

## INVESTIGATION ON POLLUTION LEVEL IN SURFACE SEDIMENTS OF COASTAL AREA, THE CASE OF NAPLES AND SALERNO GULFS, AND *IN SITU* LABORATORY RAMAN RESEARCHES

MENGHAN WANG

Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università "Federico II", Via Mezzocannone 8, 80125 Napoli

### ENVIRONMENTAL GEOCHEMISTRY STUDY OF CAMPANIA REGION, ITALY: IN THE SEA

Naples and Salerno Gulfs are located along the Eastern Tyrrhenian Sea, separated by Sorrento peninsula. Naples Gulf is semi-closed by Ischia and Procida islands at NW, Campi Flegrei and Campanian plain at NE, and Sorrento peninsula at SE, whereas Salerno Gulf locates on the coastal area offshore of Sele plain. Naples has the second population density in Italy, in metropolitan area, around 4.4 million citizen habitat, whereas Salerno has a population of 140 thousand people (Fig. 1).

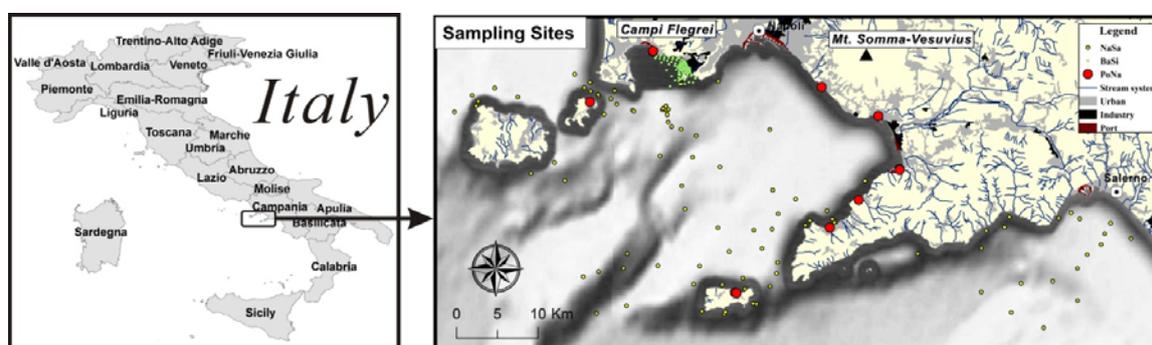


Fig. 1 - Study area and sampling sites of sediments.

The Tyrrhenian Sea is the result of Miocene-Quaternary extension contemporaneously to eastward accretion and anticlockwise rotation of the Apenninic folds and thrust belt during the roll-back of the subducting Adria plate. The Campanian Plain and Naples Gulf are integral basins, as well as Sele Plain combined with Salerno Gulf, both of which are parts of half-graben basins developed in eastern Tyrrhenian margin.

Sea floor of Naples and Salerno Gulfs are covered by Plio-Quaternary sedimentary and pyroclastic fall deposits. Two small coalescent deltas, Sebeto delta and Sarno delta, characterize eastern depositional system of Naples Gulf (Insinga *et al.*, 2008). Along Sorrento peninsula, Capri Island, and Salerno Gulf, Mesozoic-Cenozoic carbonate units also influence the composition of surface sediment.

Volcanic process during the late Quaternary has significant influence on morphology and deposits in Naples Gulf. Several volcanic eruptions happened in Campania Plain (Campi Flegrei, Ischia, and Mt. Somma-Vesuvius) during Quaternary, producing among others, Campanian Ignimbrite 39 ka B.C (De Vivo *et al.*, 2001) and Neapolitan Yellow Tuff 12 ka B.C. (De Vivo *et al.*, 2010).

Naples and Salerno provinces are among the most touristic regions around Mediterranean Sea. The port of Naples is one of the most important ports in Europe, and has one of the highest levels of passengers flow in the Mediterranean Sea. Naples is one of the most important transportation centers in South Italy, including railway, highway, and various roads. Agriculture is still the basic income of economy, being recently partially replaced by service industries. Various stream system in Campania plain and Sele plain carry related products and fertilizers into the sea.

