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A methodology for assessing the impact of the use of road salt on groundwater resources in a mountain environment (Serra da Estrela, Central Portugal)

Uma metodologia de avaliação do impacto sobre os recursos hídricos subterrâneos do uso de sal para a limpeza de estradas em ambiente de montanha (Serra da Estrela, Centro de Portugal)

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Abstract

Mountain areas are the source of high quality and socioeconomic relevance water resources. The sustainable management of such regions is fundamental to maintain the water supply to populations in wide areas all over the planet. Serra da Estrela is the origin of water resources of strategic importance to Portugal. In the highest part of the mountain, especially above 1400 m a.s.l., the use of road de-icing chemicals (NaCl and, accessorily, CaCl) may affect both groundwater and surface water as well as soils and therefore is a major environmental concern that should be investigated. This article presents a multidisciplinary methodology meant to support the study of water pollution as a result of the use of road de-icing salts in a mountain environment. This methodology encompasses contributions from Hydrogeology, Hydrogeochemistry, Isotope Geochemistry, Hydrogeophysics, GIS supported geological mapping and mathematical modelling. The main purpose of the application of this methodology in Serra da Estrela is to prepare a hydrogeological conceptual model focused in the processes related to groundwater pollution by NaCl from road de-icing. Another objective is to improve the sustainability of water resources and to provide new guidelines for water exploration and exploitation in the region.

Key words: *water pollution, de-icing salt, high-mountain hydrology*

INTRODUCTION

Mountain areas are usually the origin of water resources of exceptional quality and high socioeconomic relevance, as it is recognized by the UNESCO International Hydrological Programme (e.g., AURELI, 2002; UNESCO IHP-VI Programme: *http://www.unesco.org*) as well as by the *Millennium Ecosystem Assessment* (HASSAN *et al.*, 2005). This UNESCO Programme emphasizes the "*High Mountains as Water the World's Towers*" and their role on the hydrological system's capacity to supply freshwater for the human needs.

The mountain's role on generating and storing freshwater is a well-established fact (e.g., BANDYOPADHYAY, 1995; AURELI, 2002; GRUNEWALD *et al.*, 2007). A substantial fraction of the world's drinking water has its origin in mountains. So, the environmental management of such areas is becoming more crucial to maintain the adequate quantity and quality of water supplies to the populations living downstream (e.g., VIVIROLI & WEINGARTNER, 2008).

The understanding of mountain hydrological systems is usually difficult due to the particularly complex way how geological, geomorphologic, pedologic, hydroclimatic and anthropic processes interact and contribute to control the water cycle. Consequently, the modelling of mountain areas hydrology is a challenging task, even when relevant data are available. Yet, mountain basins provide an exceptional opportunity to increase knowledge on the relationship between those complex variables as well as their impacts on the water quality at different elevation zones, under different cultural settings (CHALISE, 1997).

The use of de-icing chemicals to maintain clear road pavements is a common practice in cold and temperate climate regions. The resulting water pollution is a major environmental concern (e.g., HAWKINS & JUDD, 1973; RISCH & ROBINSON, 2000; GODWIN et al., 2003). Several inorganic and organic chemicals may be applied in road de-icing operations (e.g., TRB, 1991; GRANATO, 1996; EPA, 2002; RASA et al., 2006). Yet, in terms of both time and budget, common salt, or sodium chloride (NaCl), is widely regarded as the most effective means of road de-icing (TRB, 1991).

Serra da Estrela is the highest mountain in the Portuguese mainland. This region shows specific climatic, geologic and geomorphologic features that play an important role on the local water cycle, where surface waters, normal groundwaters and thermomineral waters occur side-by-side. The Serra da Estrela mountain region is the source of strategic water resources: (i) high quality groundwater for agricultural and domestic uses as well as for the bottling industry and for therapeutic uses at spas; (ii) surface water stored in small and large dams, including the one that supplies the city of Lisbon (Castelo do Bode dam).

In order to understand the hydrogeological system of the River Zêzere Basin Upstream of Manteigas village (ZBUM, see fig. 1), an area of particular interest in this mountain, an integrated multidisciplinary research (comprising geology, geomorphology, climatology, hydrogeology, geochemistry, isotope hydrology, hydropedology and geophysics) has been carried out between 2003 and 2008, under the scope of the HIMOCATCH R&D Project *"Role of High Mountain Areas in Catchment Water Resources, Central Portugal"* (e.g., ESPINHA

MARQUES et al., 2005, 2006a,b, 2007; ESPINHA MARQUES, 2007; MARQUES et a*l.*, 2007, 2008a,b).

The mountain's summit is one of the most important touristic spots in Portugal mainly because of the ski courses there located. The extensive use of road salt in this region is a major environmental issue, resulting in water and soil pollution by the chemical substances used to promote snowmelt (mostly NaCl and, subsidiary, CaCl), as stated by previous studies (e.g., ESPINHA MARQUES et al*.*, 2006a; MARQUES et al*.*, 2008b; CARVALHO et al*.*, 2009). The precise nature and the extent of the problem are, at the present time, unknown. Nevertheless, at the present stage of the knowledge, it is possible to establish that the most affected area corresponds to the Nave de Santo António-Torre-Sabugueiro sector (NSATS).

