Environment and Analytical Chemistry

Maria de Fátima Araújo

The activities within the Environment and Analytical Chemistry Research Group involve the study of the Biogeochemical Cycles of Chemical Elements and Light Isotopes in the Environment. Our main skills are in the fields of Instrumental Analytical Chemistry, Environmental Geochemistry, Isotope Hydrology, Oceanography, ^{14}C Dating and Archaeometallurgy.

Instrumental Analytical Chemistry is based on the implementation of Energy Dispersive X-Ray Fluorescence Spectrometry, Mass-Spectrometry for Light Isotopes, Elemental Analysis coupled to Mass Spectrometry, ^{14}C and ^{3}H Dating techniques. These are being utilised in studies involving quantitative elemental analysis, isotopic determinations and dating of environmental and archaeological samples.

During the current year we have implemented a clean laboratory to install an ICP-MS (Inductively Coupled Plasma Mass Spectrometer) for isotopic and trace element research, financed by the "*Programa Nacional de Re-Equipamento Científico*". Also, the operation of the Elemental Analyser coupled to mass spectrometer unit allowed the development and expansion of specific working domains in Isotope Hydrology and Isotope Geochemistry, with particular emphasis the use of isotopic techniques in the assessment of aquatic resources pollution related to agricultural practises.

Environmental Geochemistry and Oceanographic research was developed under a multidisciplinary approach, including sedimentology, geochronology, absolute dating, meteorology and paleoecology. Research was focused in Sedimentary Geochemistry to evaluate: 1. consequences caused by the changes that took place during the last centuries in the main Iberian river basins, and 2. environmental changes occurred during the Late Quaternary in lagoons and interdune depressions of the SW Portuguese coast. Moreover, studies concerning the marine reservoir effect off the W margin of Iberian Peninsula, based on ^{14}C dating of marine shells and charred wood or bones closely associated, have enabled the clarification of the variability of the coastal upwelling off Atlantic Iberia and the identification of episodes of abrupt shifts in oceanic circulation.

Isotope Hydrology was extended in order to achieve the comprehension of different environments, namely: Urban Areas; High Mountain Areas; Arid and Semi Arid Zones and Gas Geochemistry in CO_2-rich Thermomineral Waters. The characterisation of these systems is being addressed in the exploitation and future development of regional water resources and the delimitation of protection areas.

Research projects have been of a particular relevance in given support to political decisions, taking into account the sustainable regional development and the appropriate use of the water resources and coastal management on the basis of several European and national directives.

The Archaeometallurgical field was strengthen via the study of pre-historical important artefact collections to characterize the technological and social conditions of Copper and Bronze Age metal production and circulation in Portugal. New studies including corrosion process in archaeological Cu-based materials and surface enrichment processes were developed by using optical metallography, micro-fluorescence and scanning electron microprobe.

Due to the specificity of the available equipment and expertise within the group, technical services are provided to Universities, Public and Private Institutions

Research Team

Researchers

M.F. ARAÚJO, Aux. Researcher, Group Leader
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Collaborators

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Environmental Geochemistry – Elemental and Isotopical Research

M. Fátima Araújo, P. Carreira, A.M. Monge Soares, P.G. Fernandes, C. Corredeira, D. Nunes, P. Valério, R. Cardoso, J. Martins, O. Margo, A. Amaro, M. Correia

Objectives

This project aims at the development and promotion of coordinate research on Earth and Environmental Sciences by implementing analytical and absolute dating techniques:

1. Multielemental characterization (Z>10) using X-Ray Fluorescence spectrometry in solid samples;
2. Light isotope (δ^2H $\delta^{13}C$, $\delta^{15}N$ and $\delta^{18}O$) determination in liquid and solid samples, including organic matter;
3. Radiocarbon dating;
4. Tritium dating of water samples.