In Bagnoli area, a large industrial area (brownfield site) had been dismantled between 1990 and 2000. The area used to concentrate various industries, such as steel production, asbestos materials manufacturing,

cement production, and fertilizer production. Although it is going through remediation by Italian Government, industrial relicts still concentrate in soil, as well as sediment in Bagnoli bay (Albanese *et al.*, 2010).

## MATERIAL AND METHODS

### *Sampling and sample preparation*

Sediments from three field sampling activities are included in this study. General survey of sea sediments in Naples and Salerno Gulfs (NaSa) provided regional information. Geochemical surveys of Bagnoli site (BaSi) and ports around Naples Gulf (PoNa) were focused on concentration of pollutants.

Sediment samples were collected (following the directives of the national program for assessment of marine pollution of highly contaminated Italian coastal areas) from 230 locations (Fig. 1). Differential global positioning system (DGPS) was used to identify each location precisely.

Among NaSa samples (May, 2000), 23 samples were collected using a box-corer with an inner diameter of 25 cm, of which superficial sediments were analyzed in this study and other 63 NaSa samples were collected by grab by C.N.R. (Istituto Geomare Sud, Naples). BaSi samples (between November 2004 and March 2005) included surface sediments (0-20 cm) of 123 boreholes along the coastline. PoNa samples (2003) included surface sediments (0-20 cm) of 11 boreholes.

From May to July 2011, 186 samples (surface and bottom) had been subset in Geomare CNR Institute (Naples), including 35 box corer sediment samples and 80 grab sediment samples. Most of box corer samples were divided into two parts, surface (or subsurface) and bottom sediment, as well as some of grabbing samples. Each sample were then subset into three parts, 30 g for metal and inorganic analysis, 100 g for organic analysis and the rest were stored in Geomare as backup.

### *Chemical analysis*

Inorganic Elements. 1) NaSa sediment samples were analyzed by Acme Analytical Laboratories Ltd. (Vancouver, Canada), through its Italian affiliate (Norwest Italia Srl, Naples) with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Emission Spectrometry (ICP-AES). 2) Analyses of elements (Al, Sb, As, Be, Cd, Co, Cr, P, Hg, Ni, Pb, Cu, Se, Sn, V, Ta, and Zn) on the ports of Naples sediment samples and metals (Al, As, Be, Cd, Co, Cr, Fe, Hg, Mn, Ni, Pb, Cu, Sn, V, and Zn) of Bagnoli site sediments were performed with Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Atomic Absorption Spectroscopy (AAS) by ICRAM Laboratories.

Polycyclic Aromatic Hydrocarbons (PAHs) and Organochlorine Pesticides (OCPs). PAHs and OCPs in sediments were concentrated to 0.2 ml under a gentle nitrogen stream and analyzed by Gas Chromatography-Mass Spectrometry (GC-MS). The analysis was carried out in Key Laboratory of Biogeology and Environmental Geology of the Ministry of Education (Wuhan, P.R.C.).

### *Numerical analysis*

Background value of PTEs for risk assessment was determined based on NaSa samples. Multivariate analyses were applied to NaSa data to group elements to speculate about the sources. Risk assessments were focused on BaSi and PoNa samples. Univariate analysis was applied to eight most concerned heavy metals of entire dataset, as well as ERA (Ecological Risk Assessment).

### *Geostatistical analysis and generation of interpolation maps*

Factor analysis help to identify relationships between different elements and get information on controlling factors. Additive Log-ratio Transformation (ALT) was used to solve the problems of dependences among elements compositions. The comparative results exhibited advantages and disadvantages of transformed data. The production of geochemical maps for Naples and Salerno Gulf sediment results, using Arcgis and GeoDAS (Cheng, 2001), is described by presenting, as an example, a complete set of geochemical maps

produced for Zn (Fig. 2A). The usefulness of this technique in environmental studies has already been demonstrated (Lima *et al.*, 2003).

