (Fig. 15). At the foot of the mountains, the piezometric level is located in the tuffs and therefore the aquifer is confined. Close to the Volturno river the tuffs are absent or very thin due to river erosion and the aquifer is semi-confined or unconfined.

The main sources of recharge are rainfall and underflow from N (Roccamonfina volcano aquifer) and E (Mt. Maggiore limestone aquifer). The Mt. Massico limestone aquifer is separated from the

\textsuperscript{h} Corniello A., Ducci D.
The groundwater sampled in wells at the foot of the mountains is the calcium bicarbonate type. The groundwater is more alkaline toward the coastline, due to the influence of the pyroclastic and alluvial aquifers of the plain;

- mineralised groundwater is present at the SE border of Mt. Massico and at the SW border of Mt. Maggiore;

- saline contamination of groundwater along the coastline is low and restricted to a sector close to the Volturno River mouth;

- nitrate contamination in groundwater is widespread.

Nitrate contamination of the aquifer is discontinuous (Fig. 15). The most seriously affected sectors are on the borders of the Plain, where often the threshold limit of 50 mg/l (WHO, 2006 guideline value, and EU, 1991 maximum admissible concentration in drinking-water) is exceeded. Toward the Volturno River, nitrate content decreases drastically (< 10 mg/l). The same happens for the SO$_4$ values, falling to about 1 mg/l, in spite of being 30-40 mg/l in the rest of the study area. By contrast, Mn and Fe increase decidedly toward the Volturno River.

These peculiar hydrogeochemical features may be related to the presence in the past in this area of extensive marshlands (recently reclaimed) and to the presence of thick peat levels, especially in the vadose zone: therefore, the groundwater moves in an environment rich in organic matter and in reducing conditions (Matthess 1982; Corniello et al. 1990; Kehew 2001).

4.2 Nitrate groundwater contamination risk assessment using the IPNOA method in the northern part of the Volturno River Plain
In the northern part of the Volturno River Plain, stratigraphic and hydrogeological data (well network for piezometric and chemical monitoring) were collected, georeferenced and standardised, especially.

Other data collected in order to assess the nitrate contamination risk are the following:

- type of animal husbandry;
- climatic and hydrologic factors;
- land cover and agricultural activities.

All the collected data were stored in a geographic database and managed by GIS (Corniello et al. 2007; Ducci, 1999).

The hazard was calculated using the IPNOA method (or ANHI - Agricultural Nitrate Hazard Index, explained in section 1.2), considering the Land Use Map obtained from the “Map of Agricultural Land Use in Campania” at the scale of 1:50,000 (SESIRCA, 2004). The Potential Risk Map \( R \) was obtained by multiplying in terms of classes, through the GIS, hazard and vulnerability, and then classifying the obtained values into risk classes (see section 1.2.1).

The Potential Agricultural Nitrate Contamination Risk Map (Fig. 16) shows a prevalent medium – high risk. The map reflects the aquifer Vulnerability map (prevalent classes: high and moderate), more than the IPNOA map (prevalent classes: low and very low). The higher risk areas are in the southern sector where the tuffs are absent and the aquifer is semi-confined or unconfined. The map, except in the coastal sector, presents a low spatial correlation with the nitrate content of the aquifer (Fig. 15). Many areas (20-30% of the whole area) present a high or very high risk and nitrate values below 10 mg/l. Almost all these areas are in the above-cited (section 4.1) reducing-conditions sector, toward the Volturno River. In this area nitrate values are low because they have been reduced in nitrite and ammonia. In the northern confined sector there are two zones with low risk and nitrate values exceeding 50 mg/l. These areas are urban areas, which suggests that the source of the groundwater nitrate is related to the leakage from the sewage network and old septic systems.
5 Hydrogeological resources, hydrogeochemistry and groundwater nitrate contamination risk assessment of the Ribera Test Site (Sicily, Italy)\(^1\)

The study area is part of the Verdura basin (Fig. 3); the Sicani mountains border it to the north and the Channel of Sicily to the south. The climate of the area may be considered Mediterranean with cool to cold, wet winters and warm to hot, dry summers. Climatic data from 1994 to 2003 show a mean annual air temperature ranging from 17.2 °C to 19.1 °C and an annual average rainfall ranging from 650 to 720 mm. The Verdura river flows in a NE-SW direction; this is a torrent defined by a flow regime with short flood events and long periods of low water level.

