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La conoscenza geochimica del territorio si è resa indispensabile dal momento che la contaminazione degli ecosistemi terrestri con sostanze ed elementi chimici tossici è divenuto un problema a livello globale. L'assunzione attraverso il cibo, l'acqua e le vie respiratorie degli inquinanti ha un impatto sulla salute che può manifestarsi anche sul lungo termine e in modi diversi. L'incidenza e la distribuzione geografica delle malattie (epidemiologia) dovute ad inquinamento ambientale è ben documentata. Queste malattie comprendono, perdita di acutezza mentale e di controllo motorio, disfunzione di organi critici, cancro, malattie croniche, inabilità e, alla fine, anche morte. La conoscenza geochimica del territorio fornisce elementi indispensabili per valutare scientificamente come "gestire" le concentrazioni anomale di sostanze ed elementi chimici tossici, sia alla sorgente che in-situ, in modo da eliminare o comunque minimizzare il loro impatto negativo sulla salute degli esseri viventi; individuare le sorgenti dell'inquinamento e sviluppare modelli per il controllo fisico, chimico e biologico relativamente alla loro mobilitazione, interazione, deposizione e accumulo negli ecosistemi terrestri. Su queste basi geologi, geochimici, chimici, biologi, ingegneri ambientalisti collaborano per sviluppare metodi e tecnologie finalizzate a preservare gli ecosistemi globali.

La collana "Conoscenza geochimica del territorio" vuole offrire ad un pubblico attento, anche se non necessariamente specialistico, gli strumenti necessari per comprendere e trattare in modo innovativo problemi di grande attualità come quelli della contaminazione ambientale e della salvaguardia del territorio e dei suoi ecosistemi naturali.

Domenico Cicchella, Daniela Zuzolo, Stefano Albanese
Enrico Dinelli, Annamaria Lima, Paolo Valera, Benedetto De Vivo

Geochemical atlas of agricultural and grazing land soil of Italy





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Introduction

The Geochemical Mapping of Italian Agricultural Soils is stemming from GEMAS (Geochemical Mapping of Agricultural Soils) (*Reimann et al., 2014*), a cooperation project between the Geochemistry Expert Group of EuroGeoSurveys (EGS) and Eurometaux. The European GEMAS project was started to produce soil geochemistry data at the continental scale consistent with REACH Registration, Evaluation and Authorisation of Chemicals — *EC, 2006*).

This work was carried out to show the results of the Italian contribution to the EuroGeoSurveys GEMAS project. The aim of the work is to define background/baseline chemical element values on a national scale, which will help State decision makers to define trigger and action limits at a local scale, bearing in mind the complex spatial variability of Italian geology (*Cicchella et al., 2015*).

In Italy, where still does not exist a national geochemical mapping at national scale, the problem of agricultural soil contamination is of utmost importance due to the fact that agriculture export is economically relevant for the Country. Mapping element distribution allows direct appraisal of the variability of potentially toxic elements (PTEs) in an area and enables rapid identification of areas that may contain excessive concentrations of PTEs. This is an essential information for site and subsequent risk assessment (*Albanese and Cicchella, 2012; Albanese et al., 2010*).

Also because of the rumors related to the national and international bad reputation of Campania agricultural products due to the illegal urban waste disposal, in the last 3 years, under the pressure of the public opinion and to the work produced by the research Group led by Prof. B. De Vivo, has been launched a regional program (Campania Transparent Project), funded by the regional Government, aimed at monitoring, with high density sampling, soils, underground waters, vegetation, air and biological matrices. This project has been managed by the Istituto Zooprofilattico Sperimentale del Mezzogiorno (IZSM) of Portici (Napoli) and will be concluded within 2018, making the Campania Region as the most, environmentally, monitored Region of Italy. Some preliminary results are reported in the Geochemical Atlas of Campania Region Soils and the SIN Litorale Domizio-Flegreo and Agro Aversano (*De Vivo et al., 2016; Lima et al., 2017*).

