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POLYPHENOLS POLLUTION BY OLIVE MILL WASTE WATERS, TUSCANY, ITALY

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The study area, characterized by the activity of several olive mills, is located in the region of Tuscany in central Italy. The research objective was to evaluate groundwater pollution caused by olive mill waste water spreading on soil. The chemical and hydrogeological characteristics of the aquifer system were studied. Particular attention was given to the presence of phenols in water samples because of their high content in these waste waters. A connection between the waste water spreading areas and local high concentrations of phenolic compounds in groundwater was found and olive mill waste waters were recognized as being the source of local groundwater pollution by polyphenols.

INTRODUCTION

One of the problems of water pollution is caused by industrial, agricultural and urban waste waters which cannot be sent to ordinary waste water treatment systems. These include olive mill waste waters, which are disposed of on the ground in waste spreading areas.

The aim of this work is to evaluate groundwater pollution by olive mill waste waters. Agriculturally these waste waters are very beneficial, because they help crops grow well by acting as fertilizers (Solinas et al., 1975; Ranalli, 1989; Lopez et al., 1993), but no one has considered their potential for pollution of groundwater.

Within a short time, groundwater can become polluted by these waste waters. By detailed analysis of the groundwater it is possible to determine pollution sources by identifying characteristic chemical contents (Goerlitz, 1984).

An area has been chosen where there are many oil mills and waste waters are disposed of indiscriminately. A study of the groundwater in this area was done with the objective of finding characteristic chemical components of these oil waste waters. We purposely chose this area because there is no other industry which could be a possible additional source of pollution.

Some of the oil mill waste constituents are very dangerous to the quality of good water because of their low rate of organic decomposition, particularly phenolic compounds which are very abundant in these wastes (Andrich et al., 1986). Following the traces of phenol compounds consequently became a guide for us to establish the direction of infiltration and groundwater movement.

HYDROGEOLOGICAL AND GEOLOGICAL STUDIES

Hydrogeologically the area includes the Zambra River, which flows into the Arno River. Figure 1 shows the study area as well as water table contours. The area is near the city of Pisa in Tuscany, Italy. It is located on the southwest side of the Pisano Mountains. The study area covers about 30 km².

Figure 2 shows the following:

- a) a geological map of the Zambra basin,
- b) the olive oil mills,
- c) the waste water spreading areas, and
- d) wells.

Geologically the rock outcrops are arranged in a chronological order, and they can be easily observed (Rau et al., 1969; Rau et al., 1974; Mazzanti et al., 1994) (see Figure 2). The sequence is:

- Paleozoic substratum and Triassic formations (“Verrucano” and “Quarziti del Monte Serra”); and
- Postcarnian carbonate formations.

These are often covered by detritus and, in the plain, there are no rock outcrops because of alluvial soil cover.

The study area is characterized by the low outcrops of Postcarnian Carbonate formations and as a result there is low percolation. Paleozoic substrata and Triassic formations have a low permeability and as a result there is little water circulation in the area.