Original concentration data, ALT and CLT (Centered Log-ratio Transformation) transformations were used to generate geochemical distribution maps with inverse distance weighted (IDW) algorithm as the interpolation method.

Concentration-area (C-A) plots (Fig. 2 B, D) illustrate a fractal analysis of data distribution in the area. In this plot, the vertical axis represents log value of cumulative pixel areas  $A(\rho)$ .  $A(\rho)$  means areas with element concentration greater than  $\rho$ .  $\rho$  is shown in horizontal axis in log value for unconverted data, whereas for ALT and CLT data,  $\rho$  is shown as it is. The C-A plot is first divided into two parts for original concentration and ALT: regional concentration and anthropogenic concentration, divided by the maximum value of NaSa data. Regional part is consequently divided based on fractal analysis. Because CLT transformation only covered NaSa samples, the results were compared to regional part in the other two maps. Divisions of C-A plot are applied as classes on interpolation maps in colour scale.

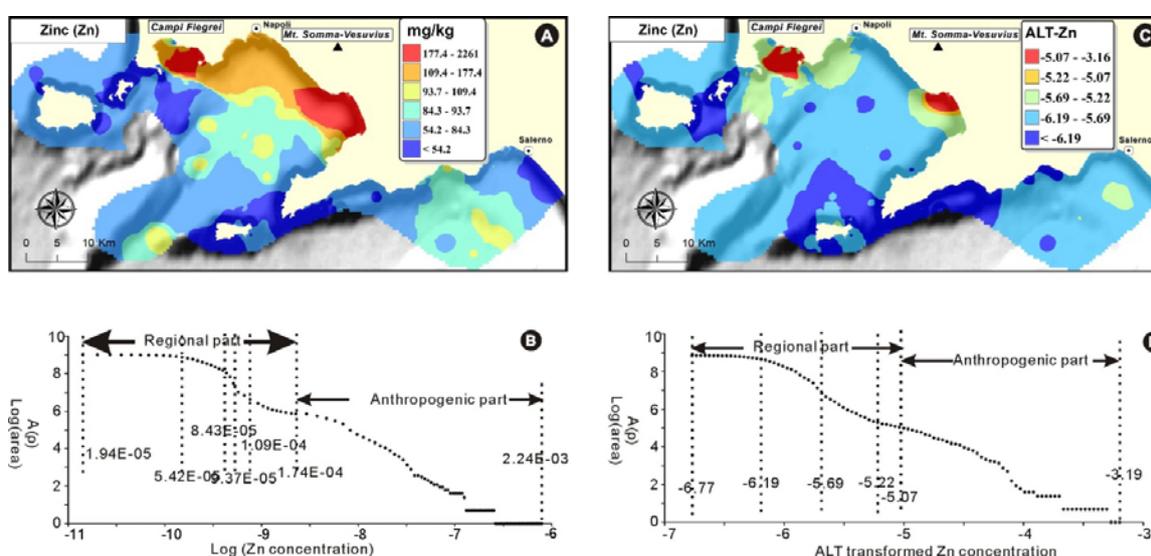


Fig. 2 - A) Interpolation map of original Zn value in mg/kg; B) Fractal concentration-area (C-A method) plot for Interpolation map of original Zn value in mg/kg; C) Interpolation map of Additive Log-ratio Transformed (ALT) Zn value; D) Fractal C-A plot for Interpolation map of ALT Zn value.

## RISK ASSESSMENTS

### Background value estimation

Bagnoli area and ports exhibit very high concentration of PTEs. The investigation of entire region set an opportunity to estimate regional background. In this study, mean value of NaSa samples is used as reference background value (eliminate the outlier near Capo Posillipo, GRNN 4).

### Estimation of pollutant impact

Numbers of factors (Abraham & Parker, 2008; Chapman & Wang, 2001; Harrison *et al.*, 2003; Lu *et al.*, 2009; Ridgway & Shimmield, 2002; Santos *et al.*, 2005) have been put forward for quantifying the degree of metal enrichment in sediments.

