Water Quality and Soil Natural Salinity in the Southern Imera Basin (Sicily, Italy)

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Abstract
The Southern Imera river crosses one of the most arid part of Sicily. The geochemical composition of the river water is due to the solubilization processes of gypsum rocks, which accounts for the particularly low quality of resources in the areas in which the presence of evaporitics deposits is highest. The geochemical composition and hydraulic parameters of river was monitored with the aim of reaching a better understanding of the relationships between lithology and water quality. The Imera river is a potential local hydric resource, but seasonal variability of salinity does not allow farmers to use its water. A geochemical monitoring of the Imera river water has been carried out in selected localities integrating a GIS analysis of the river hydrography basin and of the distribution of the evaporitic formation. During 2003 and 2005 we performed four monitoring surveys of water chemico-physical parameters (temperature, pH and electrical conductivity) and of the main ionic concentrations (Ca2+, Mg2+, K+, Na+, Cl-, SO42-). We also installed a multiparameter probe next to the hydrometrical station of Drasi, about 15 km from the river mouth. Such multiparameter probe was used to determine, continuously and simultaneously, temperature, electrical conductivity, pH, dissolved oxygen, redox potential, water level. The geochemical composition of the water allowed to confirm the results of Roda (1971) and Favara (2000), who pointed out that the main cause of degrade of the Southern Imera river are the salt-rich waters of some tributaries flowing over gypsum rocks and halite deposits. We have been able to identify which specific areas are the main contributors to the degradation of the Imera river.

Key-words: hydrochemistry, salinisation, water quality, Imera River, GIS.

Introduction
Irrigated agriculture is dependent on an adequate water supply of usable quality. Water used for irrigation can vary greatly in quality depending upon type and quantity of dissolved salts. They originate from dissolution or weathering of the rocks and soil, including dissolution of lime, gypsum and other slowly dissolved soil minerals and from intrusion of seawater into the river and underground water resources. In the case of irrigation, the salts are applied with the water and remain behind in the soil, as water evaporates or is used by the crop, contributing to soil salinisation. Salinisation can lead to desertification process, as the increasing salt levels in the top soil layers negatively affect plant growth and productivity. High salt concentrations (e.g., sodium chloride, magnesium and calcium sulphates and bicarbonates) affect plant growth directly, through toxicity, and indirectly, by increasing osmotic potential and lowering root water uptake (Yeo, 1983, Munns and Termaat, 1986, Yeo et al., 1991). Eventually, high sodium or low calcium concentrations of water, reduce the rate at which irrigation water enters...
Therefore, sufficient water cannot be infiltrated to supply the crop adequately from one irrigation to the next (Maas and Hoffman, 1977; Samemi et al., 1980; Maas et al., 1983; Mizrahi and Pasternak, 1985; Jones et al., 1989; Barbieri and De Pascale, 1992; Szabolic, 1994; Ayers and Westcot, 1994; Botrini et al., 1996; Giustiniani et al., 1997).

Salinity is a well-known issue in Sicily (Dazzi and Fierotti, 1994) and is widespread both along the coastal areas, due to the overpumping of aquifers causing sea water intrusion, and the central part of Sicily (Caltanissetta and Agrigento Provinces), due to the geological and hydrogeological conditions. In Sicily overall salinisation, primary (natural) and secondary, affects about 10% of soils (Dazzi, 2006).

The southern Imera, a torrential stream characterised by brief and violent floods during the rainy season from November to February and long periods of drought during spring and summer, crosses one of the most arid area of Sicily, an area showing the highest desertification risk of all region (Dazzi and Fierotti, 1994; Fierotti, 1997; Kosmas et al., 1999; Carnemolla et al., 2001; Basso et al., 2000; Brandt and Gee, 2003). The Imera river (Fig. 1) crosses four different provinces: Palermo, Caltanissetta, Enna ed Agrigento and its main tributaries are the Salso, Morello, Gibbesi and Torcicoda rivers and the Braemi and Alberi streams. Its spring is on the Madonie chain and its water runs for 132 km to the South, until Licata. The Licata plain is a cultivated area where specialized horticulture is the main economic activity. It is affected by low groundwater quality (Rapti-Caputo, 2005) that forces farmers to adopt multiple strategies to mitigate its effects, such as saving, storing and mixing water.

