



Hydrogeological processes and geological settings over Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystem

Deliverable D.3-4: Compilation of indicators, analyses of possible use at pan-European scale and test application in countries of contrasted main litho/geology

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1 INTRODUCTION

1.1 Objectives

Trace elements are elements present in living tissues and are found in small quantities. Some of them are known to be nutritionally essential, others may be, and the rest are considered as nonessential. Trace elements function mainly as catalysts in enzyme systems. All trace elements are toxic if consumed at high dose rates over longer periods. The difference between toxic intake and optimal intake to meet physiological needs for essential trace elements is excellent for some elements, but much less for others (National Academies Press (US), 1989). An essential element cannot be replaced by any other element and if they are not present in the necessary dose, a reduction of a certain physiological function occurs or it affects a vital function (Carretero & Pozo, 2007). With all this keep in mind, the following conclusion can be made: If we need chemical elements for our body to be healthy, we are conditioned by the presence or not of these essential elements in our environment and also by the exposure doses. It is the geological context that marks the presence and quantity of these substances (nutrients or not) around us. In other words, our health depends of the geochemical environment that surrounds us. But it is also subordinate to terrestrial dynamics, to how these elements are released from the rocks that contain them to incorporate them into water, soil or air, phases or media that we ingest, inhale or with which we simply come into contact (Giménez-Forcada, 2018).

In the field of geochemistry studies, trace elements are especially interesting because they provide important information about the processes in which they participate. According to White (2013), the study of the trace element is especially relevant for several reasons: (i) although they are in low concentrations in the earth's crust, there are always many more trace elements (more variety) than majority elements; (ii) they are sensitive to processes to which the major elements are not; (iii) each trace element has properties that can be considered unique, so its presence provides very accurate geochemical information, and (iv) its concentrations can vary in much broader ranges than the main components and, therefore, its concentration provides also valuable information.

Trace elements (in particular Potentially Toxic Geogenic Trace Elements) are also sometimes the reason why some groundwater is no longer suitable for human consumption, due to concentrations above the established threshold value. Although these are very low concentrations, the minimum excess renders the hydric resource useless as drinking water.

According to the project proposal of HOVER Project, *the challenge is to gain understanding of the controls on groundwater quality across Europe using the combined expertise and data held by member states*. The main objectives would be to address groundwater management issues related to drinking water, human and ecosystem health across Europe in relation to both geogenic elements and anthropogenic pollutants by data sharing, technical and scientific exchange between European Geological Surveys.

For natural water quality it is important to consider evaluating health risks and spatial variability of concentrations of geogenic trace elements. All of this will be developed alongside common standards, databases and maps, and project outputs will include thematic maps and pan-European-scale web service tools, as well as databases available through the Information Platform to increase political and public awareness and to improve groundwater management at EU level.



It is important to emphasize that the quantity and quality of groundwater is of great importance for the economic development of Europe, since it is the most important resource for drinking water, irrigation and industrial uses.

The quality of groundwater is linked to physico-chemical parameters such as temperature, pH, redox potential and the presence of dissolved elements of geogenic (natural) or anthropogenic origin. The objective of the project is to link the natural quality of groundwater and the risk of transfer of dissolved anthropogenic elements to aquifers with geological environments and hydrogeological processes.

The HOVER project addresses groundwater management issues, drinking water, human and environmental health, linked to the **presence and spatial variability of high concentrations of geogenic elements** and anthropogenic impacts. The project also addresses the development of common standards, databases and maps. The database, at the interface of the Information Platform Project will contain information on: soil properties, geological characteristics, hydrogeological processes, data quality and physico-chemical parameters, dominating pressure at wells or well subterranean catchments. But the geographical distribution of concentration values of trace elements harmful to human and animal health must also be analyzed, **transferring the traditional hydrogeochemical knowledge of water-rock interaction to a spatial distribution**, which relates the distribution of outcrops of different geological materials and lithologies with the quality of groundwater. And not only this, but also make other spatial geological factors intervene in the geographical analysis, such as faults or other structural elements. Only in this way, from the meticulous analysis that has been carried out between tasks 3.1 to 3.3 to the attempt **to give a harmonic response to the apparently meaningless and patchy geographical distribution of some Potentially Toxic Geogenic Trace Elements (PTGTE) on a Pan-European scale in the task 3.4.**

The HOVER project is strongly linked to the Water Framework Directive (2000/60/EC) and the Groundwater Directive (2006/118 / EC) and is developed from the extraordinary results of previous European projects (e.g. BRIDGE, BaSeLiNe, AgriAs- project, etc) that lay the foundations for the bases and development of HOVER.