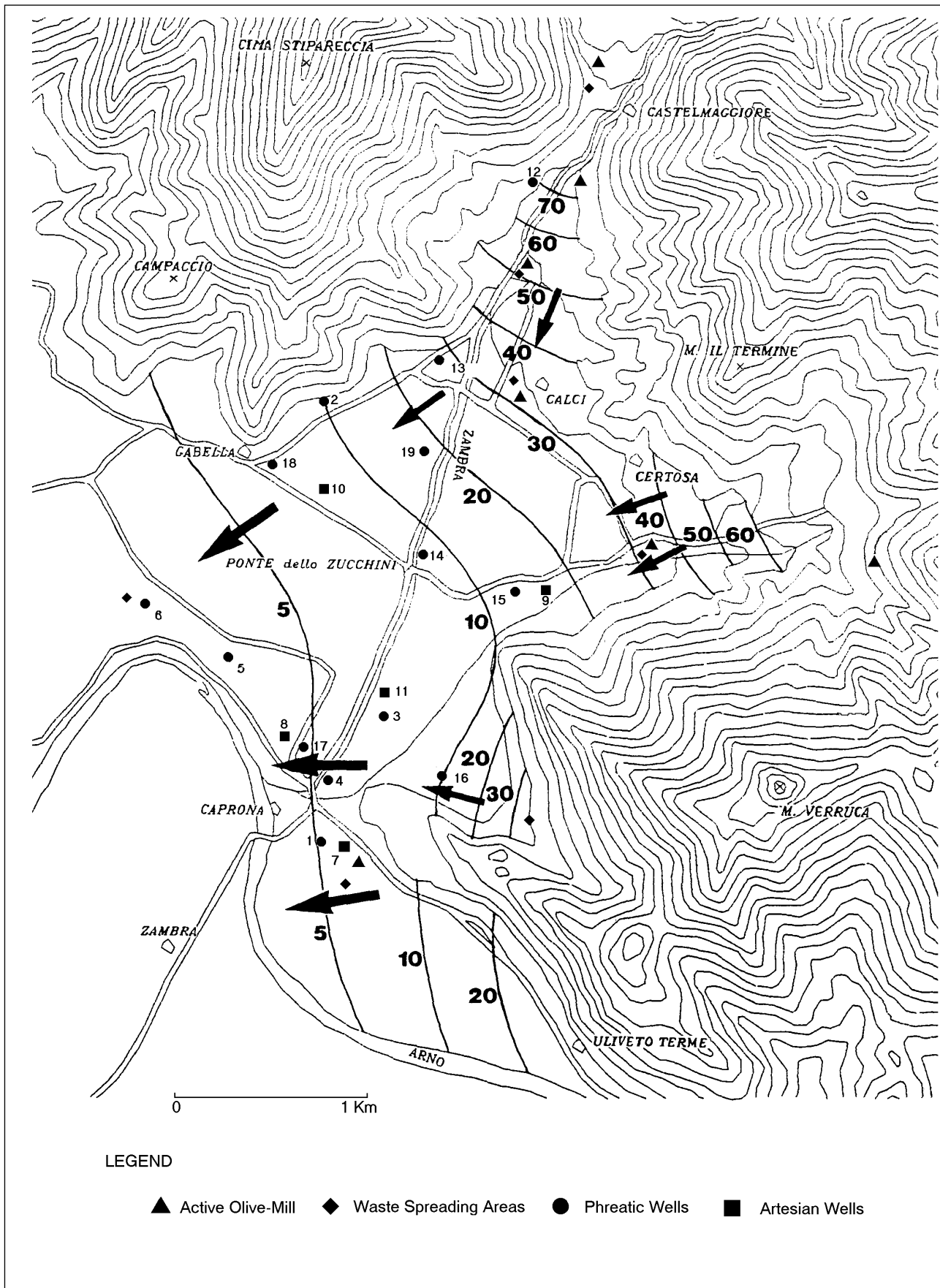


Figure 1. Map of the study area with water table contours and groundwater flow directions.