The Serra da Estrela hydrology is complex due to its particular geological, geomorphological and hydroclimatological features, requiring a multidisciplinary approach in order to establish the best methodology to study water pollution by road de-icing salts.

HYDROGEOLOGICAL FRAMEWORK

The Serra da Estrela (40º 15-38'N; 7º 18-47'W) is part of the *Cordilheira Central*, an ENE-WSW mountain range that crosses the Iberian Peninsula, and reaches 1993 m a.s.l. at the Torre plateau (fig. 1 and 2).

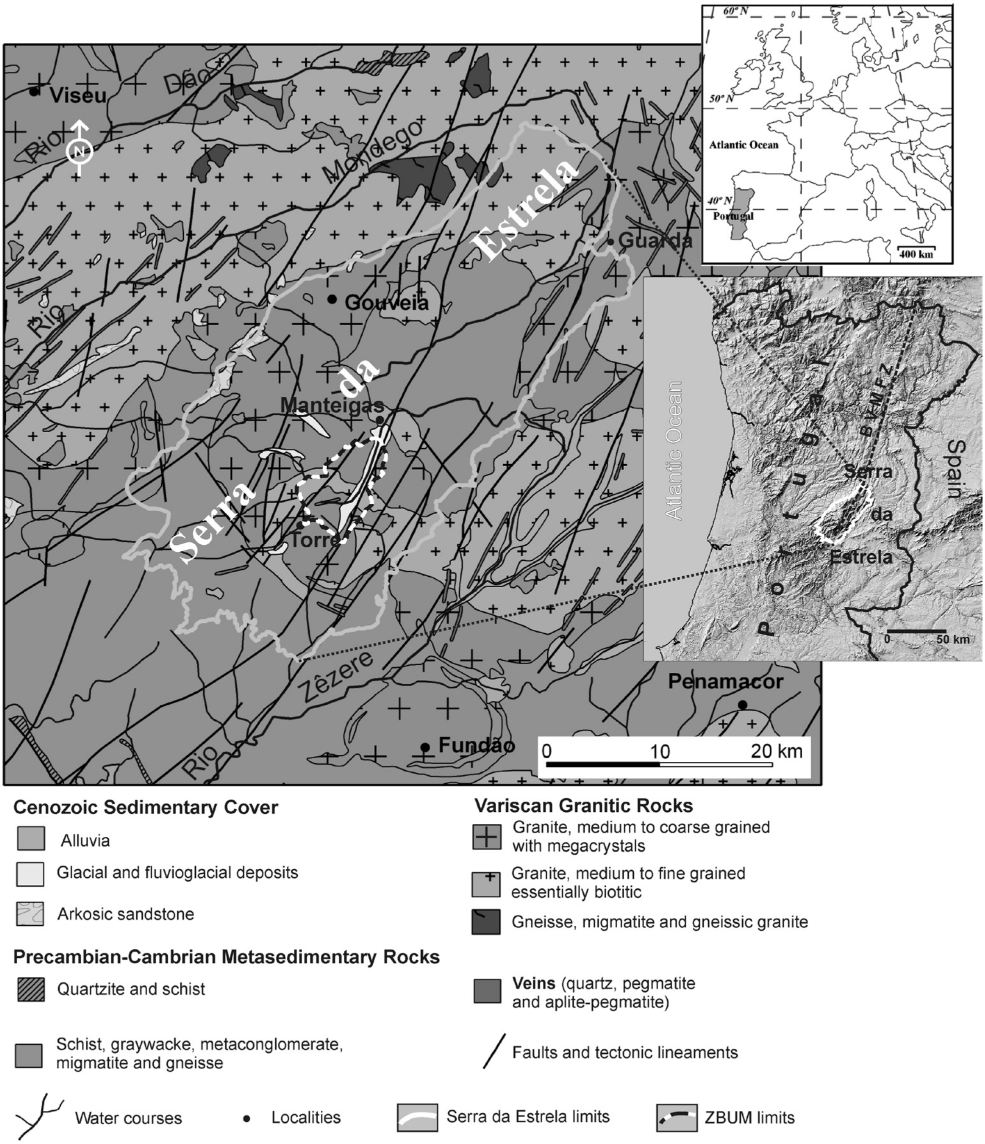

Fig. 1. Geological map of Serra da Estrela region (adapted from Geological Map of Portugal, 1/500.000, OLIVEIRA *et al.*, 1992).