In this study, three PIA parameters have been selected to study pollutant impact: Enrichment factor (EF), Geoaccumulation index ( $I_{geo}$ ), Degree of contamination ( $D_c$ ), Incremental Lifetime Cancer Risk (ILCR). Also in this study, Percentage of risk samples ( $P_r$ ) was presented.

Five PAHs diagnostic ratio were selected to infer the source of PAHs in the area: An/178, BaA/228, Fluo/Fluo+PY, IP/IP+Bghi, and  $\sum\text{COMB}/\sum\text{PAH}$ .

## RESULTS

### *Compositional analysis*

A debate on correctness of compositional data lasted for decades (Aitchison, 1982; Filzmoser *et al.*, 2009; Reimann & Filzmoser, 2000). A comparison of the original and transformed data has been performed on interpolated maps of heavy metals in Naples and Salerno Gulfs. Transformed data theoretically fit to realistic elements distribution. Transformed maps limit some heavy metals to their sources (such as Cd, Cr, Pb, and Zn) and enlarge risk area of some others (such as Hg and Ni). Statistical characteristics of transformed data are more regular than original data; this is helpful in determining better class division. However, transformed results also introduce certain difficulties for interpretation and in adapting them to environmental estimation indexes. If the investigation only analyzes certain elements other than entire elements analysis, the results are highly influenced by the choice of ratio-denominator.

### *PTEs distribution*

The R mode factor analysis points out three element associations attributed to different sources: geogenic contribution, finer deposits due to water dynamic decreasing, and anthropogenic activities. Because of the extreme high concentration in Bagnoli site coastal area and ports around Naples Gulf, the areas with concentrated PTEs due to geological process was concealed in interpolation maps of single elements. However, after ALT transformation, sub-high concentration centres of certain elements (*e.g.*, Cr, Ni, and Cu) indicate the effect of water dynamic.

### *Organic pollutants distribution*

In sea sediments, PAHs are generally concentrated in the area closer to Bagnoli brownfield site, formerly occupied by heavy steel and other industries (Albanese *et al.*, 2010). OCPs concentrations in the area are less severe than the PAHs concentrations.

### *Risk assessment*

In the sediments, Pb, Zn, Cd, and Hg are shown as the most risky elements in the area. More than 40% of the samples exhibits moderate to high degree of contamination. When considering ERA, Pb is the most risky elements in the area. For organic pollutants, most of the compounds in open sea are with concentration below the ones indicated by criteria of adverse biological effects. However, in the area closer to Bagnoli brownfield site, over 80% of samples are bonded to risk quantity of PAHs. Organisms in contact with 20% to 45% of samples in the area may have intense biological harms. Beach recreation in the Gulf of Pozzuoli and out of Capo Posillipo is potentially harmful due to ILCR estimation of skin cancer. Also beaches nearby the ports around Naples Gulf are at the risk for baseline increase of cancer incidence.

## ENVIRONMENTAL GEOCHEMISTRY STUDY OF CAMPANIA REGION, ITALY: IN LAND

Polycyclic aromatic hydrocarbons (PAHs) are a major class of environmental pollutants mainly arising from anthropogenic activities. In this paper, the behaviour and the distribution patterns of sixteen PAHs, listed as priority pollutants by the United States Environmental Protection Agency (USEPA), were evaluated in 119 soil samples collected in different areas of Campania region in the southern Italy. The study area covers about 2,400 km<sup>2</sup>, roughly corresponding to the Campanian Plain, which is a wide coastal belt that goes from the

Volturno River plain, in the north-west of the Campania region, to the Sarno River basin, southward of the volcanic complex of Mt. Vesuvius. The observation of the geochemical distribution patterns showed that both high (HMW-PAHs) and low molecular weight PAHs (LMW-PAHs) are mostly concentrated within the metropolitan area of Naples, the Agro Aversano area and, partly, the Sarno River basin. In accordance with the Italian environmental law (D. Lgs. 152/06, 2006) these areas should be considered potentially contaminated and not suitable for a residential use unless an environmental risk analysis does not demonstrate their safety. As a consequence, a preliminary quantitative risk assessment (PQRA) enhanced by the use of GIS was run revealing the existence of an incremental lifetime cancer risk higher than  $1 \times 10^{-5}$  for the city of Naples and for some other populous areas.