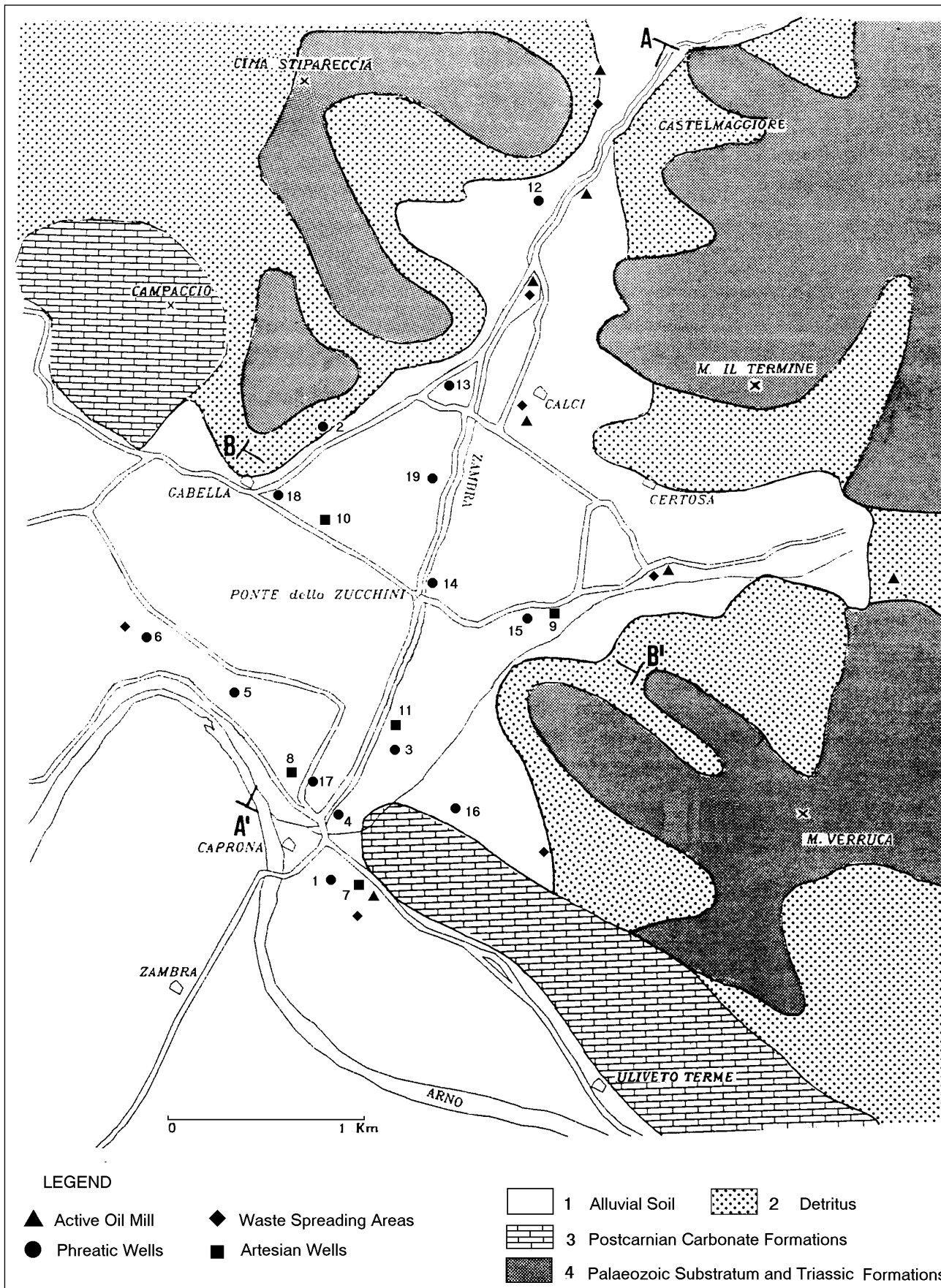


Figure 2. Geological map of the Zambra River basin.

Figure 3 shows two sections, A-A' and B-B' which illustrate the stratigraphy of the area. Alternating clays and gravels predominate. At depths of 9 and 30 meters there are gravel aquifers. There are many wells in this area; we chose 24 to sample for our study, 17 from a depth of 9 m and 7 from the 30 m depth. Most of the wells selected are from the low land.

ANALYTICAL PROCEDURE

Pollution Rate of Oil Mill Waste Waters

Every batch process of olive fruit yields 22 kg of oil, 33 kg of olive husks and 45 kg of waste water. The data available from 1985 to date show that 90,000 m³ of waste waters are produced yearly in the Region of Tuscany. The province of Pisa produces 8,000, of which 3,000 m³ are produced in the study area alone.

In Table 1 the analytical characteristics and most important constituents of oil mill waste waters are listed.

The waste water pollution rate is due to high volume of BOD₅ and COD. These parameters show that the waste has a great antimicrobial power; this feature is particularly marked by a high concentration of phenolic compounds. Typical phenols were recognized by several authors which identified the most important ones: oleuropeine, hydrossityrosole and tyrosole (Ragazzi et al., 1973; Vazquez Ronceros A. et al., 1974).

It is clear that these wastes are a significant threat to water quality. In fact, although it was verified

Table 1. Analytical Characteristics and Principal Constituents, Olive Mill Waste Waters (Andrich et al., 1986)

Suspended Substances (g/l)	5-50	Phenolic substances (g/l)	2-4
Dry residue at 105°C (g/l)	100-150	Glucidic substances (g/l)	30-60
Ashes (g/l)	20-25	Nitrate substances (g/l)	10-25
COD (mg/l)	60,000-185,000	Fatty substances (g/l)	0.5-10
BOD ₅ (mg/l)	14,000-75,000	Polyalcohols (g/l)	10-15
pH	4.8-5.4	Organic acids (g/l)	5-15
Specific weight at 20°C	1,015-1,080	Mineral substances (K ₂ O 50%; P ₂ O ₅ 15%)	20-25

that their presence in agricultural soil does not damage crops (Bonari E., 1990), a small amount of phenolic compounds in water make it not drinkable.

According to EEC regulations the maximum concentration of phenol compounds permitted in drinking waters is 0.5 µg/l, expressed as phenic acid C₆H₅OH. Generally, in waste water the concentration must be less than 5 g/l. In oil mill waste waters the high concentration is 2-4 g/l.

It is clear that a small quantity of these waste waters in contact with groundwater has the potential to cause significant pollution to drinking water sources. The problem is more serious where chlorine is used to disinfect drinking water. Chlorine in contact with phenol reacts to form chlorophenol which is even more dangerous to human health than phenol alone (Zullei N., 1981).