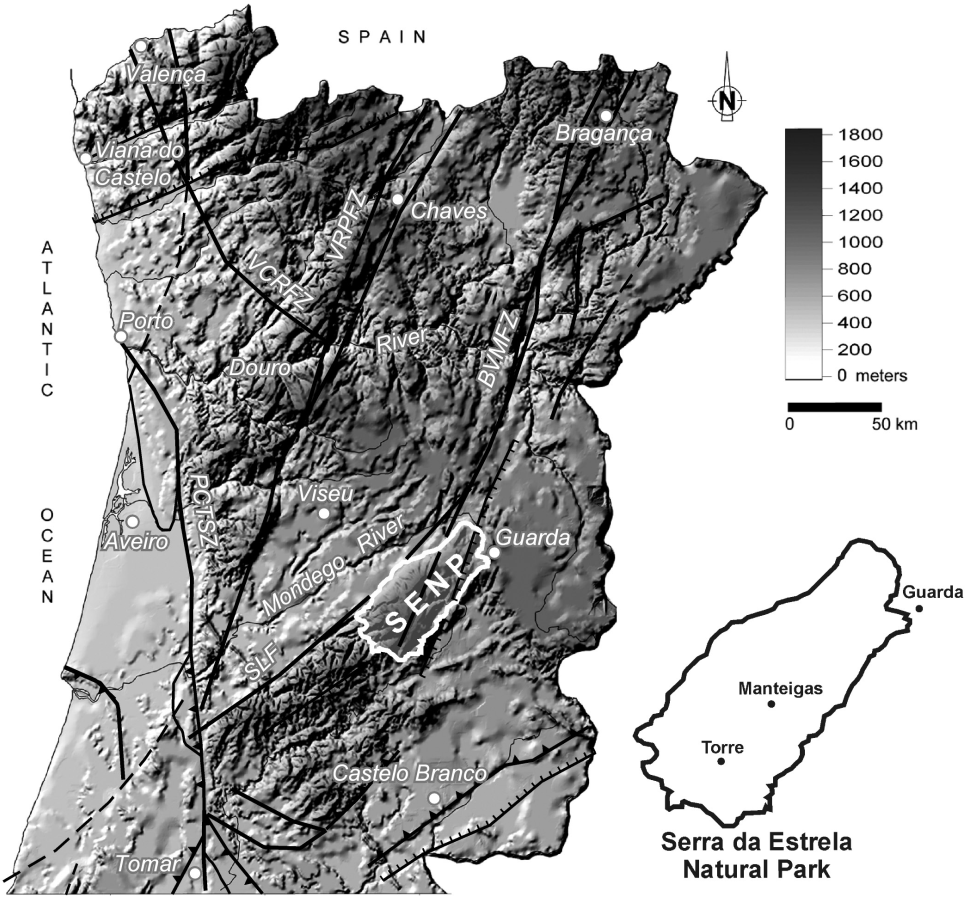

Fig. 2. Morphotectonic features from Central Portugal, Serra da Estrela mountain region. Major faults: PCTSZ: Porto-Coimbra-Tomar strike-slip shear zone; VCRFZ: Vigo-Vila Nova de Cerveira-Régua fault zone; VRPFZ: Verin-Régua-Penacova fault zone; BVMFZ: Bragança-Vilariça-Manteigas fault zone; SLF: Seia-Lousã fault zone.

The Serra da Estrela Mountain is located in the Central-Iberian Zone of the Iberian Massif (RIBEIRO *et al.*, 1990). The geological and tectonic conditions control some of the major hydrogeologic features and processes, such as infiltration, aquifer recharge, type of flow medium (porous *vs.* fractured), type of groundwater flow paths, or hydrogeochemistry.

The main regional tectonic structure is the NNE-SSW Bragança-Vilariça-Manteigas (fig. 2) fault zone, which controls the thermal occurrences. According to RIBEIRO et al. (1990), the origin of the Serra da Estrela Mountain is connected to an uplift process related to the reactivation of the Bragança-Vilariça-Manteigas Fault Zone (during Cenozoic times, by the alpine compressive tectonics, together with the reactivation of major ENE-WSW trending reverse faults (such as the Seia-Lousã fault). Serra da Estrela is mainly composed by Variscan granitic rocks and Precambrian-Cambrian metasedimentary rocks, as well as alluvium and quaternary glacial deposits (fig. 1 and 3).