The hope now, when the final results obtained for all the matrices in Campania Region will be published, is that such example is followed by other Italian Regions, to put Italy at the same level of other European Countries, in terms of territory geochemical monitoring and knowledge.

Several works, conducted in Italy, at local scale, have shown that anomalous concentrations of some elements (e.g., Be, Sn, As, Tl, V), exceeding the legislative limits, are completely geogenic (natural) (*Armiento et al., 2013*;

Cicchella et al., 2005, 2008, 2014; Frattini et al., 2006; Guagliardi et al., 2013; De Vivo et al., 2016; Lima et al., 2017). The lack of knowledge of the results reported in the latter scientific publications by the Authorities is causing, especially in South Italy, an overestimation, with no scientific ground, of the territory contamination.

Some studies, carried out mostly in the Naples metropolitan area, have shown a correlation between contamination and adverse health effects on the residential population (*Filippelli et al., 2012; Giaccio et al., 2012; Senior and Mazza, 2004*). But such localized outcomes do not justify the clamors on the media about the fact that most of Campania territory is contaminated. Such unjustified clamor was basically destroying the agricultural economy of the Campania region. The preliminary results (*De Vivo et al., 2016; Lima et al., 2017*) indicate in fact that mostly the “contamination problem” is concentrated in the metropolitan areas, and not on the entire agricultural territory. This evidence is, on the other hands, not too much different than other reality of metropolitan areas in Europe.

To give a scientific answer to the “solution” of the problem, it is basically needed a better knowledge of the state of the art of the territory and the environment, which can be achieved through systematic monitoring of different matrices (soils, sediments, waters, air). This is the most logic and not expensive solution, because to launch indiscriminated remediation projects has a cost definitely much higher than monitoring programmes.

People require, mostly based on emotional reasons with no scientific ground, an immediate clean-up of supposed contaminated lands. This makes very happy dirty businessmen which have clearly understood that the environmental remediation issue is the largest business to be taken care, using naturally the people emotions, most of the time in good faith, transferred to the politics. This involves huge amount of money to be devoted by the Government to remediation projects, which often are carried out with no proper quality controls.

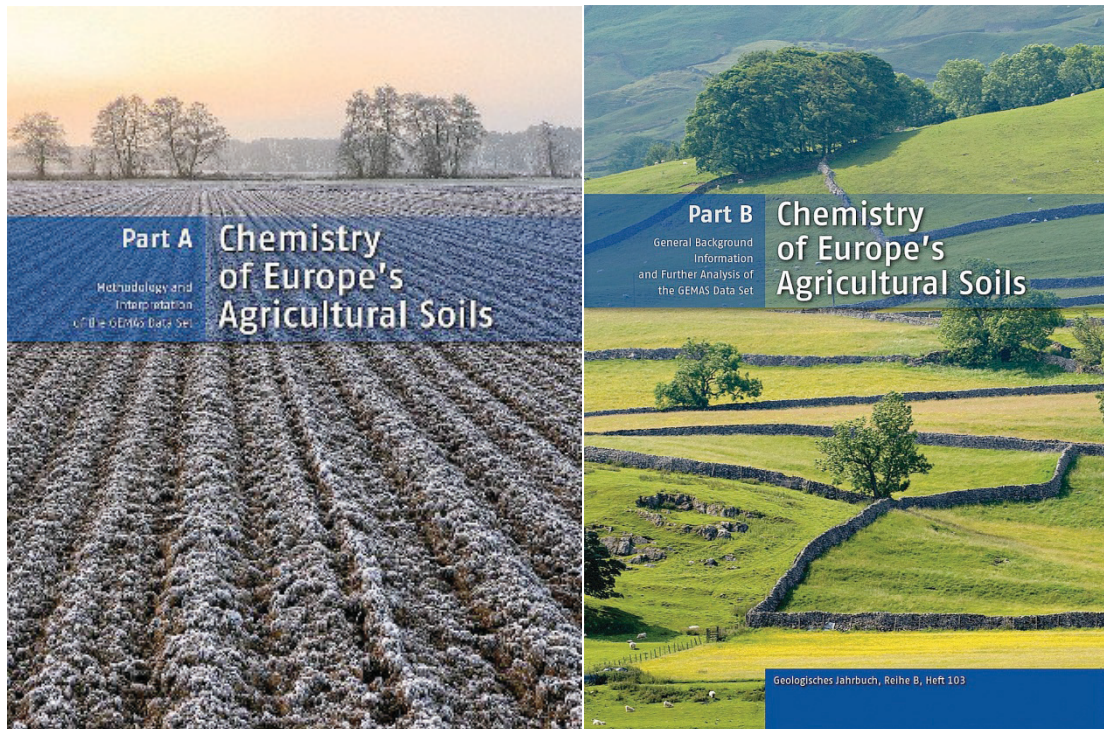
The present work – which in no way has to be considered a monitoring of the overall national territory - has a main objective to determine on a national scale the baseline values of the chemical elements in agricultural and grazing land soil, and to make them available to State Authorities and national environmental protection Agencies. In this paper, agricultural and grazing land soil data, stemming from the European GEMAS Project, resulting from XRF analysis and from a combination of ICP-AES and ICP-MS analysis after Aqua Regia (AR) and Mobile Metal Ions (MMI) extraction, are presented and discussed.