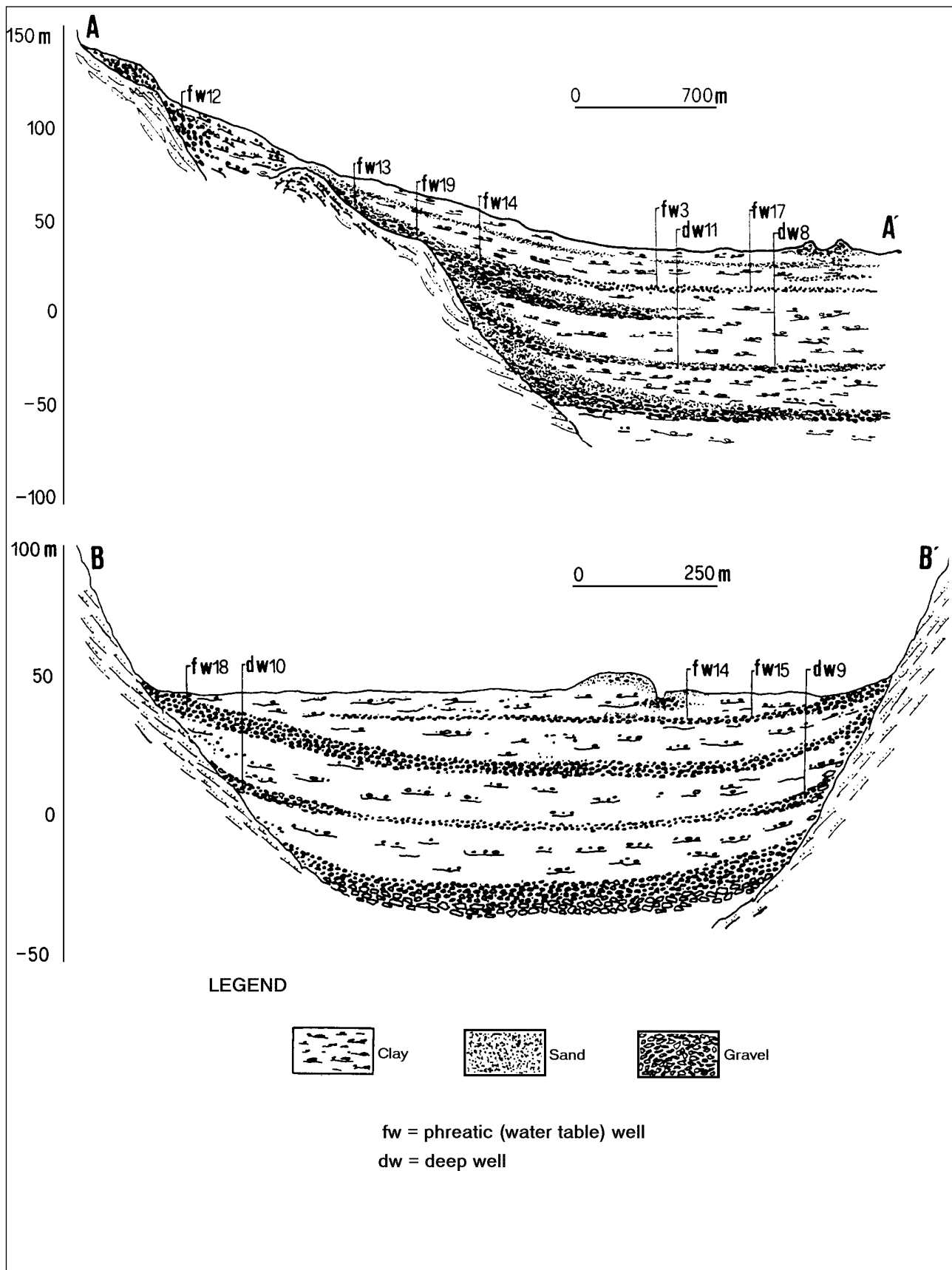


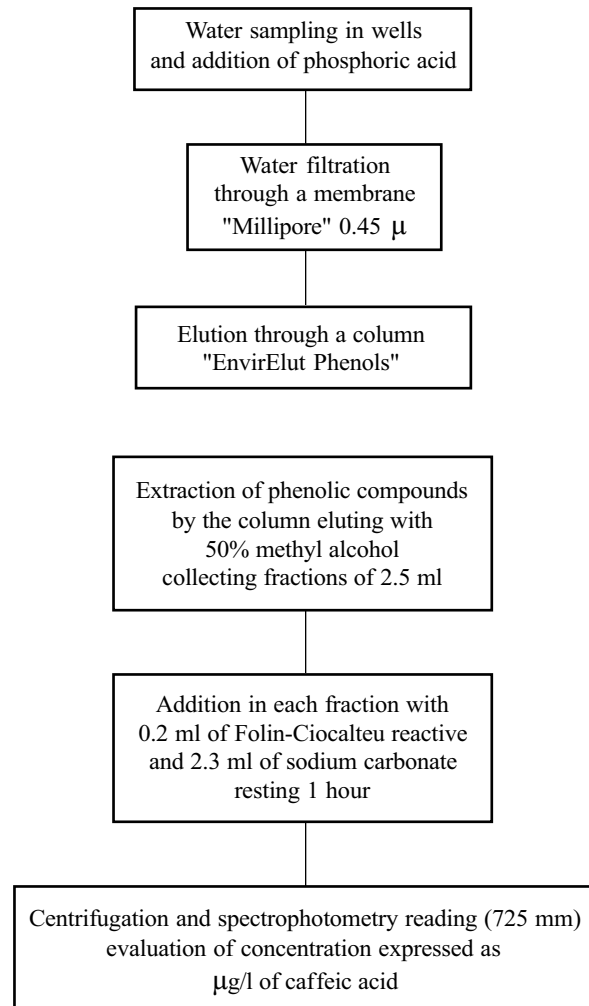
Figure 3. Stratigraphic sections.

Determination of Phenolic Compounds

To evaluate phenolic compounds present in groundwater a small volume of water samples collected in the study area were eluted through columns used in laboratory analysis which sorb phenolic compounds ("EnvirElut-Phenols"). Each column was then eluted with a solution of 50% methyl alcohol to extract sorbed phenolic compounds. In the collected fractions phenolic content was evaluated with Folin-Ciocalteu solution (0.2 ml). Lastly the absorbency at 725 nm was read using a standard obtained by treating 2.5 ml of 50% methyl alcohol in the same way as a comparison (Andreoni et al., 1994).

The quantity of total polyphenols by spectrophotometry was evaluated. Table 2 shows the procedure used to apply the test method. (Andreoni et al., 1995).

Table 2. Sampling and Analysis Procedures



RESULTS

With the described method the concentration of phenolic compounds in groundwater was evaluated dividing shallow water samples from deep ones. Sampling and analysis was conducted from Summer 1993 to Winter 1994-95. Data obtained are shown in Table 3, which lists phenolic concentrations obtained in each well during the Summer period 1993-1994, when there is no oil production, and the Winters of 1993-94 and 1994-95 during olive milling.

Table 3. Phenolic Concentration in Wells of Checked Area (see Figure 1)

Phenolic Concentration				