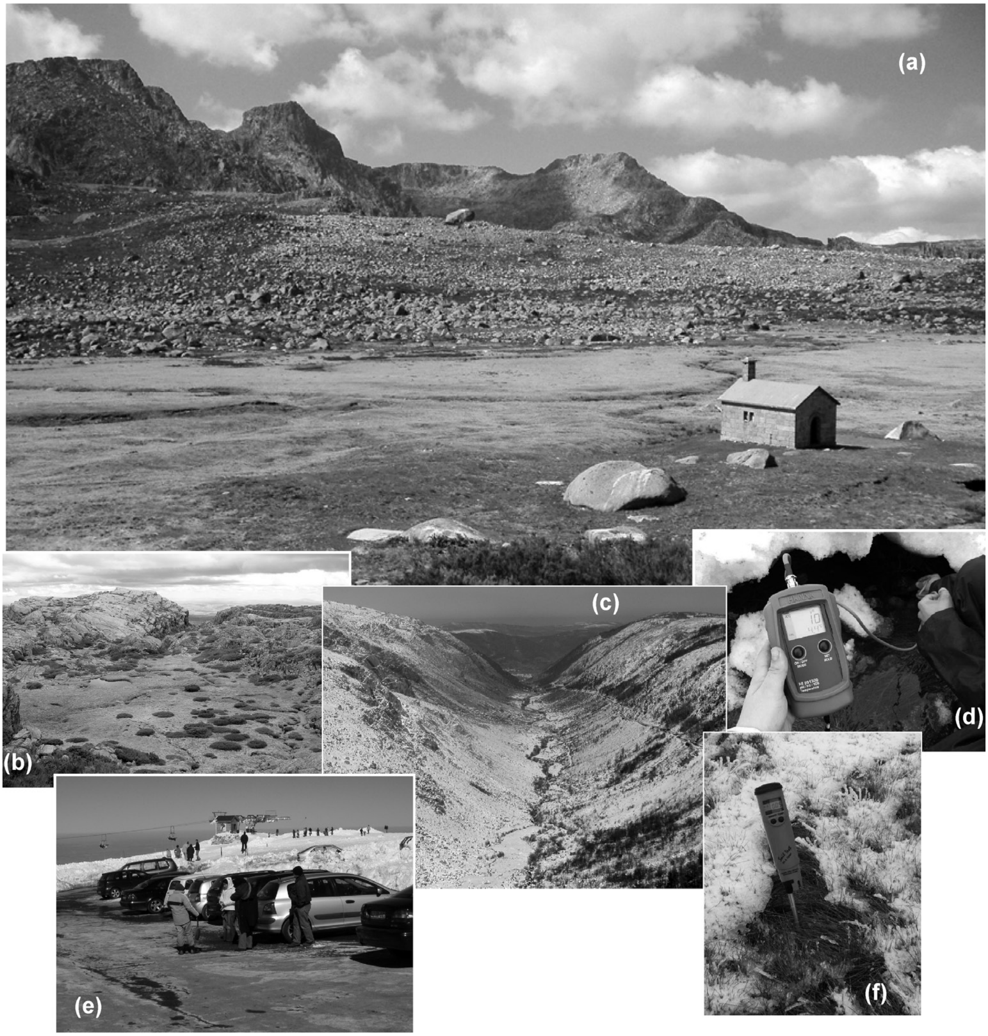

Fig. 3. Some views of the Serra da Estrela region: (a) Nave de Santo António alluvia (foreground), fluvioglacial deposits (intermediate plan) and granitic slopes (in the background); (b) granitic outcrops and vegetation near the Torre summit; (c) snow covered Zêzere glacial valley (note the road on the right); (d) in situ measurement of water pH, electrical conductivity and temperature; (e) road near the ski course; (f) in situ measurement of soil electrical conductivity.

The mountain is comprised of tectonically controlled plateaus forming steps between 1400 m a.s.l. and the summit. Late Pleistocene glacial landforms and deposits are a distinctive feature of the Zêzere catchment, since the majority of the plateau area was glaciated during the Last Glacial Maximum (e.g., DAVEAU et al. 1997, VIEIRA et al. 2005).

The spatial distribution of infiltration and aquifer recharge in Serra da Estrela is largely determined by the distribution areas of prevailing porous or fractured circulation media (e.g., ESPINHA MARQUES et al., 2005, 2006a). Porous media are dominant in the alluvium and Quaternary glacial deposits as well as in the most weathered granites and metasedimentary rocks and occur at shallower depths (usually less than 50 m). Fractured media are present in poorly weathered rocks. Such media may be present very close to the surface (especially on granitic outcrop dominated areas, with thin or absent sedimentary cover) or below the referred porous geologic materials. The regional hydrogeological units correspond to the main geological units: i) sedimentary cover, including alluvium and Quaternary glacial deposits; ii) metasedimentary rocks, which include schists and graywackes; and iii) granitic rocks.

Water resources of the ZBUM area have been evaluated by means of a semi-distributed hydrological model based on the VISUAL BALAN 2.0, a code that performs daily water balances in the root zone, the unsaturated zone and the aquifer and requires a small number of parameters (e.g., ESPINHA MARQUES et al., 2006b; SAMPER et al., 2007).

The model results suggest that interflow is the most important fraction of precipitation (41%), which is a typical result in mountain regions (e.g., GURTZ et al., 2001; WU & XU, 2005). The calculated groundwater recharge is 15% of mean annual precipitation. This value is consistent with those obtained in the last decades in Northern and Central Portugal with a wide variety of techniques (e.g., CARVALHO et al., 2000, 2007).

WATER POLLUTION BY ROAD SALT

Snow and ice control in roads may be carried out through a number of techniques like application of de-icing chemicals, ploughing and sanding (TRB, 1991).

Several inorganic and organic chemicals may be applied in road de-icing operations, such as sodium chloride (NaCl), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), potassium chloride (KCl), potassium acetate ($KC_2H_3O_2$), calcium magnesium acetate ($CaCO_3$, $MgCO_3$, and CH_3COOH), calcium magnesium propionate and potassium formate ($CHKO_2$) — e. g., GRANATO, 1996; EPA, 2002; HELLSTÉNA et al., 2005; RASA et al., 2006).

De-icing chemicals reduce the freezing point of water therefore facilitating the removal of snow and ice from road pavements and decreasing the costs related to time, man-power and equipment. In cold and temperate and climate regions, where snowfall is frequent, road de-icing operations are critical in order to maintain the normal functioning of the economy. Sodium chloride is the most widely used de-icing chemical because it is inexpensive, easily available, simple to apply and has a reliable ice-melting performance (TRB, 1991). Yet, this common practice has environmental side effects like metal corrosion in vehicles and built structures (namely bridges), soil pollution, degradation of road-side plants as well as groundwater and surface water pollution (e.g., HAWKINS & JUDD, 1973; TRB, 1991; EPA, 2002; GODWIN et al., 2003).