The elemental, isotopic and dating techniques are being dedicated to the understanding and management of natural environments, particularly aquifers, rivers, lagoons, estuaries, coastal waters and continental shelf. Our main goals are:

1) to establish the evolutionary patterns of these environments since the Last Glacial Maximum; define geochemical signatures for different marine and terrestrial contributions; evaluate changes in sediment sources; delineate local fossil background values;
2) to determine the origin of different groundwater systems; assess the vulnerability of groundwater to surface pollution; understand and determine the origin of pollution in hydric systems;

3) to assess the variability of the W Iberian coastal upwelling; identify episodes of abrupt shifts in oceanic circulation, probably coupled with abrupt climatic changes.

Results

Geochemistry and dating studies carried out in shelf, estuarine and lagoonal sediments revealed to be an important tool in the study of transitional and marine environments, giving particular indications in the marine/terrigeneous origin of the deposited materials and allowing to recognise and evaluate some temporal changes occurred during the Holocene. During this year, studies were mainly focused on: the SW Iberian shelf sediments (Gulf of Cadiz); the southwestern coastal lagoons and in estuarine region of the drainage basins of Lima, Tagus and Sado rivers.
Guadiana shelf sediments exhibit an important continental contribution. The main sources of pollution are the mineral wastes of mining activities resulting from the ore exploitation along the Iberian Pyrite Belt. Heavy metal (Cu, Zn and Pb) enrichment determined for the upper layers (from the surface down to 20 - 80cm) of sediment cores collected along the mid and out shelf indicate a continental contaminated source. Spatial distribution of the enrichment factors (using as a reference the concentration values of the deepest fractions of the cores) shows a similar behaviour in the heavy metal distribution patterns along this area of the continental shelf. Heavy metal contents and excess ^{210}Pb along core sediments indicate a clear record of the beginning of "pollution" in shelf sediments coincident with the mining exploitation reactivation during the XIX century. Geochemistry of lagoonal and estuarine sediments has permitted the establishment of background levels to derive the enrichment caused by anthropogenic factors. Lagoonal sediments were classified according the concentration thresholds published in the Portuguese legislation that regulates the degree of contamination for dredged materials (DR II, nº. 141, 21/6/1995).
Besides, environmental isotope techniques applied to surface waters have identified and characterised sources of pollution: natural, industrial, agricultural, and domestic. Isotope techniques have allowed recognising incipient pollution, providing an early warning although the chemical and biological indicators did not point to any mixture of systems or pollutants contribution (Sado/Sines basins). Agricultural practices and high industrial areas with over exploitation of the systems were identified as sources of pollution to the environment: sediment and hydrological domains (Porto region and Sado basin).

Radiocarbon dating has been used as a tool to set up chronological frameworks for the past environmental changes identified in our research. Besides this, the regional marine reservoir effect, ΔR, for the western Iberian coastal waters during the 4^{th} and 3^{rd} Millenium BC, a badly sampled time interval in previous research, was determined. The results enable a better clarification of the variability of the coastal upwelling off Atlantic Iberia. Radiocarbon dating was also applied to identify the possibility of occurrence of different age episodes of sand accumulation during aeolianite formation at the coastal region of Lisbon.

Elemental and Isotopical geochemistry of fine sediments deposited along the Iberian continental shelf
M. Fátima Araújo, C. Corredeira, D. Burdloff ,R. Cardoso, R.Calisto

The geochemical characterisation (elemental and isotopical) of fine sediments collected along the Portuguese Continental Shelf adjacent to the main Iberian river estuaries (Minho, Douro, Tagus and Guadiana), was used to assess the influence of each specific river sediment load into the coastal marine environment. The variability on the sedimentary organic matter supply results from differences in the transported sediment load, hydrodynamism and morphological environment along the continental shelf. Sediments rates determined is sediment cores demonstrate the varying sediment supply and the influence of each drainage basin (Guadiana: 0.12-0.13 $cm.yr^{-1}$; Tagus: 0.20-0.24 $cm.yr^{-1}$; and Douro 0.45 $cm.yr^{-1}$). Elemental distribution of lithogenic/biogenic elements indicates that Douro is the main source of the shelf fine sediments deposited northwards. At the northwesten shelf sediments, heavy metal contents suggest depletion by geochemical processes, probably due to a long transport and resuspension before deposition. Anthropogenic contamination detected at the shelf adjacent to Tagus is the result of urban wastes and industrial effluents from industries settled for decades in a high-populated region. Guadiana shelf sediment composition shows a significant continental contribution and the influence of the mineral wastes of mining activities. Particularly, the reactivation of the mining exploitation promoted by a British Company during the XIX century – construction of the "Pomarão" fluvial mining port (~50 km upstream) and railway connecting the mines to the ports has induced a clear metal enrichment in shelf sediments.