Well Number and Depth	Summer 93	Winter 93-94	Summer 94	Winter 94-95
1 S	23	100	19	65
2 S	n.a.	40	10	42
3 S	15	26	19	30
4 S	4	7	4	25
5 S	7	6	4	6
6 S	13	5	5	5
7 D	21	63	19	41
8 D	10	13	9	18
9 D	5	2	4	traces
10 D	n.a.	2	traces	3
11 D	3	3	3	traces
12 S	2	3	2	3
13 S	3	3	2	5
14 S	n.a.	2	3	3
15 S	n.a.	23	9	46
16 S	n.a.	18	3	23
17 S	n.a.	12	5	18
18 S	n.a.	5	4	20
19 S	n.a.	5	5	18

traces = phenolic concentration less than 0.5 µg/l
n.a. = not available
S = shallow; D = deep

In this table is clear that phenolic concentration is higher in winter than in summer as a consequence of waste water spreading on soil during olive milling.

Using these data, two maps (Figures 4 and 5) of the study area are drawn to show phenol distribution in the local aquifer system, in the water table aquifer (9 m) (Figure 4) and in the first artesian aquifer (30 m) (Figure 5). It is evident, in both maps, the correlation between some of the maximum concentration points and spreading areas.

The other possible sources of phenolic pollution, besides waste spreading, could be pesticides used in agriculture and urban waste waters. These pollution sources are generally indicated by a high concentration of nitrates (NO₃⁻) in groundwater. In 1991 a periodic pollution of nitrates, probably due to drain leaks, was located in the zone (Baiocchi et al., 1991). To identify urban pollution as a possible source of phenolic compounds, nitrate concentration and its distribution in local groundwater was evaluated.