As a result of de-icing operations, water from pavement runoff becomes enriched in NaCl. After infiltrating in roadside soils or moving as overland flow this water may reach streams and aquifers affecting its hydrochemistry, originating a major environmental concern (e.g., GRANATO, 1996).

AN ASSESSMENT METHODOLOGY

At Serra da Estrela, the NSATS (fig. 4) is the area of the most intensive use of road salt and therefore will be the main target of future environmental hydrogeology studies. The NSATS is a sector of Serra da Estrela Natural Park that includes the River Zêzere basin upstream of Nave de Santo António col and the River Mondego basin between the Torre summit and Sabugueiro village. It is located in the high valleys and plateaus with altitude ranging from *ca.* 1400 m (Nave de Santo António and Sabugueiro) to 1993 m a.s.l. (Torre summit). The results from previous studies (e.g., ESPINHA MARQUES et al., 2006b; MARQUES et al., 2008b; CARVALHO et al., 2009) suggest that, in this area, groundwater, surface water and soils are affected by NaCl from de-icing operations.

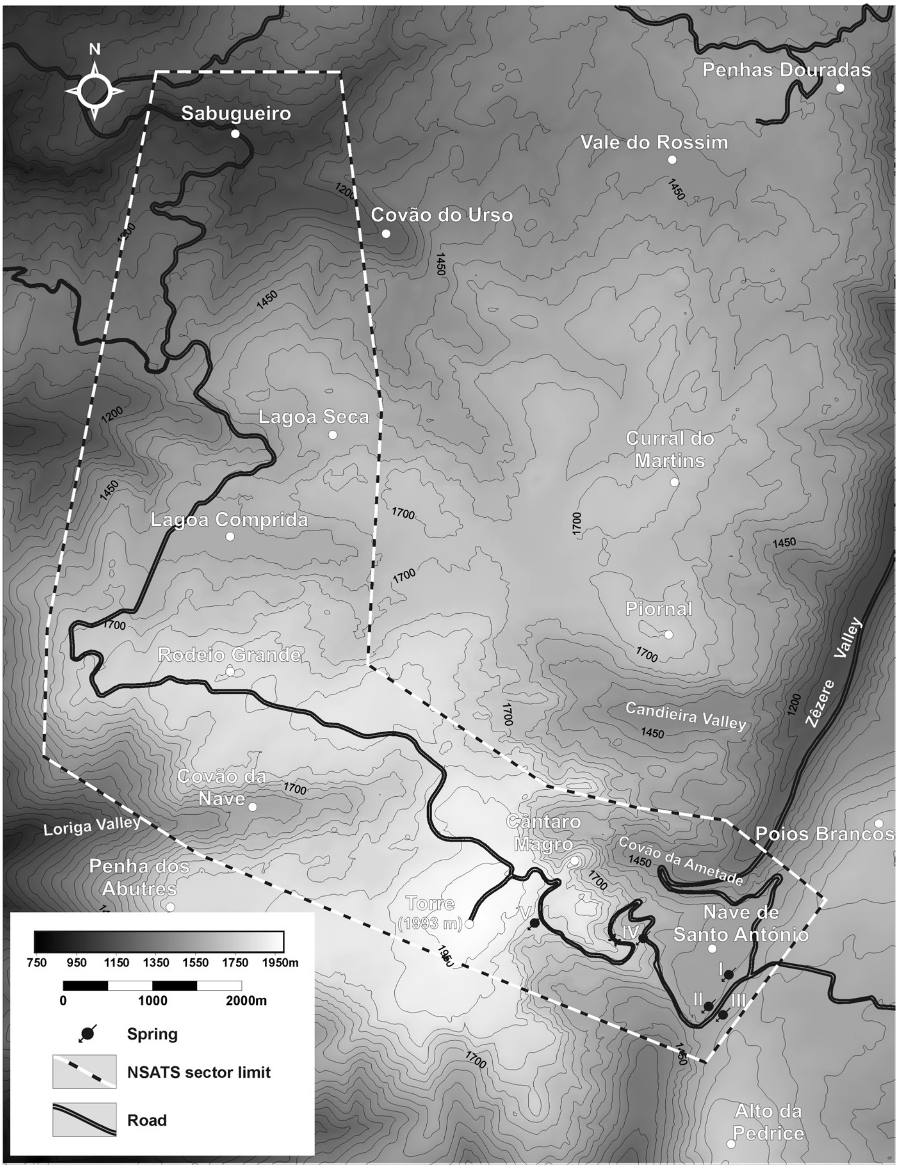

Fig. 4. Hypsometric features of the Nave de Santo António-Torre-Santo António sector. Springs considered in previous studies: (I) Nave de Santo António (north); (II) Nave de Santo António (south); (III) Saibreira; (IV) Espinhaço de Cão; (V) Covão do Boi.

In the last decades, the Natural Park's authorities established ecosystem, land use and natural resources management (e.g., SNPRCN, 1987) that seek to overcome the difficulties of protecting natural systems in a region subject to substantial human pressure. Yet, in what concerns the water resources protection and management, such plans must be substantially improved. The previous hydrological research carried out in the scope of the HIMOCATCH project (e.g., ESPINHA MARQUES et al., 2006a, MARQUES et al., 2008a) has provided very useful guidelines regarding these issues.