Geochemistry of lagoonal and interdune depressions sediments from SW Portuguese Coastal lagoons
M. F. Araújo, A. Cruces, S. Moreira, M.C. Freitas[1], C. Andrade[1]

The Albufeira, Melides, Santo André and Sancha lagoons are located in the south western coast of Portugal, the first one in the Trafaria-Espichel stretch and the others in the southern half of the Tróia-Sines bay. In spite of their geographic proximity, specific features and internal dynamics of each unit result in distinct sedimentological and geochemical patterns/signatures. The presence of sand barrier hinders the lagoon-ocean contact in all cases, although in Albufeira, Melides and Santo André, the annual artificial opening of the inlet in spring allows exchange between the lagoonal and marine environments during several days, weeks or even months.
The textural and compositional variability, as well as the concentration values of 21 chemical elements of the lagoonal superficial sediments, were determined. The heavy metals concentration was normalized using the Al as the conservative element and compared with published international reference values (RV). The heavy metals content determined in the superficial sediments was compared and classified according to the concentration thresholds published in the Portuguese legislation that regulates the degree of contamination for dredged materials (DR II, nº. 141, 21/6/1995): Class: 1 – clean; 2 - slightly contaminated, 3 - moderately contaminated, 4 – contaminated, 5 – very contaminated.

Geochemistry of sediments from Portuguese estuaries
M. F. Araújo, R. Cardoso, F.Fatela[1], M.C. Freitas[1], C. Andrade[1]

Estuaries are important transitional zones of sediment transfer between fluvial and marine systems, often acting as a sink for sediments. Therefore they may function as archives of Historical contamination and geochemical weathering. Several important rivers with many tributaries, flow across the Portuguese territory and develop estuaries with different typologies along the western coast. Drainage basins have striking differences, either natural: run-off, outcropping lithologies, climate, geomorphology and vegetation cover; and/or due to human occupation: urban centres, agricultural practises, industries, mining and dredging. Fluvial sediments, travelling throughout the Iberian Peninsula and being affected by many factors, are trapped in estuarine environments and/or exported towards the shelf. To establish the background composition it is necessary to separate anthropogenic contamination from elemental concentrations with a lithogenic origin, which varies according to the geology/geochemistry of–estuarine catchment's and must be determined individually in each estuary. The geochemical study of several transepts collected at different locations in the estuarine regions of Lima, Tagus and Sado rivers was carried out. Geochemical results combined with physico-chemical parameters and sedimentogical features allow the establishment of reference values and assessment of heavy metal contamination.

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Groundwater Resources as Indicators and Archives of Palaeoclimatic Changes

P.M. Carreira, P.G. Fernandes, J.M. Marques[1], F. Monteiro Santos[2], D. Nunes

The regional geomorphology of the region seems to favours a conceptual circulation model for Caldas de Monção thermomineral system where the recharge area is located at south of Caldas de Monção, up hill between 300 and 600 m a.s.l (based on $\delta^{18}O$ values). The underground flow paths are associated with the NNE-SSW fault systems and their NW-SE associated systems, issuing these waters when appropriate conditions are found. The geophysical models suggest that those tectonic systems may be deep and filled with mineralized water. The low ^{14}C content (between 4.82 ± 1.00 pmc and 7.43 ± 0.34 pmc) of Caldas de Monção thermomineral waters (TDIC) together with the absence of ^{3}H support the hypothesis of a long circulation path through the subsurface rocks. This hypothesis is corroborated by the minimum depth reached by the Caldas de Monção thermomineral water system (2.2 km) estimated by the geothermometric approach. The $\delta^{13}C$ determinations give values in the range of -7 to -6 $^{o}/_{oo}$, indicating a "complex" origin for the CO_2 in these waters (mixture between atmospheric CO_2, decay of organic matter and upper mantle CO_2. Geophysical, isotopic and geochemical studies performed at Caldas de Monção region have increase knowledge on the interaction between local shallow cold groundwater systems and the low-temperature geothermal waters.
This important environmental issue should be addressed either in the exploitation and future development of these low-temperature geothermal resources or/and in the delimitation of well-head protection areas.