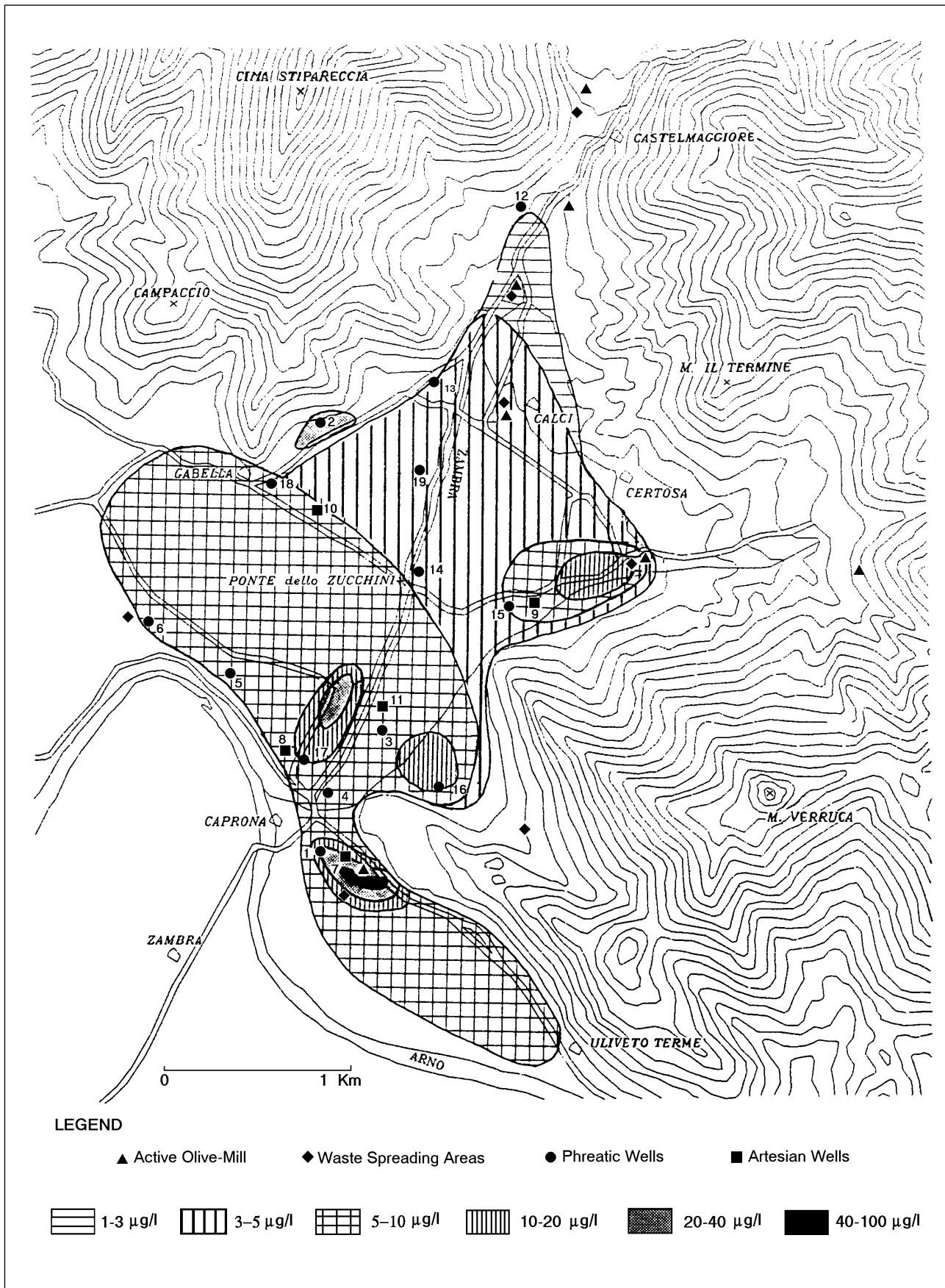


Figure 4. Phenol concentration distribution in the water table aquifer at 9 m.