Specifically, for each element and sampling medium, maps reporting interpolated data and graduated dots has been produced; univariate statistics and graphs have been associated with each map. The Atlas also contains: maps for regional variability of factor scores of elemental associations resulting from R-mode factor analysis, and 15 baseline and land use maps for some selected elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V, Zn) following the Italian intervention criteria. The Atlas shows data of Italian agricultural and grazing land topsoil extracted from the GEMAS database, and it complements the

publication of the Geochemical Environmental Atlas of Italy (*De Vivo et al., 2008, 2009*) that reports data from samples of Italian topsoil, subsoil, stream water, stream sediment and floodplain sediment extracted from the former European companion FOREGS database (*De Vos, Tarvainen et al., 2006; Salminen et al., 2005*).



De Vivo, B., Bove, M.A., Lima, A., Albanese, S., Cicchella, D., Grezzi, G., Frizzo, P., Sabatini, G., Raccagni, L., Di Lella, A., Protano, A., Riccobono, F., 2009. Atlante geochimico-ambientale d'Italia - Geochemical environmental atlas of Italy. ARACNE Editrice S.r.l., Roma, pp. 516. ISBN 978-88-548-2282-5.



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Chapter I

Italy: Climate, Vegetation, Soils, Geology, Human Activities

This chapter, with the exception of a few paragraphs, is almost entirely derived from the previous geochemical atlas of Italy (De Vivo et al., 2009).

1.1 Introduction

The territory of the Italian Republic covers 301,278 sq km. It lies between the northern latitudes of 47°05'29" and 35°39'26", and the eastern longitudes from Greenwich of 6°37'32" and 18°31'13".

1.2 Climate and vegetation

1.2.1 Climatic zone

Despite its geographical position at the centre of the temperate zone, Italy has variable climatic characteristics. This is due to the presence of both the Mediterranean Sea, whose warm waters mitigate thermal extremes, and the Alpine arc, which forms a barrier against the cold north winds. Italy is also subject to both wet and moderate atmospheric currents from the Atlantic Ocean and dry and cold ones from eastern Europe.

The Apennine chain too, comparing the wet winds from the Tyrrhenian sea, causes considerable climatic differences between the opposite sides of the peninsula. The differences in temperature between the winter and summer months are more marked in the northern regions than in the south and along the coasts.

The mean temperatures for the month of January in the Po Plain fluctuate around zero, while in the Alpine valleys the thermometer can drop to - 20°C and snow can remain on the ground for many weeks.