One of the main objectives of the HOVER Project is to determine the natural variability of concentration of elements of geogenic origin depending on the geological and hydrogeological settings. Project activities related to geogenic diversity are mainly included in the Work Package 3 on hydrogeochemistry and health: Mapping groundwater characteristics for the management of aquifers naturally enriched in dissolved elements.

High concentrations of elements in groundwater result in human health concerns and for good status objectives for groundwater itself and associated surface waters. High concentrations of Potentially Toxic Geogenic Trace Elements (PTGTEs), such as arsenic and fluoride, in drinking water can pose a serious risk to human health and therefore recommendations for best management practice in the context of naturally high concentration are proposed. A very large number of countries involved have been participating in these specific activities that are aimed to strengthen the methodology and map various management indicators (Natural Background Level (NBL) and HydroGeoToxicity (HGT) indicators).

The analysis of dissolved trace element concentrations in groundwaters is sometimes difficult, and indicators are an excellent alternative. Task 3-4, entitled "Natural background levels and health - determination and selection of indicators for WG management", led by the IGME, aims to know the Base Reference Concentration (BRC) for As and F to evaluate their hydrogeotoxicity



(HGT) levels considering Europeangeology. The NBL or reference base levels are covered in detail in Task 3.3, and here it will be taken into account only as a reference index.

The current European legislation on limits and guide values for certain chemical parameters dissolved in drinking water are included in the *Quality of water intended for human consumption European Parliament legislative resolution of 28 March 2019 on the proposal for a directive of the European Parliament and of the Council on the quality of water*, P8_TA-PROV (2019) 0320, intended for human consumption (recast) (COM(2017) 0753 – C8-019/2018 – 2017/0332 (COD)), part B of Annex I (*Minimum requirements of the parametric values used to assess the quality of water intended for human consumption*). Threshold values for arsenic (10 µg/l) and fluoride (1.5 mg/l) are defined in this legislation. However, there are other national legislation, as example, Danish legislation, which establishes a lower limit or MAC (Maximum Admissible Concentration) value for arsenic concentration in groundwater: 5 µg/l (Stockmarr, 2005; Ramsay et al., 2021).

HydroGeoToxicity (HGT) indicator is defined as the quotient between the concentration of a particular PTGTE (Potentially Toxic Geogenic Trace Element) in a specific water sample and the upper limit value for that element in potable water according to the drinking water regulations (Giménez-Forcada et al., 2017a). Hydrogeotoxicity is a sterling indicator because it relates the concentration of a PTGTE with the limits established for a safe drinking water, according to the national or international regulations; usually the limits set by the World Health Organization are taken into account.

In this part of the HOVER project (Task 3.4), arsenic (As) and fluoride (F) have been studied in relation to the geological environment, at a geological Pan European scale. Their relationship with different percentiles extracted from the analysis of the Cumulative Frequency Curve (CFC), has also been considered to calculate the Basal Reference Concentration (BRC) index. The BCR corresponds to P₉₈, corresponding to the beginning of the last section of the CFC, when it tends towards horizontality. This index signifies a maximum level of requirement for spatial analysis and its relationship with regulatory geological factors.

These values and their interrelations provide a study methodology that can be extended to other PTGTEs elements and to other geographic areas. Its use represents the ability to identify areas of high natural concentration in relation to the lithological context at EU level in a large region, as well as tectonic features (local and regional fractures).

1.2 Background

In traditional hydrochemical studies that address the analysis of trace elements (such as As and F) in groundwater, the data analysis considers their behaviour with respect to the physico-chemical parameters (as pH, Eh, etc.) that regulate their concentration in groundwater. The main process taken into account is the water-rock or sediment-water interaction in the surroundings of the sampling point. For this, the materials with which the groundwater comes into contact are analysed and contrasted with the results of the chemical analysis and physico-chemical parameters of groundwaters. They are usually very detailed studies that reveal the main mechanisms of release of trace elements to groundwater.

But the development of Task 3.4 intends to offer a new perspective, complementary and not alternative, to traditional hydrogeochemical analyses. In this task, the distribution of As and F in groundwater will be spatially analysed in relation to visible geological factors on the surface using different indices. Two PTGTEs of great importance for health, As and F, which require rigorous control of their concentration in drinking water, will be considered. It intends to do this on a pan-



European scale, joining data from all the countries that have provided their information. The final objective is to check whether, at a spatial level, geographically the European lithology could be related to the distribution of the maximum anomalous concentrations of these trace elements. But not only with lithology, but also with the structural factor that, on occasions, controls the distribution of lithology (folds) or they are preferential lines of flows, some of them preferential groundwater flow channels enriched in PTGTE.