The Imera river is a potential irrigation source for Licata farmers, but its water cannot be used due to its high salts content. Since ancient times Southern Imera waters were recognized as brackish as reported from Vitruvius (Gwilt, 1860). During dry periods some farmers do use Imera water thus increasing the risk of soil salinisation. It’s well known that along the Imera Basin there is a widespread presence of evaporitic deposits and there are many salts mines that were active until the ’90s. The geochemical composition of the river water is mainly due to the solubilization processes of gypsum rocks and halite deposits (Manzi et al., 2009), which accounts for the particularly low quality of water in the areas where the presence of evaporitic deposits is highest (Decima and Wezel, 1971, 1973). Previous studies showed that the salinity could vary according to season and flow level (Roda, 1971).

In the framework of the RIADE project (Integrated Research for Applying new technologies and processes for combating DEsertification), we monitored water quality of the southern Imera river with the aim of reaching a better understanding of the relationships between lithology and water quality. We focused our work on investigation of seasonal variability of salinity, analysing water ions concentration and identifying which areas of hydrographic network are responsible for water salt enrichment. The geochemical monitoring of the Imera river was carried out, during 2003 and 2005, in selected localities integrating a GIS analysis of the river hydrography and of the spatial distribution of the evaporitic complexes.

Figure 1. Location of samples sites along the Vaccarizzo and Imera basin.
Methods

Chemicophysical parameters monitoring

In order to characterise the quality of the Imera River waters, during 2003 and 2005 we performed four monitoring surveys of chemical-physical parameters and of the main ionic concentrations. The sampling sites, selected integrating a GIS analysis of the hydrographic system with the distribution of the evaporitic complexes and by means of information deduced from the literature (Decima and Wezel, 1971, 1973; Roda, 1971; AA.VV., 2007), are shown in the Figure 1.

We determined in situ the electrical conductivity (E.C.), pH and temperature using the Hanna Instruments portable HI8733 conductivity meter (range: .01 µS/ cm - 100.0 mS/ cm, precision: 1%) and the Hanna Instruments portable HI98150 pHmeter (range: pH - 4.00-19.99, precision ± 0.02 pH).

Afterwards in the laboratory we measured the electric conductivity (25 °C) after dilution using the Crison 30 conductivity cell, (range: 0.01 µS/ cm - 199.9 mS/ cm, precision: 1%) when the samples showed electric conductivity bigger than 100 mS/ cm, and we analysed the concentrations of the main ions (Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Na\(^+\), Cl\(^-\), SO\(_4\)\(^{2-}\)).

The water samples were put in plastic containers (polyethylene) and preserved at a temperature of 5 °C up to the moment of the analysis. The determination of ionic concentrations was performed by Suppressed Ion Chromatography with conductivity detector, using a Dionex Series 4500i chromatograph equipped with a 25ml loop, and the following columns:
- Dionex IonPac AG9-HC Guard e AS9-HC Analytical 4 x 250 mm Columns (eluent: 9 mM Na\(_2\)CO\(_3\); 1.1 ml min\(^{-1}\), electrochemical suppressor ASRS-ULTRA);
- Dionex IonPac CG 12 Guard e CS 12 Analytical 4 x 250 mm Columns, (eluent: 20 mM MSA; 1.0 ml min\(^{-1}\), electrochemical suppressor CSRS-ULTRA).

Automatic Multiparametric monitoring system

In November 2004 we installed a multiparameter probe model Minisonde 4 connected to a datalogger by cable. Such multiparameter probe, equipped with a circulator, determine, continuously and simultaneously, temperature, electrical conductivity, pH, redox potenzial, dissolved oxygen and depth. The probe was controlled by software Hydras 3 (OTT), Windows-interface, and the data are transferred to the remote control by GSM (Global System for Mobile Communications) network.