In the southern regions, the mean temperatures for January are around 10° C, with the exception of the inland mountainous zones. Mean summer temperatures throughout the whole of Italy rise to 24°-25° C for July, although they are lower in the high elevation zones. Rainfall distribution also varies considerably, due to the influence of both mountains and prevailing winds. The highest values are registered in the Alpine arc (over 3,000 mm per year in the Lepontine and Julian Alps) and on the Apennines (over 3,000 mm per year in the Apuan Alps).

The plains, however, including that of the Po, receive scarce precipitation. Generally it is less than 800-900 mm per year but in the southern regions of the peninsula (Apulia and southern Sicily) it falls below 600 mm per year. The great internal Alpine valleys and the coastal plains of the Tyrrhenian (Maremma) and Sardinia also receive little rain.

Altogether, six large climatic regions can be distinguished, mainly characterized by mountain influence (Fig. 1.1).



Figure 1.1. Climate zone map.

1) The Alpine region is strongly influenced by altitude, with long cold winters and short cool summers with an elevated day-time temperature range; precipitation is more intense in the spring and autumn months, especially in the pre-Alpine belt.

2) The Po plain region, with continental conditions, consisting of cold and sometimes snowy winters and warm and sultry summers. Precipitation is greatest in the spring and autumn months when the climate becomes milder. However, around the pre-Alpine lakes fog is frequent in the winter, due to the wetness of the land.

3) The Adriatic region. Because of the inability of the Adriatic's shallow waters to trap summer heat, the climate has a continental character, that is, winters dominated by cold north-east winds (bora).

4) The Apennine region, also with continental tendencies and cold snowy winters; precipitation is more intense on the Tyrrhenian slopes and is abundant in all seasons apart from the summer.

5) The Ligurian-Tyrrhenian region, with a maritime climate and heavy and frequent precipitation, lower in the summer and distributed irregularly; the winters are cool and the annual temperature range narrow.

6) The Mediterranean region, also with a limited annual temperature range; precipitation is frequent, especially in winter, and the summers are hot and dry. The interior and the mountain zones of the islands and Calabria also have an Apennine type climate due to the altitude.

1.2.2 Vegetation zone

Due to the thousands of years of intense exploitation by human beings the original vegetation cover has been greatly altered, as have been the high mountain zones of the Alps and Apennines, which were subject to systematic deforestation until the end of the last century. Despite attempts to protect the mountains, which began at the beginning of this century, many of Italy's mountain regions still remain without tree cover and are therefore susceptible to hydrogeological disaster, especially in the zones with particularly unstable rock types. At the present time little more than a fifth (21.2%) of Italy is covered by trees, which altogether occupy an area of about 64,000 sq km. In the strictly floral category, the Italian territory includes unites Mediterranean and central European species. When these are combined with morphological and altimetical influences there is a varied floral landscape, that is due to climatic conditions rather than soil types.

Thus it is possible to identify at least four principal floral regions:

1) the Alpine region, divided into bands according to height, with oaks and other broadleaved trees prevailing in the lower areas and valley bottoms, followed up to about 1,000 m by chestnuts and then beeches followed still higher up, but not beyond 2,000 m., by a mixture of needle-leaved trees (firs, larches and Scotch pines); the summit areas are dominated by meadows and pastures with shrub vegetation (rhododendrons and dwarf pines) or, on the margins of permanent snow (circa 2,400-2,800 m.), by Alpine tundra with mosses and lichens. Olives and cypresses grow around the around the southern shores of the major Alpine lakes, and on the hills at the edges of the Adige plain.

2) The Apennine region, similar in character and sequence to the Alpine but with the presence of temperate species in the valley bottoms and a lesser spread of conifers in the upper levels.

3) A Po region, dominated by broad-leaved trees (willows, alders, poplars and oaks), which still form small woods but only along the river banks, while on the upper plain there survive extensive stretches of the original heath with American acacias, heathers and brooms and, along the Adriatic coast, some forests of maritime pine.

4) The Mediterranean region, covering the Ligurian and Tyrrhenian coasts as well as those of the central and southern Adriatic and the islands, dominated by a mixture of maritime pine and evergreen undergrowth (with olives, cypresses, corks, etc.) derived from the spoliation of the original ilex groves.