The results obtained by the PQRA in this study together with the epidemiological evidence of an increased incidence of some cancer types in Campania pose the need of developing a detailed and multi-media based geochemical characterization of the regional territory to define, at least at regional scale, a conceptual model considering all the exposure pathways followed by contaminants to reach the human target from the emitting source. Soil, water, air, and food should be taken into account and concentrations of metals and organic compound, such as PAHs, should be determined within these media to allow the development of an environmental risk analysis based on the effective concentrations of contaminant likely to come into contact with humans.

Although in case of an objective risk to human health, little could be done to clean up the soils of a territory covering more than 1,000 km<sup>2</sup>, the location and the control of the sources of emission of contaminants could be of crucial importance to recover the environment in the long term and the results of a risk assessment could be used, at least, to establish a priority order in the implementation of safety measures and remediation plans consistent with the available resources.

## LABORATORY RAMAN *IN SITU* RESEARCHES OF FLUID SYSTEMS AND IRON MINERALS CHANGES

### *In situ* researches apparatus

Capillary high pressure optical cells (CHPOC) were used in this study to carry on *in situ* experiments and observation. CHPOC was constructed from square or round cross-sectioned fused silica-capillary tubing (I.D. is from 50  $\mu\text{m}$  to 300  $\mu\text{m}$  whereas O.D. is from 100  $\mu\text{m}$  to 600  $\mu\text{m}$  respectively) and a high pressure valve plus heating-cooling stage that allows *in situ* Raman studies at pressures up to 100 MPa and temperature ranges from -80  $^{\circ}\text{C}$  to 400  $^{\circ}\text{C}$ . The same study conditions may be achieved by diamond anvil cells (DAC) but in the need of a

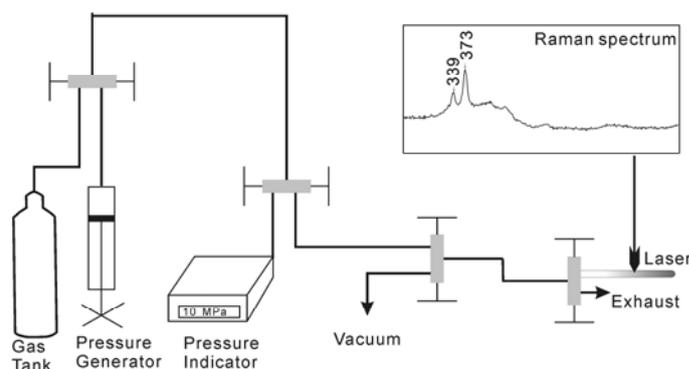


Fig. 3 - A schematic diagram of the experimental set up for collecting *in situ* Raman spectra of the sample in a CHPOC. The example Raman spectrum was derived from pyrrhotite.

much more complicated device. Several key features of this cell include: 1) the ability to directly load sample fluids and monitor pressure during investigation, 2) the lack of optical distortion, 3) the small cell volume suitable for samples of limited supply, 4) the high pressures that can be achieved, 5) the high-magnification and high-numerical wall of the capillary tube, 6) the heating-cooling stage that allowed for temperature controlling, and 7) the observation of metastable transition phase of reactions (Fig. 3).