Results and discussion

Hydrochemical characterization of the Imera river

The aim of our work was to study the seasonal variability of river salinity, analyse the water ion concentrations, identify which areas of the hydrographic network are responsible for water salt enrichment and define if the river waters can be used for irrigation purposes. Therefore we carried out the investigation of the main river tributaries by mean hydrochemical characterization.

Sampling October 2003

In this first monitoring surveys (Tab. 1) we identified some streams with high electric conductivity (maximum value 35.0 mS/cm) and other characterized by low values (about 1.0 mS/cm.).

We observed high salinity in the northern areas, especially for the Vaccarizzo stream (6), where some tributaries flow over gypsum rocks, while low salinity were observed for the southern Imera river (9).

The conductivity value was 15 mS/cm between Cinque Archi bridge (5) and Capodarso bridge (4) and decreased in the area between Capodarso bridge (4), Besaro bridge (3) and Drasi (2). The salinity decrease was caused by the intake of tributaries with low salinity water.

Table 1 shows the ionic concentrations (Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Na\(^+\), Cl\(^-\), SO\(_4\)\(^{2-}\)) and the SAR values.

As we can observe we found a very high nitrate value at station 6 (145.6 mg/l) very probably due to the common presence of cattles along the river banks. The SAR values are very
low in the northern area and shows a sudden increase at the confluence between Vaccarizzo stream and Imera and than decrease from Cinque Archi Bridge until Drasi station due to some tributaries with better quality water.

The Ion Chromatography analysis indicated that the ions with highest concentrations are sodium, calcium, sulphate and chloride and calcium and sodium concentrations are much higher than magnesium and potassium concentrations respectively (Ca/Mg and Na/K > 1).

Sampling June 2004

During June 2004 we performed the second monitoring surveys of chemicophysical parameters and of ionic concentrations of the Imera river. We collected eight samples (2-9) near the sites sampled in the October 2003 and eleven samples at new monitoring stations.

The new samples allowed recognizing other areas that contribute to increase the river’s salinity.

High E.C. values were observed in the samples collected near: Morello river bridge (4A, E.C. = 11,91 mS/cm), Cinque Archi bridge (5, E.C. = 11,91 mS/cm), Vallone Salito (5A, E.C. = 30,60 mS/cm and 5C, E.C. = 7,35 mS/cm). High conductivity and ion concentrations, but lower than the values of Vaccarizzo stream, were determined in the Morello river waters (4A, E.C. = 11,91 mS/cm and 5D E.C. = 7,12 mS/cm), but his intake in the Imera river doesn’t seem to influence the conductivity.

In comparison to the samples collected in the October 2003, samples 6, 7, 8 show higher conductivity values, samples 2, 3, 4 and 5 show lower values, while sample 9 shows the same value (Fig. 2). Table 2 shows the ionic concentrations (Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Na\(^+\), Cl\(^-\), SO\(_4\)^{2-}\) and the SAR values. Chloride and sodium ions are present in all samples with the highest concentrations and in both samplings, June and October, the ionic concentrations are similar.

The Ca/Mg and Na/K ratios are bigger than 1 except for the samples 6 and 6A (Vaccarizzo stream) that show low Ca/Mg values (Ca/Mg = 0,3). The SAR values show the same trend observed during the sampling October 2003: the values are very low in the northern area and increase at the confluence between Vaccarizzo stream and Imera and than decrease from Cinque Archi Bridge until Drasi station.

Sampling November 2004

In November 2004 we sampled again the sites analysed in June 2004 moreover we collected the water of the Garisi stream and Gibbesi river.

A comparison of the electric conductivity in the samplings of June and November 2004, showed a similar trend (Fig. 2).

The ionic chromatography analysis pointed
out that the cations and anions concentrations ratio change along the river, confirming that the low water quality is due to the presence of evaporitics deposits in several areas. Table 3 shows the ionic concentrations (Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\), Na\(^{+}\), Cl\(^{-}\), SO\(_4^{2-}\)) and the SAR values measured in the water samples during November 2004. The SAR values and the Ca/Mg and Na/K ratios show the same trend observed in the previous samplings.