The antecedents of this approach are several studies carried out in Spain, which have yielded good results. For example, the application of statistical analysis techniques in the study of the spatial distribution of trace elements in groundwater of a coastal area with complex salinization processes (Castellón and Sagunto coastal plains) (Giménez-Forcada and Vega-Alegre, 2015). But, definitely, the example that can better illustrate the approach to the analysis that will be read below, throughout the report, is the one carried out in the south of the Duero Basin.

In 2014 Giménez-Forcada and Smedley published the first work (Giménez-Forcada and Smedley, 2014) about the control of arsenic distribution in the area by structural faults. This work was the precursor to two others that were published three years later: Giménez-Forcada et al., 2017a, 2017b. The first of them statistically analysed the chemical results and as a consequence the presence of As was related to a particular type of groundwater (NaHCO_3), named cold-hydrothermal flows. In particular, these flows were the primary source of As contributions to the detrital aquifer of the Duero Basin. The analysis of the spatial distribution of these results, gave as a result that these waters were closely related to the structural directions of the mountainous massifs of the southern Duero Basin (metamorphic and igneous rocks, which constitute fissured basement aquifers), which extended into the sedimentary basin. Its distribution in the sedimentary aquifer followed the prevailing fault guidelines (NW-SE and NE-SW). In this mentioned work it was also seen that As was accompanied by other PTGTEs such as V, U, or Cr. In the 2014 study, it was detected in some of these waters also the presence of F, B, Li, and Mo, all of them trace elements that are usually related to hydrothermal flows or related to deep aquifers (Giménez-Forcada and Smedley, 2014).

Another aspect that the 2017 work addressed (Giménez-Forcada et al., 2017a) was that these waters contributed as primary As to increase the occurrence of As in the surface aquifer when they were used for irrigation and that this practice initiated an escalation in the dispersion process in the sedimentary environment. In this superficial environment, it is where research work has been carried out in the last 20 years on the subject of arsenic in groundwater in the Duero Basin. Most of them focused on sediment-water reactions and the role of iron oxy-hydroxides in controlling As concentration in groundwater.

A further step was taken in the following work in 2017 (Giménez-Forcada et al., 2017b): where hydrogeotoxicity (HGT) by As and U in the groundwater of the south of the Duero Basin were analysed. HGT_{As} and HGT_{U} sometimes went hand in hand (coincided with some relevant fracture lines), configuring a combined and complex hydrogeotoxicity by arsenic and uranium, $\text{HGT}_{\text{As,U}}$. Other times this was not the case and each element showed its own behaviour.

In all these analysis, it was a great advantage that the study zone was located right in the area where the great fault-dike of Messejana-Plasencia, which begins in the south of Portugal and has a route of 550 km, is lost under the sediments of the south Duero Basin. The main anomalies were in the deep wells that had been drilled along its extension in the Cenozoic aquifer of the Duero.

The results of these studies could be valid in other scenarios and also for large areas of territory because the geology could be observed on small scales covering large territories. Hydrochemical



studies would be done with a **new perspective** as a whole (*geo-hydrochemistry*), also seeing the distribution of As and F in groundwater as a consequence of the Geotectonic evolution of Europe: lithology and fault structures were elements to take into account in the spatial analysis of the distribution of PTGTE As and F on a Pan-European scale.

A good result would mean having a valuable tool at hand: geological knowledge would lead to prediction, prevention, and improvement of groundwater management and public health.



2 HYDROGEOTOXICITY BY POTENTIALLY TOXIC GEOGENIC TRACE ELEMENTS (AS AND F) AND OTHER INDEXES

2.1 Concept of HGT by PTGTE

Water is an essential resource and in many arid and semi-arid regions groundwater is the only available resource for public supply. For drinking water, the Drinking Water Directive of the European Union imposes stringent quality criteria. High concentrations of Potentially Toxic Geogenic Trace Elements (PTGTE) (as arsenic, chromium, uranium, boron, fluoride, etc.) in drinking water can pose a risk to human health and impose restrictions on the use of safe drinking water.