*Diffusion coefficients of methane in aqueous systems*

Raman spectroscopy has been used for quantitative analysis for several decades. At constant temperature the concentration of dissolved methane is proportional to the Raman band intensity ratio of methane and water. Thus, we can use the quantitative Raman spectroscopic method to monitor *in situ* the concentration changes during methane diffusion in water under high pressure and elevated temperature. We have previously applied such quantitative Raman spectroscopic methods to determining the diffusion coefficients of methane in water at room temperature and under two pressures. In this study, the work was extended to the wider temperature and pressure ranges, from 273 to 473 K and from 5 to 40 MPa, to study the temperature and pressure effects on the diffusion coefficients of methane in water. It is concluded that, diffusion coefficients of methane in water show Arrhenius behaviour only at higher temperatures, the temperature dependence of the diffusion coefficients of methane in water can be fitted with Speedy-Angell power-law. The pressure effect is very small (Fig. 4).

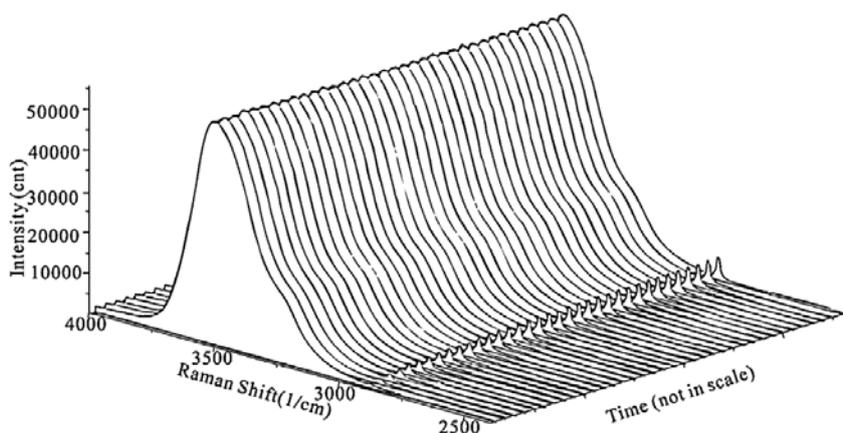


Fig. 4 - Time-dependent Raman spectra of dissolved methane (CH<sub>4</sub>, around 2,910 cm<sup>-1</sup>) and water (H<sub>2</sub>O, around 3,520 cm<sup>-1</sup>) collected at the spot B (3,000 mm away from the spot A, and 14,911 mm away from the end of the tube), at different times after the after the water was pressurized by methane at 20 MPa and 473 K.

*Asymmetric bands of methane dependences of temperature and pressure*

Raman spectroscopy is also a powerful tool to study the properties of gas phase in fluid inclusions. Besides the most intensified C-H symmetric stretching band ( $\nu_1$ ), asymmetric stretching band ( $\nu_3$ ) and asymmetric bending band overtone ( $2\nu_2$ ) are two primary bands with mediate intensity (~ 2% intensity of  $\nu_1$ ).

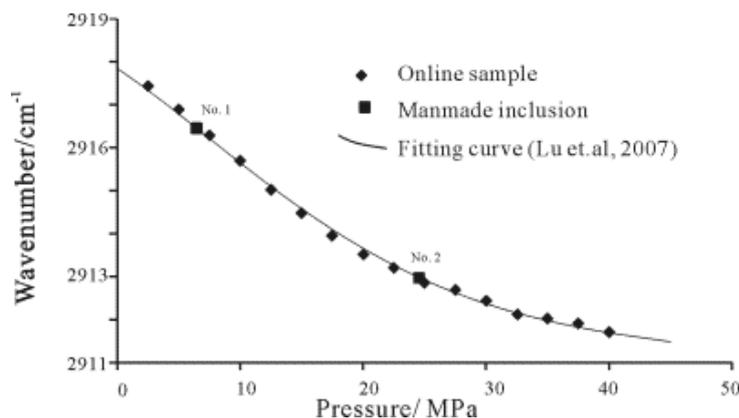


Fig. 5 - The fitting curve (solid line) followed the form of calculating methane vapour pressure with  $\nu_1$  peak position. Least square method is used to fit the laboratory standard  $\nu_0$ , which is determined as 2,917.849 cm<sup>-1</sup>. The corrected  $\nu_1$  peak position of manmade methane inclusions (solid squares) are 2,916.456 cm<sup>-1</sup> and 2,912.972 cm<sup>-1</sup> for No. 1 and No. 2 methane inclusion respectively. Followed Eq. 3, inner pressures of inclusions are 6.45 MPa and 24.54 MPa, respectively.