1.3 Soils of Italy

This paragraph is derived from (*Costantini et al., 2013*).

The unconsolidated mineral or organic matter on the surface of the Earth that has been subjected to and shows effects of genetic and environmental factors of: climate, macro and microorganisms, conditioned by relief, acting on parent

material over a period of time. A product-soil differs from the material from which it is derived in many physical, chemical, biological, and morphological properties and characteristics.

One of the main factors influencing the soil formation in Italy is the climate. Italy is located in the middle of temperate zone, the elongated shape of the Italian peninsula stretching along 11 parallels and two main morphological barriers (e.g. the Alps and the Apennines) result in great local climatic variations. Actually, in Italy there are 14 of the 35 climatic regions occurring in Europe.

Different rock types and various landform types from alluvial and coastal plains via hilly regions to large mountain chains all contributed to the abundance of different soil types.

Soil regions on hills are the most lithologically and climatically variable environments, and host the greatest soil variability and endemisms. Alluvial soils form in the Po plain and in main river valleys, in strict correlation to corresponding landforms: Luvisols on terraces and high plains, Cambisols and Fluvisols in the low plains, with Gleysols in depressed areas (*Bini 2013*).

Three main domains may be recognized in the peninsular Italy: Northern Apennine with large sandstone outcrops, Central Apennine dominated by calcareous formations, and Southern Apennine with prevailing clayey flysch formations. Widespread water and mass erosion rejuvenate soils of these landscapes. Luvisols (Terra rossa) from limestone and Umbrisols or Cambisols from granite rocks are the typical soils of Apulia and Calabria, respectively (*Bini 2013*). Peculiar soilscapes are related to particular lithotypes such as ophiolite and volcanic rocks, which outcrop disseminated in various parts of the peninsula, the former with general steep slopes and thin soils and the latter with andic properties (*Bini 2013*). Besides actual Andosols, volcanic materials spread off over the land may contribute to form soils with some andic properties, not sufficient to meet criteria for Andosols, but able to affect significantly soil chemistry and hydrology and, in turn, soil fertility and landslide risk (*Bini 2013*).

A vast majority of the WRB (World Reference Base) reference soil groups (25 out of 32), as well as soil orders of Soil Taxonomy (10 out of 12) are represented in the main Italian soil typological units (STUs). In particular, more than a fourth of STUs belong to Cambisols, more than a half to only four reference soil groups (Cambisols, Luvisols, Regosols, Phaeozems), and 88 % to nine Reference Soil Group (RSG) (the former plus Calcisols, Vertisols, Fluvisols, Leptosols, and Andosols), while the remaining 16 RSGs are represented in 12 % of STUs. Ferralsols (Oxisols for Soil Taxonomy) and Durisols are the only main kind of soils that have not yet been found in Italy. Thus, in Italy there is about three-quarters of the global pedodiversity. Although the most common qualifiers (that is Calcaric, Haplic, Skeletic, Eutric) are all related to the nature of parent material and to incipient pedogenesis, a second group (namely Chromic, Calcic, Stagnic, and

Luvic) indicates the main soil forming mechanisms that typify current Italian pedogenesis.

1.4 Geological framework

1.4.1 Geology

The complexity of its geological history combined with the wide variety of its substratum rock types, often dislocated by numerous fault-lines, folding and thrusting of the rocky Units by orogenic forces, have contributed to Italy's extremely diverse morphology. Less than a quarter (23%) of its total territory is formed by plains, while mountainous areas occupy over a third of its surface (35%) and, over two-fifths (42%) consists of hill zones. Italy's maximum height above sea level corresponds with the summit of Mont Bianco, 4,810 m., on the border with France. In the far eastern section of the Po valley there are some zones which are slightly below the sea level and which are often subject to subsidence phenomena. However, physically, the Italian territory, generally speaking, can be considered to consist of the following regional units, characterized by a certain morphological and at times climatic similarity: the Alpine system and Po-Venetian Plain in the continental section; the Apennine system and anti-Apennine reliefs in the peninsula section; and the large islands of Sicily and Sardinia.