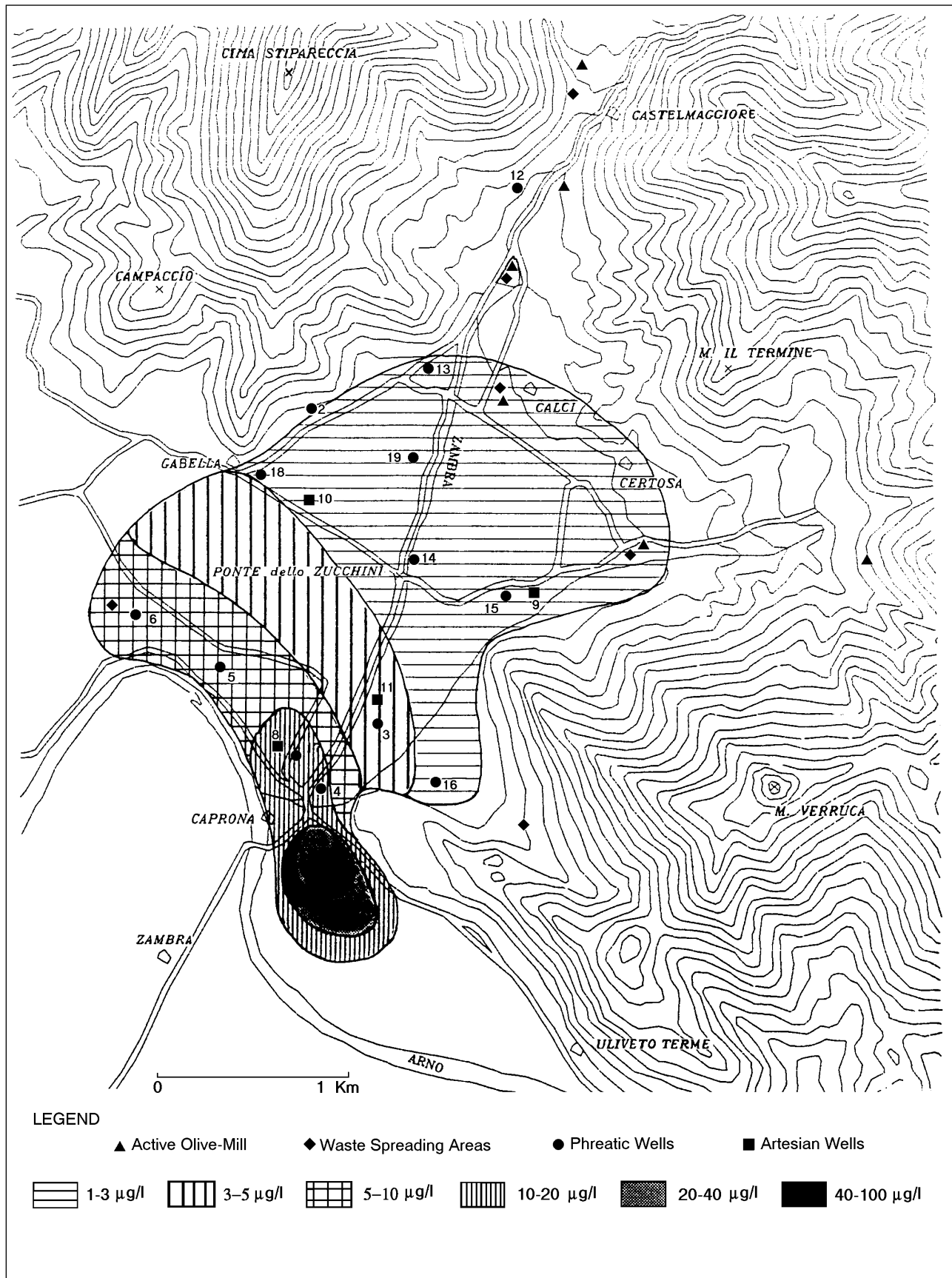


Figure 5. Phenol distribution in the first artesian aquifer at 30 m.