The morphology presents a flat trend with three sea terrace orders from 300m above sea level. The area occupies part of the Caltanissetta and Castelvetrano foredeep (Catalano and D’Argenio, 1978). The geology setting of the study area is represented by the Messinian Gessoso-Solfifera formation (clay/gypsum sequences and Pasquasia gypsum second cycle): it includes Messinian evaporitic sediments deposited during the drying up of the Mediterranean Sea after a relative sea level change, which isolated the Mediterranean Sea from the open ocean. The study area is covered with plio-pleistocene outcrop deposits (terraced calcarenite) and younger deposits. The pleistocene blue clay and the Messinian clay represent the aquiclude of the main aquifers, the plio-pleistocene deposits and the river terrace.

There are several aquifers, albeit overexploited for grapefruit irrigation. The major aquifers are:

1. **Alluvial complex** (alluvial terraced deposits, mainly heterogeneous gravel). Permeability for porosity depends on the thickening and/or the presence of sandy and silty layers;

2. **Arenaceous-sandy deposits complex** (Grande Terrazzo Superiore, Pleistocene, Ruggieri et al., 1975). This complex is divided into several bodies (silt, sand and conglomerate, 14m thick). The permeability for porosity is medium low.

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\(^1\) Cusimano G., Hauser S., Pisciotta A., Vassallo M.
Calcarenitic complex (yellow organic calcarenite partially cemented with interbedded clayey and clayey-sandy). The high permeability for porosity depends on the granulometry and degree of cementation. Locally it is covered by marine terrace deposits (a few metres thick).

These aquifers are on the same impermeable complexes:

4 Clayey-gypsum complex: it includes the clayey gypsum layers of the “Gessoso-Solfifera” Messinian succession. The gypsum outcrops (selenitic gypsum banks and re-sedimented and tectonized gypsum-arenite) have a low permeability due to jointing and porosity.

5 Clayey marly complex: it includes the “marly arenaceous formation of the Valle del Belice” layers (blue clays with marly arenaceous interbedded changing to quartz sands and calcarenites) and marly limestones and white globigerina marls “Trubi”. The permeability is very low; in some cemented layers it is low due to jointing.

In the last part of the Verdura basin there is an important alluvial aquifer. The terraced deposits are in hydraulic connection with the youngest alluvial deposits, and the flow directions are mostly NE-SW. Several wells, about 10 metres thick, mainly exploit the alluvial groundwater, while the calcarenitic groundwater has low productivity.

In conclusion, hydrogeological investigation of the last part of the Verdura river basin was carried out on two main aquifers. The first is located in the alluvial deposits with an unconfined aquifer, in hydraulic connection with the Verdura river. The second is sited in the calcarenite pleistocenic complex.

5.1 Geochemical context of the Ribera test site

Two geochemical field surveys were conducted, one during May 2006 and the other during January 2007, water samples were collected, and chemical and physical parameters were measured. 26 groundwater samples and two river water samples were analysed by High-performance liquid
chromatography (HPLC) to determine the major constituents and by mass spectrometry to measure the isotopic rates $^{18}\text{O}/^{16}\text{O}$ and D/H.

In Fig. 17a the Langelier-Ludwig diagram (1942) shows two main different families of waters: the first is the chloride-sulphate alkaline-earth water, the second is chloride-sulphate alkaline water. The water composition has a slight loss in carbonate, calcium and magnesium.

The diagrams $\text{Ca}^{2+}-\text{SO}_4^{2-}-\text{HCO}_3^-$ (Fig.17b) and $\text{Ca}^{2+}-\text{SO}_4^{2-}$ (Fig.18a) indicate a weathering process of carbonate and gypsum rocks. Moreover, the $\text{Ca}^{2+}-\text{SO}_4^{2-}$ ratio close to 1 (black line), probably due to the dissolution of the gypsum deposits, shows a steady input of sulphate waters into the alluvial complex. The red line identifies the carbonate source of the calcarenitic complex. The groundwater nitrate concentrations are over the limit range provided by International Laws, mostly exceeding 50 mg/l as NO$_3$.