Among the samples collected near the Garisi stream (6D and 6E), only the sample 6E had high conductivity (13.52 mS/cm) and high ionic concentrations. Finally, the sample collected near Gibbesi river (6D) showed an electric conductivity equal to 3.15 mS/cm.
Sampling May 2005

The previous sampling allowed to identify the areas of the Imera basin that cause the water salt enrichment. The tributaries with the highest ion concentration are localized in the northern area. In particular, very interesting is the Vaccarizzo stream. This small stream, crossing an area of Sicily characterised by a widespread presence of clays, gypsum rocks and evaporitics deposit, seems to contribute to a large extent to the water salt enrichment. In fact, salt concentration of the Vaccarizzo stream is ten times higher than that of the other tributaries (Na+ 6932 mg/l, K+ 2463 mg/l, Ca+ 56,42 mg/l, Cl- 13289 mg/l). During the Summer, when the water flow is lower and evaporation is higher, it is possible to observe salt crusts along the river banks.

In May 2005, we collected seven samples (Tab. 4) and examined the Vaccarizzo basin in detail (Fig. 3 and Tab. 4). Because of the high salinity, for some samples collected in the Vaccarizzo basin we could not determine in situ the conductivity. In these sites the conductivity was higher than 100 mS/cm, the maximum value detectable by our portable conductivity meter.

During the survey we could clearly identify the stream segment where we observe a sudden increase of salinity. We went up the Vaccarizzo riverbed, starting from sampling site 6A (Fig. 3), measuring water conductivity every one hun-

| Samples Date | E.C. mS/cm (25 °C) |
|--------------|-------------------|
| 1A 9 November| 3.65              |
| 1B 9 November| 1.75              |
| 2 9 November | 3.66              |
| 2B 9 November| 3.15              |
| 2A 9 November| 2.57              |
| 3 9 November | 7.36              |
| 4 9 November | 11.21             |
| 4a 9 November| 12.02             |
| 4B 9 November| 9.22              |
| 5 9 November | 10.59             |
| 5A 9 November| 41.60             |
| 5B 10 November| 34.30            |
| 5C 10 November| 9.61              |
| 5E 10 November| 12.36             |
| 6 10 November | 85.30             |
| 6A 10 November| 57.60             |
| 6B 10 November| 14.39             |
| 6D 10 November| 3.15              |
| 6E 10 November| 13.52             |
| 6C 10 November| 4.29              |
| 7 10 November | 6.74              |
| 7A 10 November| 5.78              |
| 8 10 November | 7.46              |
| 9 10 November | 0.88              |

Table 4. Sampling May 2005. E.C. in the water samples.

| Samples Date | E.C. mS/cm (25 °C) |
|--------------|-------------------|
| 1A 22 May    | 17.40             |
| 1 22 May     | 5.22              |
| 2 22 May     | 8.98              |
| 4 22 May     | 16.32             |
| 4A 22 May    | 7.90              |
| 4B 22 May    | 9.72              |
| 5 22 May     | 15.55             |
| 6A 24 May    | 37.10             |
| 6B 24 May    | 9.82              |
| 6D 24 May    | 4.04              |
| 6E 24 May    | 2.60              |
| 6F 24 May    | 6.00              |
| 6G 24 May    | 3.60              |
| 6H 24 May    | 39.10             |
| 6I 24 May    | 6.78              |
| 6L 24 May    | 4.78              |
| 6M 24 May    | 20.90             |
| 6O 24 May    | > 100.00          |
| 6P 24 May    | > 100.00          |
| 6Q 24 May    | > 100.00          |
| 6R 24 May    | > 100.00          |
| 6S 24 May    | > 100.00          |

1 Maximum value detectable by portable conductivity meter.
dred meters until we found the salty resurgence where EC grows suddenly from 14.0 mS/cm up to 100 mS/cm. The area was clearly detectable by the sudden change in the vegetation pattern along the riverbed.