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Groundwater Resources Assessment by Anthropogenic and Natural Contamination Sources

P.M. Carreira, P.A. Fernandes, O. Margo, D. Nunes, L. Ribeiro[1], E. Peralta[2]

The work is being focused on the study of the quality of groundwater sources for Human supply and groundwater resources protection and management, through the identification and quantification of pollution sources traced by environmental isotopes ($\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $\delta^{2}H$ and ^{3}H). Isotope techniques can assess the vulnerability of groundwater to pollution from the surface by determining how rapidly it moves and where it is being recharged. Surface waters of pollution can then be determined, e.g. natural, industrial, agricultural, or domestic. Isotope techniques can also identify incipient pollution, providing an early warning when the chemical or biological indicators do not give cause for concern. Some of the projects developed under this aim have to consider the agricultural practices and high industrial areas must be seen as new inputs of pollution in the environment (sediments and hydrological domains) through demographic density increase and growing of organics and toxic contamination. In the particular case of nitrogen isotopes, this tool can offer a direct means of source identification, since the two major sources of nitrate in agricultural areas, fertilizer and manure, have an isotopically distinct $\delta^{15}N$ values. The relative contribution of these two sources to groundwater or surface water can be estimated by mass balance. The analysis of $\delta^{18}O$ of nitrate in conjunction with $\delta^{15}N$ improves the ability to trace nitrate sources and cycling. Preliminary results confirm that major source of nitrate-N in groundwater comes from agriculture and small percentage from natural N cycle and biochemistry origin.

The projects carried out by QAA research group will give scientific proves to support political decisions, taking into account the sustainable development of the region and the appropriate use of Nitrogen fertilizers on the basis of several European and national directives, namely vulnerable regions and EC Water Framework Directive.

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High Mountain Areas in Catchment Water Resources

P.M. Carreira, D. Nunes, J.M. Marques[1], J. Espinha Marques[2], H. Chaminé[3]

Mountainous areas are usually the source of most of the larger river systems all over the world, and represent some of the "black boxes" in the hydrological cycle. The seasonality and spatial variability of local groundwaters and the complex role of soils, geomorphology, geology, climate, land use and Human activities on the hydrology of mountain areas are rather particular. Special emphasis is dedicated on high mountains and their role and impact on surface water/groundwater interaction at Serra da Estrela region - Central Portugal in order to i) increase knowledgment on recharge and discharge processes in this high mountain area and ii) assess snow as a source of thermal water resources, with the aid of isotopic techniques.

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National Network for Isotopes in Precipitation

P.M. Carreira, M. Fátima Araújo, D. Nunes, P. Valério, M.Correia, L. Araguas-Araguas[1]

Interpretation of the isotopic composition in terrestrial water (groundwater resources and superficial waters) requires knowledge about the meteoric water that feeds them: rain and snow. Their isotopic composition is quite variable in time and space, and depends on climate, geography, nuclear fallout and other factors. In the follow up of these for more than a decade we are participating in the Global Network for Isotopes in Precipitation (GNIP) in a close collaboration with the Isotope Hydrology Section of the IAEA. The work carried out aims to provide basic isotope data (^{2}H, ^{3}H and ^{18}O), for hydrological investigations, by determining the temporal and spatial variations of environmental isotopes. The correlation between the water vapour samples and precipitation events in most cases is not clear probably due to the different characteristics of the sampling periods, although a similar evolution can be observed. The large depletion in the isotopic composition found in vapour and rain event samples are associated to the depressions over Atlantic (in front of the Portuguese coast – Mid North Atlantic) or over the British Islands, crossing Portugal mainland from W to E. The atmospheric weather depressions induce a progressive depletion both in rain and water vapour. Regional variations in the ^{3}H content (monthly data) between littoral and interior stations are probably a result of the oceanic dilution of the tritium content in the atmospheric water vapour. The Isotopic results are compiled and gathered in the IAEA Data Base and disseminated via IAEA publications (www.iaea.org/programs/ri/gnip/gnipmain.htm), to be used in international hydrogeological and climatologic studies.