Italy is a country whose variegated characteristics are strictly controlled by its peculiar geology (*Doglioni and Flores, 1997*), whose main lineaments reflect the constraints of the Alpidic structural setting (Fig. 1.2).

From a geographical and geological point of view it is useful to distinguish between former European basement (Sardinia), Alps (Northern and Southern), Apennines, bigger (Po plain, Tavoliere delle Puglie) and smaller plains, the variegated volcanic districts, including also many islands groups. The Italian crust is continental, apart from the Tyrrhenian abyssal plain and the Ionian Sea. Its maximum thickness occurs in the Alpine chain (about 50÷60 km), and its minimum along the Tuscan and Latium coastal belt. The pre-Alpine Basement is well exposed in the Alps, in the island of Sardinia, and locally in Calabria and Sicily.

It consists of variously metamorphosed sedimentary successions, associated to minor Caledonian and far more widespread Variscan magmatites.

Post-Variscan stratigraphy in Italy from the Permian to Cretaceous, exhibit the typical characteristics of a passive margin, reflecting the geodynamic evolution of the Central Mediterranean. Sedimentary sequences both in the Alps and the Apennines record the rifting and drifting history of the Tethys margins.

Italy was part of the passive margin of the western and northern Adriatic plate during the opening of the western Tethys. The inversion and relative motion between Europe and Adriatic plates began during Cretaceous and generated

compression at the western margin or dextral transpression at the northern margin of the Adriatic plate.