One of the aims of our study was to define the water quality for irrigation purpose. The SAR and E.C. values observed (SAR > 40 and E.C: > 3.0 mS/cm) during October 2003-May 2005 showed that the waters of the Southern Imera cannot be used for agricultural purpose, except for those of site 9 (Imera bridge) located in the northern areas before the Vaccarizzo stream intake (5).

Automatic Multiparametric monitoring system

The multiparameter probe was installed in November 2004 next to the hydrometric station of Drasi (sampling site 2, Fig. 1) managed by the Sicily Hydrographic Services, about 15 km from the river mouth (56 m a.s.l.).

The probe installation in this site allowed to compare the hydrometric values determined by the probe with those detected by the hydrometric station, to compare electric conductivity values obtained by Roda in 1971 with those detected by the probe and to define the Drasi station water quality.

The temperature, pH, dissolved oxygen and redox potential values detected from November 2004 to April 2007 by the probe were compatible with agricultural purposes. At Drasi the conductivity was lower than that of the northern areas thanks to the contribution of tributaries with better quality waters. The seasonal variability of electrical conductivity showed some high values related to precipitation event, when salts along riverbanks and riverbed are quickly mobilized. Figure 4 shows the electric conductivity and the daily rainfall measured from July 2006 to April 2007: higher conductivity values were observed a few days after the precipitation events. It is quite difficult to understand and explain time delay between precipitation and water conductivity increase. During dry periods it's quite common to observe large white salt crusts along riverbed and when it rains those crusts melts and ions are dissolved.
in the river. The ECw that we measure in Drasi is the result of precipitation events and subsequent solubilization and mobilization processes that happen in the northern areas, but we do not know exactly where because there is no a dense network of pluviometrical station along the Imera basin.

Finally, the conductivity values measured from July 2006 to April 2007 shown that the Imera waters can rarely be used for agricultural purposes. The average conductivity was high (5.9 mS/cm) with peaks of 14 mS/cm and only for 10 days we observed E.C. values compatible with irrigation uses (<3 mS/cm).

Conclusions

Water characterization allowed to confirm the result of Roda (1971), who pointed out that the main causes of degrade of the Southern Imera river are the salt-rich waters of some tributaries flowing over gypsum rocks. The ionic concentrations measured in the four samplings allowed to recognise the tributaries characterised by high salinity (Cava, Vaccarizzo, Salsò, Morello and Vallone Salito streams) and to identify, in agreement with Favara (2000), in the Vaccarizzo stream the main cause of degrade of Southern Imera river waters. This small basin of 58 km², showed the highest sodium and chloride concentration during all the surveys, and can contribute, depending on the season, to more than 40% of total Imera ions concentration. In fact, the electric conductivity and the ionic concentrations (the ions which present highest concentrations are sodium, calcium, sulphate and chloride) increase below Salsò bridge and Imera bridge, because of the Vaccarizzo stream intake, and decrease in the area between Capodarso bridge, Besaro bridge and Drasi thanks to the intake of tributaries with low salinity in the river. All over the area salinity is widespread and strong differences in ions concentration are observed along river network. To better understand the differences we have to take into account the basin extent, its geological complexity and the development, since ancient times till last century, of salt mines devoted to dug minerals as kaynite, sylvinites, halite and sulfur for industrial uses and that caused deep geomorphological changes altering natural water flows (Liguori et al., 2008).

Then, the chemical analyses showed that only the water before Vaccarizzo stream intake can be directly used for irrigation purposes.

At Drasi, we observed seasonal variability of conductivity; in fact during Winter the electric conductivity increased, because of precipitation events and subsequent mobilization of salt deposits formed along the riverbanks during the dry period. From July 2006 to April 2007 we observed conductivity values compatible with irrigation uses only for a short period (ten days). Moreover, the values detected continuously by the multiparameter probe installed in this site could allow farmers to manage properly river water withdrawals.
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