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Hydrology in Urban Areas

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One of the most crucial water-related research issues at the turn of the millennium "Water and Society" with special emphasis dedicated on "Land habitat hydrology in urban areas" and their role and environmental impact on surface water/groundwater recharge and circulation. In urban regions the application of environmental isotope geochemistry includes the assessment of recharge from leaking water mains and sewers, from in situ sanitation, from waste water and from influent surface watercourses. The isotopic techniques most commonly employed are ^{2}H and ^{18}O in water and ^{15}N and ^{18}O in nitrate (in liquid and solid samples), in combination with major and trace hydrogeochemical indicators.

Rainfall, surface water systems, rivers and lagoons are possible sources of recharge related to groundwater systems. Thus, one question may arise: what is the relative importance of these several potential sources of recharge? To assess the quality/quantity based in hydrogeochemical, isotopic and ecotoxicological parameters and relate them with the underground circulation with the main goal to provide information to support water management and land use planning. A better understanding of urban hydrological cycle will contribute to a proactive management of urban groundwater resources.

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Gas Geochemistry in CO_2-rich Thermomineral Waters

P.M. Carreira, D. Nunes¸ M.R. Carvalho, J.M. Marques[1], G. Capasso[2], F. Grassa[2]

In the Portuguese mainland, the greatest number of hot (≈76ºC) and cold (17ºC) CO_2-rich thermomineral waters are situated in the Northern part of the country, occurring along or near major faults. Such faults should be considered important targets for geothermal exploration in Portugal. A new geochemical approach on the study of the nature of these thermomineral waters will be focused on the geochemistry of the gas associated with those waters. Gas chemical and isotope analyses Gas geochemistry will be used to improve knowledge on subsurface reservoir temperatures using several gas geothermometers. Gas isotopes will give new insights on the sources of gas constituents (crustal rocks, mantle, etc.). Chemical and isotopic signatures of the waters, together with the gas characteristics, will be used to confirm and/or update the preliminary conceptual models of the local and regional fluid circulation, producing new data on the geothermal potential of the northern part of Portuguese mainland. Trace elements in waters will expand the possibilities of quantitative interpretation of specific mineral-solution equilibrium conditions.

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Arid /Semi Arid Zones Hydrology

P.M. Carreira, P. Galego Fernandes, D. Nunes¸ F.M. Santos[1], A. Pina[2], A.M. Gomes[2], J.M. Marques[3], M. Bahir[4]

Geophysical studies when combined with isotope techniques and geochemical data can provide comprehensive information on groundwater dynamics and recharge history, in order to assess arid zones hydrology. On the following up of Research Projects started in 2005 at Santiago Island (Cabo Verde) and in Esssaouira Basin (Morocco) such a multidisciplinary approach has been applied to evaluate the hydrogeological potential of arid zones and environmental / climatic changes. The combination of these different methodologies have been applied in this island with the goal of monitoring fresh-water – salt water interface. The $\delta^{18}O$ and $\delta^{2}H$ data will be used to i) the identification and characterization of the recharge areas and ii) the quantification of amount (%) of mixture between seawater and fresh water. Besides, tritium content measurements will allow obtaining the mean residence time of the water system. ^{3}H and stable isotope data, together with the accumulation of chloride in the unsaturated zone, can be applied (under piston flow conditions) to provide a record of past recharge and help to reconstruct the antecedent climatic conditions. The obtained data may act as an additional climatic archive of the region. It is important to have in mind that the hydrological balance shows that the rainfall that falls on the islands is distributed in medium periods like following: 67% is evaporated, 20% is drained away as superficial drainage and only 13% recharges the aquifers.