Isotopic results, the Global Meteoric World Line (GMWL) (Craig, 1961) and Mediterranean Meteoric Water Line (MMWL) (Gat and Carmi, 1970) are plotted in Fig. 18b. The isotopic composition range is from - 6.3 to - 3.8‰ for oxygen and from -36 to -21‰ for hydrogen (V-SMOW). The linear interpolation of the data is between the GMWL and MMWL lines; its equation is: $\delta D = 4.8 \delta^{18}O - 5.5$. Non-equilibrium processes, such as evaporation process (Gonfiantini, 1986), cause a shift from the main lines. The negative isotopic values show a far higher recharge area. Moreover, the positive ones exclude salt-water interaction. Although the isotopic groundwater composition shows a meteoric source, evaporation processes probably shift the linear interpolation data from the main meteoric water lines (GMWL and MMWL). Moreover, the results do not point to salt water intrusion on the coastal area due to low human pressure.

5.2 The map of intrinsic nitrate contamination risk from agricultural sources at the Ribera Test Site

Fig. 19a shows the SINTACS map, with about 62% of the area falling into the high value, where the depth-to-water index is less than 5 metres in the alluvial plain, the value being high on the
thalweg (8%). Aquifer vulnerability was for the most part high, owing to the very shallow depth of the two groundwaters, never over 10 metres.

The IPNOA index is obtained as explained in section 1.2. The annual nitrate load from mineral fertilisation for each crop is: 180-240 (kg/ha) for grapefruit, 100-120 (kg/ha) for olive, about 100 (kg/ha) for vines. Organic fertilisation and sewage sludge have no major effect on the nitrate load in these agricultural areas.

The soil classes in this area were used to assign the soil nitrate factor (CFa), the relative range being 1.00-0.98. Rainfall and temperature data from the weather stations at Ribera, Sciacca, Cianciana and Calatabellotta were used to calculate the type of climate (CFc), the related value being 0.98. The main tillage in this area is traditional with a value of 1.00 and the no-tillage area has a relative value of 0.94. The irrigation method (CFi) is sprinkler with a relative value of 1.02.

The hazard of nitrate contamination from agricultural sources (IPNOA) is obtained from the sum of the three hazard factors (HF) multiplied by the product of the four control factors (CF). The final values of each cell (50m) are classified into six classes which represent six degrees of nitrate contamination hazard from agricultural sources (Fig. 19b). Fig. 19c shows the map of the potential risk from agricultural sources: 68% of the area falls into Very High (class 5) and 4% into Extremely High (class 6). The results obtained are strongly influenced by the intrinsic aquifer vulnerability.

In conclusion, the quality of water resources are mainly influenced by the intensive crop farming and by aquifer vulnerability as shown in the map of the potential nitrate contamination risk from agricultural sources.

Conclusions

The research was developed to assess the contamination risk by nitrates in groundwater originating from crops and livestock or from municipal and industrial sources.

Joint application of the SINTACS vulnerability model and the IPNOA hazard model represents a valid method for assessing the potential risk of contamination by nitrates of agricultural origin. This
risk assessment method was tested on four areas in the province of Cuneo (NW Italy), in the Cecina Plain (central Italy), in the Volturno River Plain (southern Italy) and in the Ribera area (Sicily). The IPNOA risk index proved a valid tool for public administrations to use in their own water resources management and protection policies concerning nitrate contamination and agricultural planning, as required under current European law (91/676/EC).

In the Cecina plain we applied a new method to assess the potential risk of contamination by nitrates from household sources, the IPNOC method (Hazard Index for Nitrates of Household Origin). By combining the IPNOA and IPNOC method the main factors causing the nitrate contents observed may be determined, as highlighted in some areas by isotopic studies. The methods can be used as an alternative (in large areas) or as a complement to commonly used isotopic investigation to evaluate nitrate source in groundwater.

In conclusion, the parametric method to evaluate the contamination risk by nitrates in groundwater was successfully used. Nevertheless, in some cases the hydrochemical facies influences the nitrate content in the aquifer: dilution and reduction phenomena make risk maps appear less reliable.

The use of a groundwater nitrate contamination risk map makes it possible to account for the spatiality in the on-ground nitrogen loadings and allows the realistic allocations of the different nitrogen sources present in the area of concern, especially if coupled with in-depth hydrogeochemical studies.

References


SESIRCA (Settore Sperimentazione Informazione Ricerca e Consulenza in Agricoltura della Regione Campania) 2004. Carta dell’Utilizzazione Agricola dei Suoli della Campania. Carta in scala 1/50.000. Map of Agricultural Land Use in Campania at the scale of 1:50,000.


Figure 1. The Nitrate Vulnerable Zones in Italy (source: http://www.crpa.it/media/documents/crpa_www/Progetti/OptiMa-N/it/CI_20070914/Mundo.pdf)

Figure 2. Scheme for the IPNOA calculation.