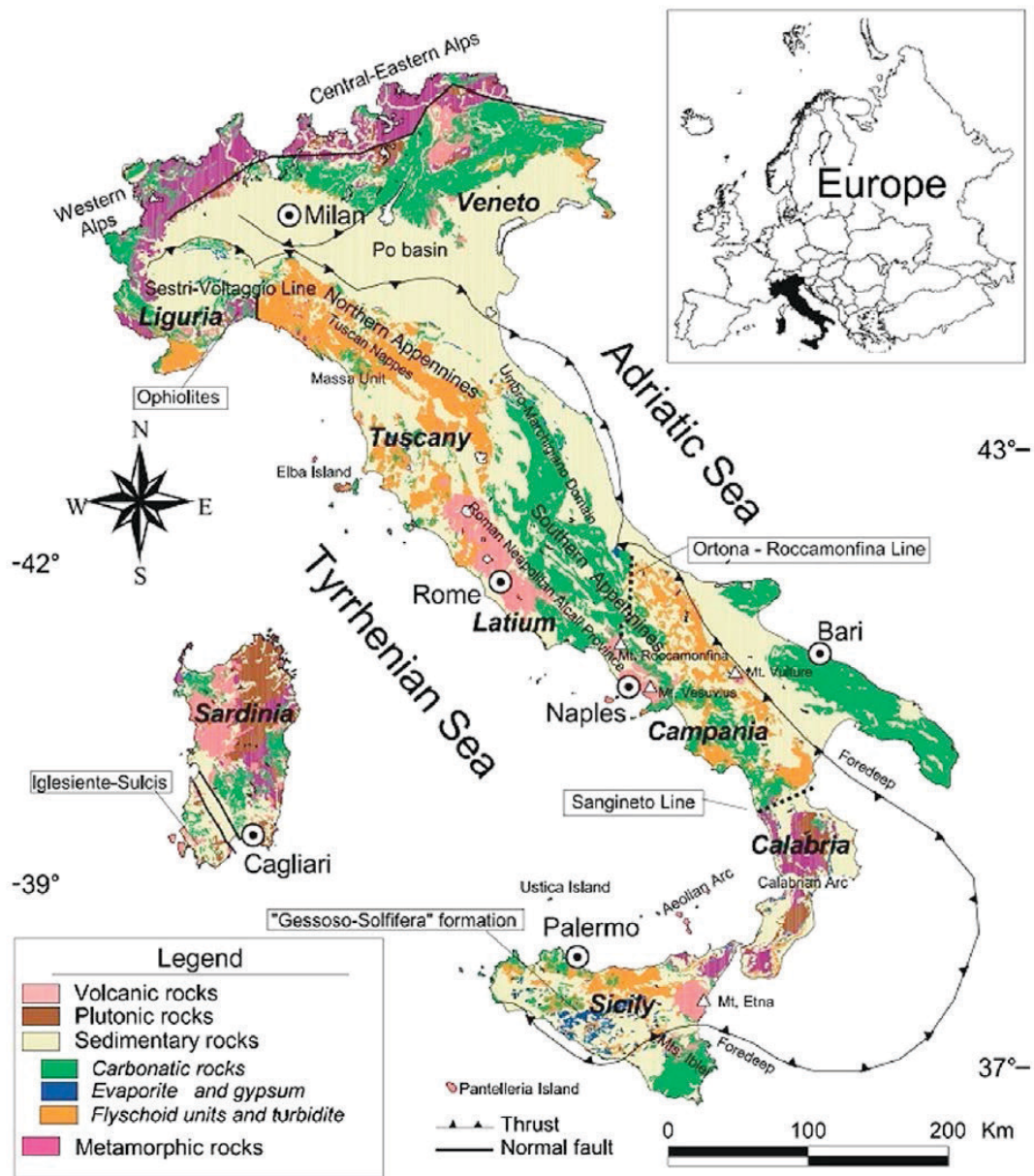


Figure 1.2. Geological sketch map of Italy. Modified after *Doglioni and Flores (1997)*.

The spatial and temporal evolution of the Alps and later of Apennines during the Tertiary is recorded by clastic sediments, flysch and molasses which overlain the earlier passive margin sequences.

From Triassic to Recent, several magmatic episodes with different geodynamic significance occurred in Italy. The most significant are: the middle Triassic calc-alkaline and the Eocene-Oligocene riolitic-trachitic and basaltic, both effusive and subvolcanic magmatisms of the Central-Eastern Southern Alps; the Tertiary calc-alkalic magmatism, which marked the Oligo-Miocene rifts in Sar-

dinia; the Plio-Quaternary volcanism with variable character, occurring, in Sardinia, in several districts of Central and Southern Italy and in the Aeolian islands.

1.4.2 Lithological description of Italy.

The evolution of the geology of Italy spans from the early Paleozoic orogens throughout the Mesozoic opening of the Tethys oceans to the later closure of these oceanic embayments during the Alpine and Apenninic subductions. All these phenomena are reflected in the lithological characteristics of the different Italian regions.

We will present here a short summary of these variable characteristics.

The alpine regions, from Piedmont, Lombardy, Trentino-Alto Adige, Veneto to Friuli, where the soil samples have been collected, are characterized by a combination of lithologies comprising the metamorphic-magmatic rocks of the basaments of the different Alpine thrust sheets, the extensive Permo-Triassic to Oligocene-Miocene sedimentary covers and the widespread sediments of the foreland plains (Po-Adige-Piave river plain). In Piedmont region the most northerly lithologies are the pre-Triassic crystalline rocks, and in part Mesozoic ophiolitic-sedimentary series, comprised in the Penninic tectonic Units, separated by the Canavese and Centovalli Lineaments (westernmost part of the Insubric Line) from the southern Late- to post-Variscan magmatites and associated calcareous-dolomitic and terrigenous Anisian to Eocene sediments. More to the south there are late orogenic molasses and the alluvial deposits of the Po plain.

In the Liguria region the ophiolite deposits, associated to deep sea sediments, both of Jurassic age are common. In the easternmost regions, from Lombardy to Friuli, the sub-latitudinal Tonale-Giudicarie-Pusteria-Gail Lineament (easternmost part of the Insubric Line) separates, to the North, the rocky crystalline Units of the Austroalpine Complex, from the sequences of the Southalpine Complex.