The relationship between groundwater quality (which is closely related to the geological setting) and environmental health particularly takes into account the distribution of PTGTE (mainly metals and metalloids) due to their possible influence on public health. Natural waters play a fundamental role in the transfer of these trace elements from the physical environment to the biosphere and, therefore, are fundamental for the dynamic interrelation between the natural environment and human health. The geological environment is the one that largely determines the presence of certain trace elements in groundwater and, although rocks and minerals do not necessarily contain high concentrations of these elements. However, it is relatively common to find groundwaters that contain concentrations above the permissible limits. Moreover, the legality of the reference limits established for these elements in drinking water are commonly very low (in the order of tens of micrograms per liter). Paying sufficient attention to the HydroGeoToxicity (HGT) potential of certain areas is part of the optimal management of groundwater resources in areas affected by high concentrations of PTGTes.

The concept of HydroGeoToxicity (HGT) (Giménez-Forcada et al., 2017) needs to be introduced to speak not only of concentrations, but rather of the concentration of a particular element compared to its limit value for the supply of drinking water. HGT is defined as the ratio between the concentration of a particular PTGTE in a specific water sample and the upper limit value for that element in drinking water in accordance with drinking water regulations (WHO):

$$HGT_{PTGTE} = [PTGTE_{water}] / [PTGTE_{WHO}]$$

HGT_{PTGTE} values > 1 indicate that the concentration exceeds the allowable limit for drinking water. Also, not only the HGT of an element should be taken into account, but the possibility of a combined or multiple HGT, which is the sum of more than one individual HGT_{PTGTE} (Giménez-Forcada, 2017).

2.1.1 Arsenic

Arsenic is identified as a problem in a number of large aquifers in various parts of the world, occurring at concentrations above 50 mg/L, and often significantly higher. The most noteworthy cases occur in parts of Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Romania, Taiwan, Vietnam and many parts of the USA, particularly the SW (Smedley and Kinniburgh, 2002). Groundwaters with elevated concentrations of arsenic are not necessarily linked to areas with high As concentrations in the source rocks. In Europe, countries such as Austria, Denmark, France, Hungary, Romania, Portugal or Spain have groundwaters with concentrations of As above the EC drinking-water limit of 10 µg/L.

Arsenic is a strongly chalcophile element and occurs as a major constituent in arsenates, sulphides and sulphosalts, oxides, arsenides and arsenites. The most common As minerals are

ore minerals or their alteration products (i.e., secondary mineral precipitations such as ferrihydroxides or goethite). Although arsenopyrite (FeAsS) is the most abundant As ore mineral, arsenian pyrite ($\text{Fe}(\text{S},\text{As})_2$) is probably the most important source of As in ore deposits (Nordstrom, 2000). Arsenic is incorporated into primary rock-forming minerals to a limited extent, for example, by the substitution of As^{3+} for Si^{4+} , Al^{3+} , Fe^{3+} and Ti^{4+} . Arsenic concentrations in silicate minerals are typically $\sim 1 \text{ mg kg}^{-1}$ or less (Smedley and Kinniburgh, 2002).

Arsenic is a ubiquitous element, widely distributed in the environment. It is considered to be a bio-essential trace element at a very low dose, but, in general, it is potentially toxic. Arsenic is one of the 10 chemicals that the WHO considers most dangerous to public health. The International Agency for Research on Cancer (IARC) has classified arsenic and arsenic compounds as carcinogenic to humans. Similarly, the arsenic present in drinking water has also been included in this category by the IARC.

The WHO recommends $10 \text{ }\mu\text{g/L}$ for the concentration limit in drinking water, but when there are problems to respect the guideline value, countries can set higher or lower limits. These recommendations are made taking into account local circumstances. In the EU the limit value for drinking water is $10 \text{ }\mu\text{g/L}$, although in Denmark drinking water limit is $5 \text{ }\mu\text{g/L}$. In the Netherlands, drinking water companies aim to supply water with As concentration of $<1 \text{ }\mu\text{g/L}$ (Ahmad et al., 2020).