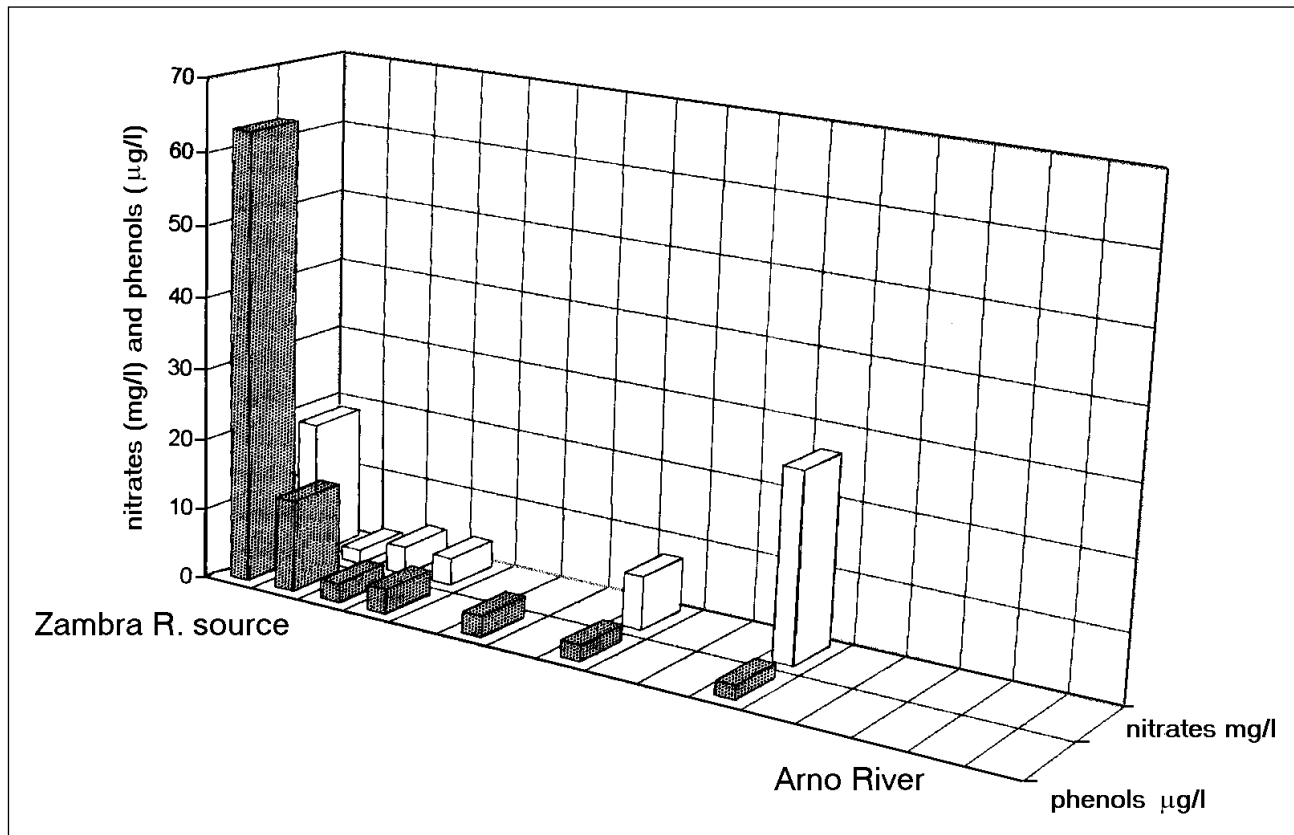


Figure 6. Phenol and nitrate concentration in the Zambra River, winter 1993/94.

A graph of the values of phenol and nitrate concentration, referring to winter 1993-94, was developed (Figure 6). This figure shows the concentration trend of these two pollutants in wells placed along the section A-A' that follows the course of Zambra River from its source to where it flows into the Arno River.

Phenol concentration decreases progressively from mountains to valley unlike the nitrate concentration, which has a u-shaped trend. It is possible to deduce that there is no correlation between the two pollutant trends and it is concluded that there is no influence of urban waste waters or pesticides on the concentration of phenolic compounds in the local groundwater.

CONCLUSIONS

The present research is a water control pattern applied to a real situation in which each factor that interferes and exerts an influence on the system was considered. In this work several assumptions were made to limit the scope of the research. These were:

1. Phenolic compounds in oil mill waste waters do not alter their characteristics when they infiltrate and are diluted in groundwaters.
2. These compounds accumulate in soil, saturating it with time, and can be mobilized and transported by infiltrating rain water.
3. Phenolic compounds found in each water sample are from oil mill wastes that are spread on soil.

The first assumption is based on the fact that in an anaerobic environment phenols are removed by oxidation (Servili et al., 1989). The second assumption is true because phenolic compounds fix heavy metals and consequently bind themselves to soil (Marsilio et al., 1991; Madrid et al., 1993).

The third assumption is based on the fact the rain waters mobilize and transport natural phenols from the decomposition of leaves. The same mechanism can carry phenolic compounds from oil mill wastes.

As previously described, direct research in the study area, confirms the following (see Figures 4 and 5):

- olive oil mills spread the most of their wastes directly on the soil;
- groundwaters have locally high concentrations of phenolic compounds; and
- there is a correlation between places of olive oil mill waste spreading and wells with high phenolic concentration.

These facts tend to confirm the assertion that oil mill wastes are responsible for pollution by phenolic compounds in this zone.

These results enable us to conclude that local groundwaters are not protected against the yearly infiltration of pollutants present in the area by continuous impermeable clay beds or other impermeable strata. Poor well construction practices, stratigraphic discontinuities, sand and gravel that alternates with the clays, and spreading of wastes on permeable gravelly areas results in the degradation of groundwater quality by olive mill waste waters.

More detailed analytical methods could, without doubt, help to evaluate the mill wastes responsible for the high concentration of phenols in groundwater through the separation and recognition of different classes of compounds by HPCL analysis.

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