Peak intensity ratio (PIR) of  $\nu_3$  and  $2\nu_2$  is found to systematically change with pressure at room temperature and the relationship between PIR and pressure seems to be independent to composition of natural gas. It is worthy to know how the relationship between the PIR and pressure is affected by temperature and the composition of the fluid samples, when we use PIR to accurately determine the pressure of methane-bearing fluid inclusion.

In this study, the PIR is studied for pure methane system at elevated pressures and temperatures. The relationship among peak intensity ratio,

temperature, and pressure/density were derived with numerical equations. As a demonstration, the inner pressure and density of two methane inclusions were determined by Raman spectroscopic measurement of the peak intensity ratios of  $\nu_3$  and  $2\nu_2$  (Fig. 5).

#### *Sulfidation of iron minerals*

Various valences of iron sulfide minerals commonly appear at the transient depth between iron oxide reduction zone and sulfate reduction zone in marine sediments. Reactivity of iron oxide minerals towards sulfide is solely ascribed to various crystal structures. However, large discrepancy of reaction rate exists between different studies. The discrepancy is assumed as a result of different interstitial compositions and geochemical environments. For example, organoclastic related iron sulfides reflect concentrations of S and Fe in pore water (Haese *et al.*, 1997), whereas methanotrophic source of iron sulfides indicate concentrations of methane and carbon dioxide in pore water. Combined with high pressure optical cells, Raman spectroscopy shows advantages to monitor the evolution of minerals. Optical images and Raman spectra could demonstrate that under  $\text{CH}_4$  atmosphere, pure  $\text{Na}_2\text{S}$  solution could coexist peacefully with iron oxide minerals. If  $\text{CO}_2$  partially replaces  $\text{CH}_4$ , intense reaction occurs not only to sulfide solution but also triggers iron oxide minerals sulfidation. The products in solution and vapour phase are different: in solution only appears iron monosulfide; in the vapour phase pyrrhotite is detected. The results serve as a possible explanation to anoxic environmental iron sulfide minerals (Fig. 6).

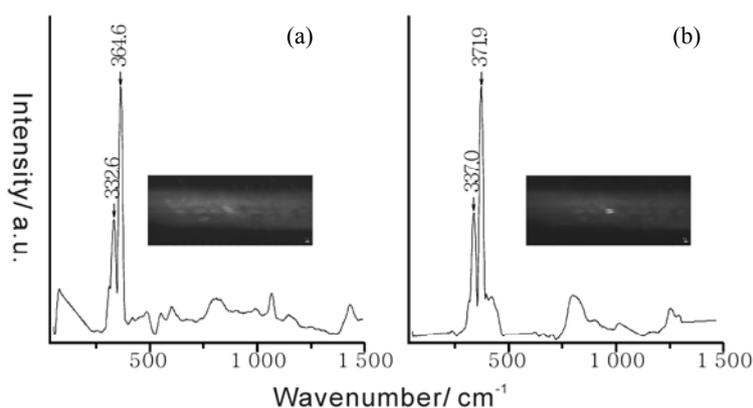


Fig. 6 - Raman spectra of iron sulfide minerals. Peaks at  $\sim 333 \text{ cm}^{-1}$  and  $\sim 363 \text{ cm}^{-1}$  (a), or  $337 \text{ cm}^{-1}$  and  $\sim 372 \text{ cm}^{-1}$  (b) indicate the occurrence of pyrrhotite. The white sample spot shined after excited by laser.