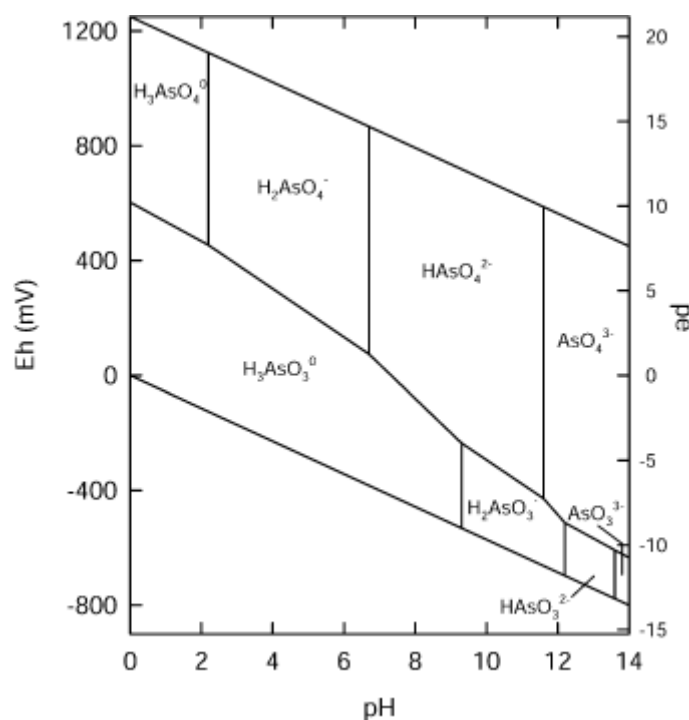


Figure 1. Eh-pH diagram for aqueous As species in the system As–O₂–H₂O at 25 °C and 1 bar total pressure (Smedley and Kinniburgh, 2002).

In natural groundwaters arsenic occurs as arsenate, As(V) and arsenite, As(III). Under reducing conditions, the prevailing species is arsenite (H_3AsO_3) over a wide pH range. Under oxidizing



conditions, arsenate oxyanions (H_2AsO_4^- or HAsO_4^{2-} , according to water pH) are dominant (Figure 1).

Arsenic mobilization is frequently controlled by adsorption/desorption equilibria, and redox and pH conditions. Clay minerals and oxides and oxyhydroxides of iron and manganese have strong sorption capacities for arsenic and so their presence is a significant factor in defining the behaviour of arsenic in natural groundwaters (Smedley, 2008).

Arsenic is also recognized as a tracer in geothermal systems. In such settings, it appears alongside B, F, Hg, Li, Sb, Se, Tl, and H_2S , which are all recognized nowadays as contaminants with a geothermal origin (Webster & Nordstrom 2003). According to Baur and Onishi (1969), Ballantyne and Moore (1988), and other authors, many hot springs contain appreciable amounts of arsenic, and it is considered as an important trace constituent in geothermal fluids, ranging in concentration from less than 0.1 to nearly 50 ppm. Moreover, the sedimentary environment plays an important role in the As geochemical cycle and great amounts of arsenic are present in these materials Baur and Onishi (1969).

A common feature of many aquifers contaminated by arsenic is the pronounced spatial variability of As concentrations in groundwater, making it difficult to predict their concentration in a particular zone or well based on the results of nearby wells (Smedley and Kinniburgh, 2002). The lack of understanding about the present pattern of arsenic concentrations may lead to inadequate or inefficient approaches for regulation. These solutions also generate high costs for both the public administration and users. If we knew the geological factors that control the distribution and mobility of arsenic in groundwater at regional, country or European level; that is, we would have to identify the factors and how they regulate the distribution of arsenic, we would have prediction tools lead to an adequate and efficient management of water resources.

2.1.2 Fluoride

Fluorine is a chemical element from the group of halogens, which is a gas (F_2) at room temperature, and which in water occurs as a fluoride ion (F^-); it is also an essential element in the human diet (Edmunds and Smedley, 2005).

Oral health today is largely based on prevention, which has a lot to do with the use of fluoride. This is because fluoride deficiency is linked to the incidence of cavities. The cycle of demineralization and remineralisation on the surface of the teeth occurs continuously in the mouth. Whether we are in one part or another of it depends above all on the pH in the mouth. If the acidity on the tooth surface is below 5.5, demineralization occurs, but if the pH rises above 5.5, remineralisation occurs. Well, in this cycle of demineralization and remineralisation of the tooth, fluorine facilitates the remineralisation process by the formation of fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), which is more resistant to acidic pHs than hydroxyapatite, because it begins to dissolve at lower pH values (of 4.5) (Carretero and Pozo). For this reason, fluoride is considered essential as resistance to tooth decay is an important physiological function. In fact, for the prevention of dental caries, the Public Health Service (PHS) has recommended, since 1962, that public water supplies contain fluoride in a concentration range between 0.7 and 1.2 mg/L (ATSDR, <https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=212&tid=38>).