Figure 3. Location of the study areas: F = Fossano area; C = Cecina Plain; V = Volturino River Plain; R = Ribera area.

Figure 4. Fossano area: flow pattern of the unconfined aquifer and hydrogeologic setting.

Figure 5. Map of the aquifer vulnerability in the Fossano area.

Figure 6. Map of the IPNOA index of nitrate hazard in the Fossano area.

Figure 7. Map of the potential nitrate contamination risk from Agricultural sources in the Fossano area.

Figure 8. Map of isoconcentration of the NO₃⁻ in the unconfined aquifer in the Fossano area.

Figure 9. Comparison between usual vulnerability SINTACS (A) and vulnerability SINTACS executed for the sewerage system (B).

Figure 10. Risk of nitrate pollution from agriculture and livestock (A) and (B) from sewer waters.

Figure 11. Langelier-Ludwig diagram of the ground waters from the Cecina Plain.

Figure 12. NO₃/Na vs. Cl/Na molar diagram for the Cecina Plain groundwaters. Communal input and agriculture fields are from Roy et al. (1999).

Figure 13. δ¹⁸O-NO₃ vs. δ¹⁵N-NO₃ binary diagram for selected ground waters from the Cecina Plain.

Figure 14. Hydrogeological map and location of the northern part of the Volturino River Plain area. The piezometric surface of the aquifer (June-July, 2006) is in m a.s.l. Hydrogeological units: Dt: Slope deposits; al: Alluvial deposits (-a: prevalently silty; -an: prevalently silty of marine origin; -s: prevalently sandy); TG: Campanian Ignimbrite tuffs; TA: old tuffs; MC: marly-calcarenitic flysch; AM: marly-arenaceous flysch; C: limestones.

Figure 15. Nitrate (NO₃) distribution in groundwater of the northern part of the Volturino River Plain area in mg/l (June-July, 2006); highlighted areas with nitrate values exceeding 50 mg/l.

Figure 16. Potential Agricultural Nitrate Contamination Risk of the northern part of the Volturino River Plain aquifer derived from the IPNOA (Agricultural Nitrate Hazard Index) map and the Vulnerability map.

Figure 17. Chemical composition of the Ribera groundwater: a) Langelier-Ludwig diagram; b) Ca²⁺-SO₄²⁻-HCO₃⁻ diagram.

Figure 18. Chemical and isotopic composition of the Ribera groundwater a) Ca²⁺ - SO₄²⁻ diagram b) δD - δ¹⁸O diagram.

Figure 19. a) Map of the aquifer vulnerability (SINTACS); b) Map of the IPNOA index of nitrate hazard; c) Map of the potential nitrate contamination risk from Agricultural sources.
Table 1. SINTACS classification.

<table>
<thead>
<tr>
<th>SINTACS</th>
<th>classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>very low (vl)</td>
</tr>
<tr>
<td>2</td>
<td>low (l)</td>
</tr>
<tr>
<td>3</td>
<td>moderate (m)</td>
</tr>
<tr>
<td>4</td>
<td>high (h)</td>
</tr>
<tr>
<td>5</td>
<td>very high (vh)</td>
</tr>
<tr>
<td>6</td>
<td>extremely high (eh)</td>
</tr>
</tbody>
</table>

Table 2. Nitrogen supply from different fertilisation types and relative hazard classes.

<table>
<thead>
<tr>
<th>Nitrogen supply from inorganic fertilisation (kg/ha)</th>
<th>Nitrogen supply from organic fertilisation (kg/ha)</th>
<th>Nitrogen supply from sludge (kg/ha)</th>
<th>Hazard classes (HF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1-25</td>
<td>1-150</td>
<td>1-150</td>
<td>2</td>
</tr>
<tr>
<td>26-100</td>
<td>151-300</td>
<td>151-500</td>
<td>3</td>
</tr>
<tr>
<td>100-180</td>
<td>300-500</td>
<td>500-1500</td>
<td>4</td>
</tr>
<tr>
<td>&gt;180</td>
<td>&gt;500</td>
<td>&gt;1500</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3. Control classes for the soil nitrogen content.