#### SURFACE ENHANCED RAMAN SCATTERING APPLIED TO *IN SITU* GEOCHEMISTRY

Intense development of industries during last century has created thousands of synthetic organic compounds, such as plastics, lubricants, fuels, pesticides and etc. All of these compounds, along with organic byproducts and residues, constitute a new category of contaminants to natural environment. Among all the organic contaminants, persistent organic pollutants (POPs) are believed to be the most harmful compounds. POPs include variety of pesticides (OCPs), chlorobenzene species (PCBs and HCBs) and polyaromatic hydrocarbons (PAHs). POPs exhibit following four characteristics: 1) high toxicity: small quantity of POPs may cause severe damage; 2) persistency: POPs are resistant to photolysis, chemolysis and biolysis; 3) accumulation: POPs are hydrophobic and lipophilic, which helps POPs accumulate in soil, sediment and biological adipose tissue; 4) mobility: most POPs are semi volatile and easily migrate in the atmosphere.

Clean water, which is free from toxic chemicals, is essential to both human health and economic development, when considering its different uses, as 1) drinking water, 2) water for agriculture, 3) water for zoo-technique, and 4) water for industrial systems. Moreover, the demand for pure water is continuously rising due to the global industrialization and the socio-economical growth of emerging countries. Unfortunately, aquifers as sources of drinking water can undergo pollution, due to 1) atmospheric contamination, 2) discharge

of liquid contaminants, and/or 3) percolation from contaminated soils. At the same time, water pollution can provoke soil contamination, by accumulating both heavy metals and toxic or carcinogenic compounds in marine and fluvial sediments. In marine waters, as well as in flow waters and aquifers, chemical compounds, usually used as herbicides, pesticides, and antibacterial agents in agriculture and zoo-prophylaxis, can be present. Many of these have molecular structures similar to natural products and are degraded naturally or through their own chemical or photochemical instability. On the other hand, when these compounds are stable, they can alter the ecosystem, accumulating in living organisms or diffusing through the environment by volatilization, dissolution or percolation from contaminated soils. As a consequence, the effects of the pollution can manifest themselves very far from the original site.

Raman spectroscopy allows the identification of different molecules on the basis of their vibrational bands, providing an unambiguous molecular fingerprint. However, the low sensitivity of Raman scattering, along with possible spectral interference due to fluorescence emission, impairs the use of this technique for the recognition of molecular traces. In these cases one can use the SERS (Surface-Enhanced Raman Scattering) effect, which is able to enhance the Raman intensity of molecules adsorbed on metal substrates by many orders of magnitude and to promote a drastic quenching of fluorescence. Huge magnifications of the Raman signal are observed when a molecule adheres to nanostructured surfaces of metals with high optical reflectivity, such as Ag, Au, and Cu. The SERS enhancement factors are generally up to  $10^7$  with respect to the Raman intensities of non-adsorbed molecules. By means of experimental procedures that combine microscopy and spectral observation beyond the light diffraction limit,  $10^{14}$ - $10^{15}$  enhancement factors are reached, thus ensuring single-molecule detection. Thanks to its peculiar properties, SERS spectroscopy, since its discovery at the beginning of the seventies, has achieved a leading role in the analytical investigation of very low traces of contaminants, allowing the spectroscopic detection at sub-picogram level. Actually, aromatic nitroderivatives could be identified by means of SERS spectroscopy when adsorbed on silver nanoparticles, as demonstrated in the literature by observing strong enhancements of their Raman bands.

Determination of POPs and other organic contaminants in marine environment inspires the study of *in-situ* detection approaches. An intension of applying such advanced techniques into field survey is consistent with the object of environmental geochemistry. Integration of field survey, rapid analysis and geochemical mapping extends the future of geochemistry and serves effectively to governing and management.

In this study, an integrated approach of surface enhanced Raman scattering (SERS) and solid phase extraction (SPE) is considered. Organic pollutants were firstly concentrated into solid phase with silver nanoparticles embedded, and following micro (macro) Raman detection of SERS spectrum. Lower concentration of nitroaromatic compounds (lower than  $10^{-6}$  M) is easily detected. Thanks to polymer layers, silver nanoparticles are protected, which extends the period of silver nanoparticles availability.

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