The Austroalpine Units consist of various Paleozoic sedimentary and volcano sedimentary poly-metamorphosed series, locally with autochthonous strips of Mesozoic sedimentary cover, that exhibits only the effects of the Alpine tectono-metamorphic cycle. In the northernmost Lombardy and Trentino Alto Adige areas some strips of the Penninic Units outcrop in tectonic windows across the Austroalpine belt.

The Southalpine Complex includes:

- 1) a Variscan crystalline basement, mostly outcropping along the Insubric Line, made up of prevailing paragneisses in Lombardy and of phillites in Trentino-Alto Adige and Veneto, in both cases with intercalated minor quartzites, porphyroid-gneiss and metabasites;

- 2) a wide sedimentary Permo-Miocene unmetamorphosed sedimentary cover, several thousand meters thick, consisting of both shallow water carbonates and basinal deposit, with major calcareous-dolomitic sequences in the Dolomites. Late- to post-Variscan granitic-granodioritic bodies are intruded along the Insubric Line, as well as in the Southalpine crystalline basement (mainly in the

Trentino-Alto Adige region) as plutonic and epi-plutonic masses; very large effusive, often ignimbritic deposits evolving from andesite-dacite to riolite (Piattaforma Porfirica Atesina) are products of the same magmatic event. Across the southern sedimentary covers are also widely present sub-volcanic and effusive calc-alkaline to shoshonitic products of the Ladinian-Carnian magmatism. At the edge or in the near Po-Adige plain, outcrop abundant alkali-basaltic rocks (Lessini-Berici Mountains) and sub-volcanic trachi-andesitic to riolitic bodies (Euganei Hills) of the Eocene-Oligocene age. In Tuscan region, there are quite distinct complexes, which include both the Liguridi Units, consisting of flyschoid successions, often associated to ophiolites, and the successions of terrains of the Tuscany thrust sheets.

These consist of a carbonate platform as well as of pelagic sediments, with their related flysch deposits. The deeper tectonic units are the crystalline (parautochthonous) deposits of the Apuane metamorphic carbonates.

The same tectonic situation, but with strongly variable lithological types, is found in southern Tuscany and parts of the Umbria-Marche-Lazio-Abruzzo regions. Here the pelagic successions of the Umbria-Marche domain are quite important and they are accompanied by their late-orogenic flysch deposits, grading toward Abruzzi to carbonate platform deposits. Along the Tyrrhenian coastal belt, there occur the thick volcanic deposits of the Southern Tuscan-Roman province with high-K magmas, whose volcanoes were emplaced along grabens with an Apenninic trend.

In Sardinia outcrop most of the Paleozoic lithotypes recorded in Italy. In the north, high grade metamorphic rocks of Variscan age prevail (amphibolites and migmatites), associated to syn- to post-kynematic granites. Tertiary volcanites of calc-alkalic character occur both in the north and in the south of the island, often in association with Tertiary continental sediments. In the southern part of the island, the metamorphic character of the Paleozoic Thrust Complexes is lower. In the South-West of the island, the Cambrian and Ordovician platform carbonates of the External Zones, hosted important base metal ores resources.

The central-southern Sardinia, also share many common lithological characteristics. They comprise the Southern Lazio-Campania and the uppermost Apulia district. Common lithologies are the widespread Mesozoic platform carbonates (limestone>dolomite) and their associated silicoclastic flysch deposits. Upper Tertiary post-orogenic pelitic successions and marine to continental Pleistocene deposits are also present, mostly in easternmost Campania and Abruzzi regions. In the southernmost Campania the pelagic deposits of the Lagonegro Units, mostly Mesozoic in age, start to occur.

They consist of pelagic carbonates with chert nodules, evolving to radiolarite sequences. Volcanic rocks with potassic character occur mostly in the Campania region, forming the Roccamonfina, Vesuvius and Phlegrean Fields complexes. Another volcanic center is the Vulture complex, between Apulia and Lucania.

In Apulia region carbonate sequences of foreland environment prevail. In Campania-Lucania and northern Calabria the most characteristic deposits are