Further investigations are fundamental to expand the knowledge concerning the impact of the use of road salt on the water resources. Starting from the available hydrological conceptual model (ESPINHA MARQUES et al., 2006a,b) the main purpose of the proposed study methodology is to achieve a new conceptual model focused on the processes involved in groundwater pollution by road salt. This new model is meant to trace the dynamics of water pollution by road salt in the NSATS sector.

Other objectives of the application of this methodology are:

(i) To provide a multidisciplinary approach capable of embracing the complexity of high a mountain hard rock aquifer system. This approach will include contributes from Hydrogeology, Hydrogeomorphology, Hydrogeochemistry, Isotope Hydrology, Hydropedology, Hydrogeophysics, and Mathematical Hydrologic Modelling.

(ii) To establish the nature and the spatial extension of the groundwater and, accessorily, surface water pollution by road salt.

(iii) To determine hydrogeochemical signatures associated to road salt, in order to distinguishing polluted and unpolluted waters.

(iv) To determine isotopic signatures of groundwater and to identify aquifer recharge areas and flowpaths.

(v) To understand the role of the unsaturated zone in water pollution by road salt, namely the infiltration and interflow processes; to carry out a hydropedological characterization including the hydraulic, mineralogical and geochemical features of soils, as well as the water flow and the NaCl transport through the unsaturated zone.

(vi) To carry on the scientific research achieved during previous Projects on the assessment of Portuguese groundwater resources.

(vii) To provide new insights into the water management, water quality protection and land use planning in high mountain areas.

(viii) To contribute to the knowledge on the hydrology of high mountain areas.

(ix) To increase the interest of local authorities and private companies in exploring and exploiting groundwater resources in the region, potentially leading to the local creation of income and jobs.

The referred multidisciplinary approach (fig. 5) is required because of the high complexity of the natural system affected by the road salt pollution and comprises the following components:

(i) Hydrogeology — hydrogeological, hydrogeomorphological and hydrogeomechanical features of the rock and soil units.

(ii) Hydrogeochemistry — major and minor element composition of snow, rain, groundwaters and surface waters; the chemical analysis of waters will be used to understand the pollution processes and to determine the spatial extent of the water pollution.

(iii) Isotope geochemistry — in mountain regions the air masses are orographically uplifted, they cool and precipitate preferentially the heavier isotopes; it is possible to use the altitude effect to help locating the recharge area (^{18}O and ^{2}H), to determine the residence time (^{3}H) and to quantify the recharge by snowmelt of the groundwater systems based on the ^{18}O and ^{2}H composition.

(iv) Hydropedology — the hydrological features of soils, such as the hydraulic conductivity, the water content, the water retention, will be investigated by means of field and laboratory techniques; other soil physical and chemical properties (such as electrical conductivity, pH and texture), as well as mineralogy and geochemistry will also be studied.

(v) Hydrogeophysics — electric resistivity and ground penetrating radar techniques will be applied in order to study the unsaturated zone structure.

(vi) Hydrogeological GIS mapping — aquifer vulnerability to pollution and aquifer risk assessment mapping.

(vii) Mathematical modelling of hydrological processes — the CORE^{2D} code (e.g., SAMPER *et al.*, 2000) will be applied to perform calculations in the unsaturated zone and in the aquifer concerning water flow and solute transport (especially NaCl).