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Archaeometallurgy – Provenance, technology and use of metallic artefacts

M. Fátima Araújo, P. Valério, E. Figueiredo, A.M.M. Soares, J.C. Senna-Martinez[1], A. Ávila de Melo[2]

This field combines analytical and archaeological studies concerning the metallurgical activities of the Copper and Bronze Ages in the Portuguese territory. The relationship between archaeometallurgy research with historical, cultural and economical contexts will ultimately enhance our knowledge of those prehistoric societies. The research conducted in Late Bronze Age sites from *Beira Alta* (*Castro da Senhora da Guia, Castro de Santa Luzia, Castro do Outeiro dos Castelos de Beijós, Canedotes e Castro da Senhora das Necessidades*) establishes the preponderance of artefacts with an Atlantic typology although constituted by copper-tin alloys instead of the typical Atlantic leaded bronzes. The latter alloy is particularly scarce in this region, probably due to the fact that this is an area exceptionally rich in tin ores, namely cassiterite (SnO_2). The absence of leaded bronze artefacts in Late Bronze Age *Beira Alta* is also a proof of the reduced exchange system of metallic commodities with the Atlantic world. Contacts with Oriental Mediterranean Cultures are also established by the presence of a few characteristic copper-tin artefacts, namely from the *Castro da Senhora da Guia (Baiões).*

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Non invasive elemental characterization of pre-historic copper-based artefacts
P. Valério, M. Fátima Araújo, A.M.M. Soares, I. Silva

Research concerning archaeological items requires the use of non invasive techniques in order to protect this significant part of our collective History. Energy Dispersive X-Ray Fluorescence spectrometry is therefore being used in the Archaeometallurgy field. Our work involves the elemental characterization of copper-based artefacts and related materials (e.g. crucibles, slags, etc.) from the Portuguese territory dated from the end of the IV millennium BC until the first half of I millennium BC. Several metallic artefacts from *Castro de Palheiros (Vila Real)* were analysed in order to establish the type of alloy, as well as its major impurities. Chalcolithic materials could be divided into copper with low and high arsenic content, as well as copper with different impurities of tin. Artefacts from the Iron Age occupation of the site are made from copper-tin alloys with low and high lead contents. In a different study, Copper Age materials from *Porto das Carretas (Évora)* provide significant results regarding the arsenical copper metallurgy of this period – artefacts are made from copper with high arsenic content, whereas analysed ore fragments from the same period, are constituted by copper without any traces of arsenic. The slag composition from *Castelo Velho de Safara (Moura)* point out to the local smelting of lead ores.

The reservoir effect of coastal waters off the western margin of the Iberian Peninsula
A.M.M. Soares, J. Martins, A. Amaro, J.A. Alveirinho Dias[1]

Marine shells have not been used as extensively as charcoal or bone samples in absolute chronologies due to the unknown variability of past oceanographic conditions. At present, along the western coasts of Europe active upwelling is restricted to the western margin of the Iberian Peninsula. ^{14}C content of marine shells can be used a proxy of the upwelling intensity. However, present and past oceanographic conditions must be known in order to use radiocarbon dating of marine shells accurately. Sample pairs (marine shell – charred wood or bone) collected at the same stratigraphic level (and closely associated) from several western Iberian archaeological sites, representing different periods of time, were dated and the regional reservoir effect (ΔR) calculated: 940±50 to -160±40 ^{14}C years. This considerable variation suggests a significant fluctuation in the strength of the Iberian coastal upwelling, which may be the result of fluctuations in the latitudinal migration of the subtropical front or of the North Atlantic Oscillation – the strength of northerly and northwesterly winds depends on these factors – or on the summer insulation – higher summer insulation results in increased sea breezes that strengthen the northerly component of the wind. Those data also enable, not only a clarification of the eventual variability of the coastal upwelling off Atlantic Iberia, but also the identification of episodes of abrupt shifts in oceanic circulation, probably coupled with sudden climatic changes. On the other hand, the viability of using radiocarbon dating of marine shells in order to get reliable chronologies was consequently tested out in this research.

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