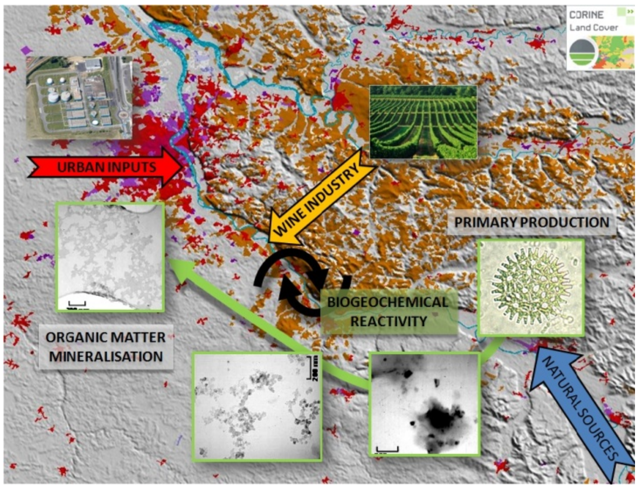
Anthropogenic activities have modified the geochemical cycle of Metallic Trace Elements (MTE, formerly known as heavy metals) by increasing tremendously their flux towards surface environments, causing long term potential exposure to living organisms and affecting ecosystems. Pollution by MTE is also critical for a number of social and economic issues as well as human health. In coastal systems, including estuaries and bays with intensive seafood production, multiple anthropogenic sources of MTE contribute to the pollution at a given site, leading to problems in developing emission controlled strategies and remediation targets. In addition, biogeochemical processes may affect the bioavailability and the mobility of pollutants and need to be accounted for. Source, fate and behaviour of metallic trace elements need to be fully understood so that remediation and regulation policies can be appropriately targeted.



ISOGIRE aimed at investigating heavy stable Cu, Zn and Ag isotope fractionation in the large scale (80000 km²) Gironde Watershed and Estuary. The objectives were to use metallic trace element (MTE) isotopes to identify and discriminate different sources of pollutions, their evolution in time, accounting also for biogeochemical processes and biological uptake of MTE that may modify their isotopic signatures. The ISOGIRE project aimed at developing the analytical methodology for Ag isotopes to evaluate their potential for identifying and discriminating Ag and Ag nanoparticles urban sources and follow their environmental route using their isotopic compositions.

New Ag, Cu and Zn isotopic data have successfully provided new geochemical models to interpret geochemical and isotopic variations in river and estuarine systems connected with their watersheds and in sentinel organisms for coastal pollution assessment (oysters). Cu and Zn isotopes have given insights into several biogeochemical processes affecting metallic trace elements, such as uptake by phytoplankton, addition of dissolved Cu by the mineralisation of organic matter; adsorption of Zn dependent on the amount of suspended particulate matter and assimilation pathways in natural oysters in the context of isotopically contrasted natural and anthropogenic sources of metals (urban, natural, industrial,...).

The Gironde Estuary and its maximum turbidity zone (MTZ) developing in the Garonne Branch, exhibit strong physicochemical and biogeochemical gradients. These changing physicochemical and biogeochemical characteristics strongly affect dissolved Zn and Cu concentrations in two contrasted ways: Cu is characterized by a continuous addition from the particulate to the dissolved phase whereas Zn is strongly absorbed (= subtraction) onto particles in the Estuary. These processes affect isotopic compositions of dissolved Cu and Zn, as well. Elemental and isotopic biogeochemistry of Cu in the Gironde Estuary was strongly linked to that of organic matter: phytoplankton assimilated light Cu isotopes while the mineralisation released preferentially heavy Cu isotopes in solution, corresponding to a reactive mixing following grossly a Rayleigh process. In contrast, dissolved Zn showed a strong removal by adsorption onto suspended particulate matter (SPM) and displayed a progressive enrichment in heavy isotopes with increasing SPM concentrations varying from δ^{66}Zn = -0.02 ‰ at 2 mg/L to +0.90 ‰ at 1313 mg/L. The range of variation in zinc isotopic composition in the Garonne River and Gironde Estuary overlapped data on World Rivers, suggesting that Zn geochemical reactivity by adsorption onto particles might be the driving process explaining the isotopic composition of dissolved Zn on Earth.

New constraints on the meaning of metal isotopes signatures in bioaccumulating *Crassostrea Gigas* oysters used to monitor spatial and temporal trends for the contamination of French coastal areas (RNO/ROCCH program) are also provided. The constant isotopic signatures of Ag, Zn and Cu in the Gironde oysters with time (from 1981 to 2012), suggested a control by geochemical reactivity of these metals in the estuary rather than by the temporal evolution of their environmental sources. Gironde oysters were characterized by enrichments in light Cu and Ag isotopes and a strong enrichment in heavy Zn, compared to either seawater or natural or terrestrial isotopic compositions of these metals. Unlike zinc, Cu and Ag are mostly characterized by additions (i.e. release of dissolved metals towards the dissolved phase). Therefore, we propose that dissolved Ag in the estuary could be enriched in light isotopes, as recorded in RNO oyster samples.

Anthropogenic and natural sources could be discriminated on the basis of isotopic signatures. The natural background, i.e. the “Geogenic” reservoir (δ^{65}Cu ≅ - 0.2 ‰; δ^{66}Zn ≅ + 0.35 ‰) has different isotopic signatures than anthropogenic sources related to (i) viticulture (δ^{65}Cu ≅ - 0.4 ‰; δ^{66}Zn ≅ + 0.12 ‰), (ii) former metallurgical activities (δ^{66}Zn ≅ + 1.3 ‰) and (iii) urban/domestic activities from the Bordeaux city (δ^{65}Cu ≅ -0.8 ‰; δ^{66}Zn ≅ +0.12 ‰). In contrast, high recoveries of Ag by nanoAg production and electroplating, small range of isotopic fractionation in metal compared to terrestrial samples and small relative contribution from PCP to urban Ag flux and to the Garonne River strongly limited the use of δ^{109}Ag to trace nanoAg in the environment.

One of the primary societal goals of the ISOGIRE project was to investigate the use of isotopic signatures to discriminated sources of Cu, Zn and Ag (and nanoAg) in the environment and thereby providing scientific tools to identify levers for regulation/remediation of metal contamination in the environment. Results from the ISOGIRE project have allowed identifying several anthropogenic sources from Cu and Zn signatures, especially with respect to urban activities and wine production. Clearly limited by its variability on Earth, the isotopic composition of Ag may have a limited interest to trace nanoAg sources, unless nanoAg producing industries are constrained to develop isotopically labeled nanoparticles (made with artificial isotopic composition, strongly enriched in one of the heavy or light Ag isotope). However, Ag is not yet recognized as a priority contaminant (European Directive 2000/60/EC) and a very broad range of Ag-NP containing products are not recognized as biocidal substances (EU Biocidal Products Directive BDP 98/8/EC). Yet, unambiguously there are environmental and sanitary risks due to Ag and Ag-NP. Beyond the ISOGIRE project, the social and political construction of these risks related to nanoAg being a very long process, we recommend that more effort should be given to dissemination of scientific results be directed towards water managers, industrials, health authorities, agencies and committees responsible for expert evaluations, environmental associations, and potential users of silver or nano-silver.