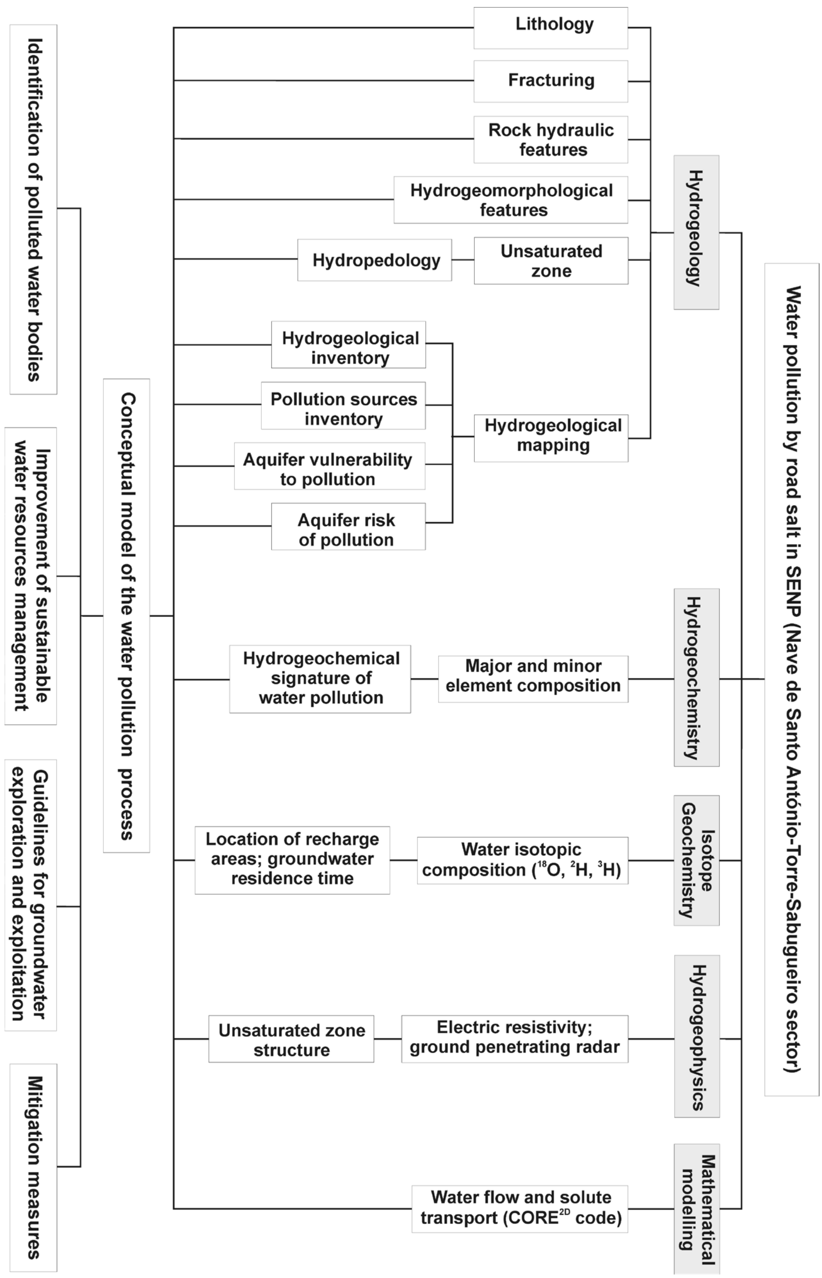

Fig. 5. Scheme of the methodology for assessing the impact of the use of road salt on water resources in Serra da Estrela Natural Park (SENP)

The starting point is the compilation of the available scientific data and the definition of the local and regional hydrogeological framework. The next step is the hydrogeological inventory including springs, wells and surface water bodies. Afterwards, field campaigns for water and soil sampling, for geological, hydrogeological, hydrogeochemical, isotope hydrology, hydrogeomorphological, hydrogeophysical and hydropedological characterization will be carried out. During these field campaigns, water pollution sources will be inventoried and mapped.

A preliminary conceptual model will be created involving the comprehension of the hydrological system nature, its broad characteristics as well as the physical and chemical processes implicated. As new results arise, the conceptual model will evolve and improve its capability of explaining the natural systems functioning. Mathematical modelling of flow and solute transport will aim at simulating the part of the conceptual model related to the water flow and the NaCl transport. Aquifer pollution vulnerability and risk assessment will be GIS mapped.

The results from the application of this methodology are expected to provide a new conceptual model representing the most important processes regarding water pollution by road salt in a high mountain environment, bringing significant improvements to the water resources management in the Serra da Estrela region. The extent of water pollution — including the identification of the affected water bodies — will be recognized, allowing the adoption of future mitigation measures. Contaminated wells, springs and streams will be identified to prevent public health damages. Future groundwater exploration and exploitation in the studied region will be carried out more rationally due to the provided knowledge.

PRELIMINARY RESULTS

The hydrogeological studies carried out under the scope of the HIMOCATCH project have provided some results suggesting that the use of road de-icing salts could be affecting groundwater and soil in the Nave de Santo António-Torre area (e.g., ESPINHA MARQUES et al., 2006b; MARQUES et al., 2008b; CARVALHO et al., 2009).

In this area, several field observations based on measurements of groundwater electrical conductivity have revealed some anomalous situations corresponding to springs situated downstream of roads where de-icing operations are frequent (see fig. 4, fig. 6 and table 1). These springs tend to exhibit electrical conductivity values much higher (usually above 60 μS/cm) than the ones measured in springs upstream from the roads (usually bellow 20 μS/cm). In these cases, laboratory analysis confirmed the presence of relatively high concentrations of Na and Cl ions.