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<thead>
<tr>
<th>Soil nitrogen content (%)</th>
<th>Control classes (CF_n)</th>
</tr>
</thead>
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<tr>
<td>&gt;0.5</td>
<td>1.04</td>
</tr>
<tr>
<td>0.22-0.5</td>
<td>1.02</td>
</tr>
<tr>
<td>0.15-0.22</td>
<td>1.00</td>
</tr>
<tr>
<td>0.1-0.15</td>
<td>0.98</td>
</tr>
<tr>
<td>&lt;0.1</td>
<td>0.96</td>
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</tbody>
</table>

Table 4. Control classes for the climate.

<table>
<thead>
<tr>
<th>Rainfall (mm/year) and Temperature (°C)</th>
<th>Control classes (CF_c)</th>
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<tbody>
<tr>
<td>&gt;1200</td>
<td>1.10</td>
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<tr>
<td>1050-1150</td>
<td>1.08</td>
</tr>
<tr>
<td>950-1100</td>
<td>1.06</td>
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<tr>
<td>800-1000</td>
<td>1.04</td>
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<tr>
<td>600-1000</td>
<td>1.02</td>
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<tr>
<td>600-800</td>
<td>1.00</td>
</tr>
<tr>
<td>500-900</td>
<td>&gt;16</td>
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<tr>
<td>600-700</td>
<td>0.96</td>
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<tr>
<td>&lt;600</td>
<td>0.94</td>
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</table>

Table 5. Control classes for the agronomic practices.

<table>
<thead>
<tr>
<th>Tillage</th>
<th>Type of fertilisation</th>
<th>Control classes (CF_ap)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fertirrigation</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>traditional total surface</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>through leaves</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>minimum localized</td>
<td>0.96</td>
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<tr>
<td></td>
<td>no tillage</td>
<td>0.94</td>
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Table 6. Control classes for the irrigation systems.

<table>
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<th>Irrigation system</th>
<th>Control classes (CF_i)</th>
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<tr>
<td>basin</td>
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<tr>
<td>border</td>
<td>1.04</td>
</tr>
<tr>
<td>sprinkler</td>
<td>1.02</td>
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<tr>
<td>no irrigation</td>
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Table 7. Hazard indices, IPNOA and relative classification.

<table>
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<th>Hazard Index</th>
<th>IPNOA</th>
<th>Classification</th>
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</tr>
<tr>
<td>3.19-5.88</td>
<td>2</td>
<td>very low (vl)</td>
</tr>
<tr>
<td>5.89-7.42</td>
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<td>low (l)</td>
</tr>
<tr>
<td>7.43-9.31</td>
<td>4</td>
<td>moderate (m)</td>
</tr>
<tr>
<td>9.32-11.10</td>
<td>5</td>
<td>high (h)</td>
</tr>
<tr>
<td>11.11-17.66</td>
<td>6</td>
<td>very high (vh)</td>
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Table 8. SINTACS and IPNOA correlation for the potential risk assessment.

<table>
<thead>
<tr>
<th>IPNOA</th>
<th>SINTACS</th>
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<td>vh</td>
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Table 9. Average leakage of sewer pipes.

<table>
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<tr>
<th>MATERIAL</th>
<th>AVERAGE LIFE-TIME, years</th>
<th>LEAKAGE %</th>
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<tr>
<td>gres</td>
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<td>3</td>
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<tr>
<td>pvc</td>
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</tr>
<tr>
<td>cement</td>
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<td>10</td>
</tr>
<tr>
<td>steel</td>
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<td>5</td>
</tr>
<tr>
<td>polyethylene</td>
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<td>8</td>
</tr>
<tr>
<td>asbestos cement</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>cast iron</td>
<td>25</td>
<td>4</td>
</tr>
<tr>
<td>lead</td>
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<td>3</td>
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Table 10. No. of heads of livestock raised per Municipality

<table>
<thead>
<tr>
<th>TOPONYM</th>
<th>BOVINES</th>
<th>SHEEP</th>
<th>GOATS</th>
<th>HORSES</th>
<th>PIGS</th>
<th>POULTRY</th>
<th>RABBITS</th>
<th>OSTRICHES</th>
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<td>33283</td>
<td>14008</td>
<td>36740</td>
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<td>Fossano</td>
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<td>68</td>
<td>76</td>
<td>84725</td>
<td>362862</td>
<td>31427</td>
<td>77</td>
</tr>
<tr>
<td>Genola</td>
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<td>3</td>
<td>2804</td>
<td>423000</td>
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<tr>
<td>Marene</td>
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<td>29</td>
<td>28</td>
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<td>18794</td>
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