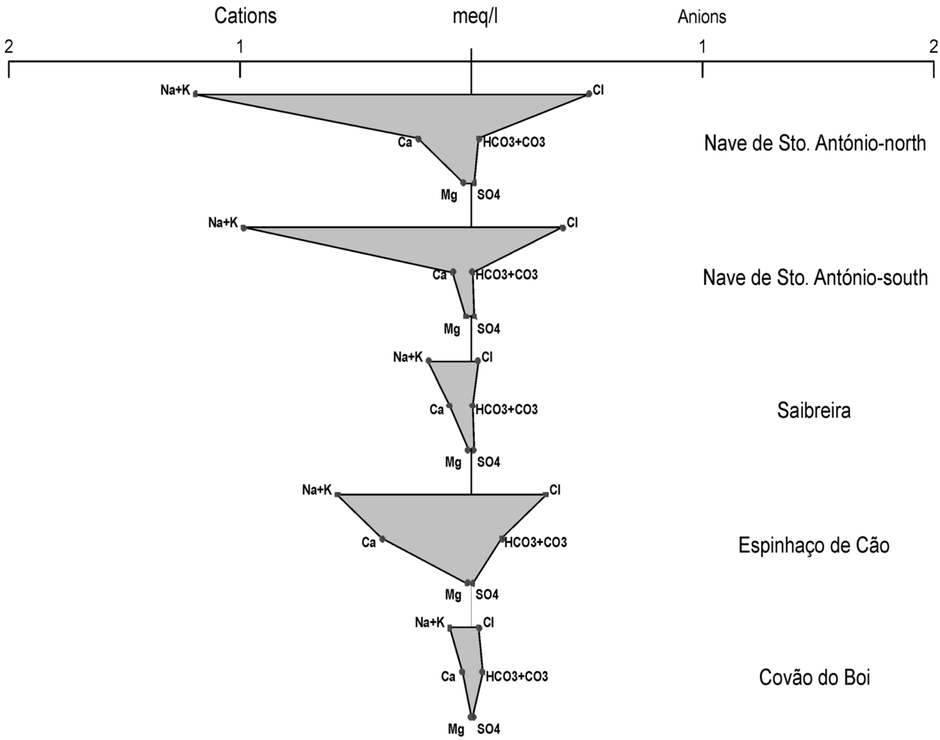

Fig. 6. Stiff diagrams of some groundwaters from the NSATS sector.

	pH	Electrical conductivity (μS/cm)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	Cl^- (mg/L)
Nave de Sto. António (north) (1)	5,2	84	27	0,8	4,6	0,4	2,0	0,6	1,0	18,0
Nave de Sto. António (south) (1)	5,9	68	22	1,2	1,6	0,3	0,2	0,6	0,3	14,0
Saibreira (1)	5,2	8	4	0,5	1,9	0,2	0,3	0,5	n, d,	1,0
Espinhaço de Cão (2)	6,2	150	13	0,6	7,8	0,2	8,0	0,3	1,7	11,5
Covão do Boi (2)	5,7	9	2	0,2	0,8	0,0	3,0	0,4	0,1	1,2

Table 1. Composition of groundwaters from the NSATS sector.

(1) Measured in June 2008

(2) Measured in Abril 2004

The typical composition of groundwater not affected by NaCl is represented by the Covão do Boi and Saibreira springs (HCO_3-Ca and Na-Cl *facies*, respectively, with low Na and Cl contents) whereas the composition of the polluted water is represented by the Nave de Santo António (north and south) and Espinhaço de Cão springs (Na-Cl *facies* with much higher Na and Cl contents). Especially interesting is the comparison between the composition of the Saibreira spring (situated *ca.* 5 m upstream from the road and having low electric conductivity and Na and Cl concentrations) and the Nave de Santo António-south spring (situated *ca.* 50 m downstream from the road and having higher electric conductivity and Na and Cl concentrations) since they are both connected to the same shallow aquifer (see fig. 4, fig. 6 and table 1).

According to Carvalho *et al.* (2009), in the vicinity of the Torre summit, soil salinity evaluated in A horizon through electrical conductivity tends to be higher along the roads where snow mixed with de-icing salts usually melts. Polluted soils present electrical conductivity values that may reach 0,3 бS/m while unaffected soils presents values usually under 0,05 бS/m.

Recent and unpublished exploratory studies performed in the Torre-Covão da Nave sub-sector (fig. 4) suggest that surface waters are also being affected by road salt. Water electric conductivity measured in streams and lakes also exhibit higher values most likely associated to pollution by de-icing chemicals. In this area, measurements taken from 5 m to 30 m upstream from the roads revealed electric conductivity values under 10 μS/cm (in some cases around 2 μS/cm) as measurements taken up to 100 m downstream from the roads supplied values above 100 μS/cm (occasionally above 300 μS/cm). Since sampling campaigns are still in course, laboratory results for these waters are not yet available.

CONCLUDING REMARKS

Mountains are the source of water resources of great quality and socioeconomic importance. The environmental management of such areas is becoming more crucial to maintain the adequate quantity and quality of water supplies to the world population. Mountain hydrological systems are hard to understand due to the complex way how geological, geomorphologic, pedologic, hydroclimatic and anthropic processes interact and contribute to control the water cycle.

In cold and temperate and climate regions, including mountains, where snowfall is frequent, road de-icing operations are very common. Sodium chloride (NaCl) is the most widely used de-icing chemical. The use of NaCl has environmental side effects including groundwater, surface water and soil pollution.

Serra da Estrela is the highest mountain in the Portuguese mainland and is the source of strategic water resources including high quality groundwater for agriculture, for domestic use, for the bottling industry and for therapeutic uses at spas, as well as surface water stored in dams, including the one that supplies the city of Lisbon. The extensive use of road salt in Serra da Estrela is a major environmental concern, resulting in water and soil pollution by the de-icing chemicals (NaCl and, subsidiary, CaCl), as stated by previous studies. A multidisciplinary approach is proposed as the best alternative to overcome the high complexity of the natural system affected by the road salt pollution. This approach comprises hydrogeology, hydrogeochemistry, isotope geochemistry, hydropedology, hydrogeophysics, hydrogeological GIS mapping and mathematical modelling of hydrological processes.

The main purpose of the proposed methodology is to achieve a new conceptual model focused on the processes involved in groundwater pollution by road salt in a high mountain environment, bringing significant improvements to the water resources management in the Serra da Estrela Region. This new model is meant to trace the dynamics of water pollution by road salt in the NSATS sector.

The knowledge of the spatial extent of water pollution should help to decide on which mitigation measures are to be adopted. Contaminated wells, springs and streams will be identified to prevent public health damages. Finally, new guidelines for sustainable groundwater exploration and exploitation will arise and contribute to a more rational management of the regional water resources.

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