In order to improve the strength of the teeth, the water supply is sometimes fluoridated. This apparently good measure has a risk because fluoride is one of those essential elements that has a very narrow range of optimal dose. Excessive doses of fluoride cause dental fluorosis and, in extreme cases, skeletal fluorosis. The adult intake of amounts greater than 5 mg of fluoride per day from all sources probably represents a significant risk of skeletal fluorosis.



The maximum guideline value set by the World Health Organization (WHO) for fluoride in drinking water is 1.5 mg/L.

Many countries also use this value as a national standard for drinking water; others, such as China and India, require lower values (1.0 mg/L), while others allow higher values, such as the USA, where the Environmental Protection Agency (EPA) has established a mandatory limit of 4 mg/L for fluoride in drinking water, or Tanzania, where the national standard is 8 mg/L. These high values reflect the difficulties in complying with the values established by the WHO, either due to water shortages or high regional concentrations.

The distribution of fluoride in the earth's crust and in the waters is uneven. In groundwater, its concentration is closely related to the abundance of this element in the minerals and rocks with which the water is in contact. It has been found that there are high concentrations of F in groundwater associated with crystalline basement rocks (particularly granites), active volcanic areas and in geothermal environments (Edmunds and Smedley, 2005). It has also been found that high concentrations of fluorine are related to long residence times in aquifers and in the deeper areas of them. On the other hand, when fluorine cannot be incorporated in crystalline phases during crystallization and differentiation of magmas will be accumulated in hydrothermal solutions. These fluids may form hydrothermal fluorite deposits and veins. The most abundant fluorine mineral in the hydrothermal cycle is fluorite, which often forms fluorite veins and is in many instances associated with sulphide ores. In waters, the mean concentration of fluoride in ocean water is 0.03 to 1.35 mg/L, whilst in hot spring waters can reach until some tens of mg/L (Allman and Koritnig, 1978).

2.2 Other indexes: BRC vs. HGT by PTGTE

The natural baseline of groundwater chemistry (NBL) shows a range of concentrations for each dissolved element that depends on the aquifer mineralogy, facies changes, flow paths, and residence time, among other factors (Edmunds et al., 2003). According to these authors, knowledge of the natural reference quality of groundwater is an essential prerequisite for the understanding of pollution and for imposing regulatory limits, however it is also a needed starting point to show positive anomalies of some trace elements, especially the PTGTE.

Nowadays, opinions differ on the precise meaning of the concept of *baseline* (BL) in the context of groundwater chemistry. In the British Geological Survey line of work denominated *Defining and investigating the groundwater quality baseline* (BGS, <https://www.bgs.ac.uk/research/groundwater/quality/BaselineUK/baselineMore.html>), the *baseline* in a specific system is defined as the concentration range (within) of an element, species or chemical substance present in solution that is derived by natural processes from natural geological, biological or atmospheric sources.

When the perspective of health is included into the analysis of Natural Background Level (NBL) or Background Level (BL) and the concentrations of the elements dissolved in groundwater are analyzed taking into account the guidelines established by the regulations for drinking water, these concepts take on a new scope. It is necessary to take into account a threshold that involves the highest level of demand in the spatial analysis of the distribution of concentrations of As and F. A spatial analysis on European geological cartography that defines the natural environment seems opportune and necessary.

There is an index that could be considered as essential for the interpretation of the geographical distribution of PTGTE in groundwater on a geological basis. It is about the **Basal Reference Concentration (BRC)** for a given PTGTE in an area, which use the highest PTGTE concentrations to

create a geographical pattern of hydrochemical anomalies, so that they can be related to the geological or hydrogeological patterns to find correlation.

For this purpose, the BRC is chosen by being the governing highest threshold value, above Q_3 (75th percentile) and NBL/BL (90th percentile, according to the analysis done in Task 3.3) and, located at the point that marks the beginning of the last section of the curve, when it tends towards horizontality.

Regarding other percentiles, **the BCR means a maximum requirement level when considering the highest anomalies in the PTGTE distribution pattern (As and F) and their probable relationship with governing geological factors.** In other words, interpreting these significantly high concentrations means identifying the factors that have the greatest impact on the occurrence and distribution of PTGTE in groundwater.

Ruling out large-scale contamination, the geographic pattern created by the distribution of the highest concentrations only can be interpreted in a natural context to find answers about the geological (natural) control that exists in the distribution of these hydrochemical anomalies. The most significant geological factors are lithology (types of rocks and water-rock interaction processes) and the structural features (faults and folds) (see e.g. Giménez-Forcada and Vega-Alegre, 2015; Giménez-Forcada et al., 2017a).

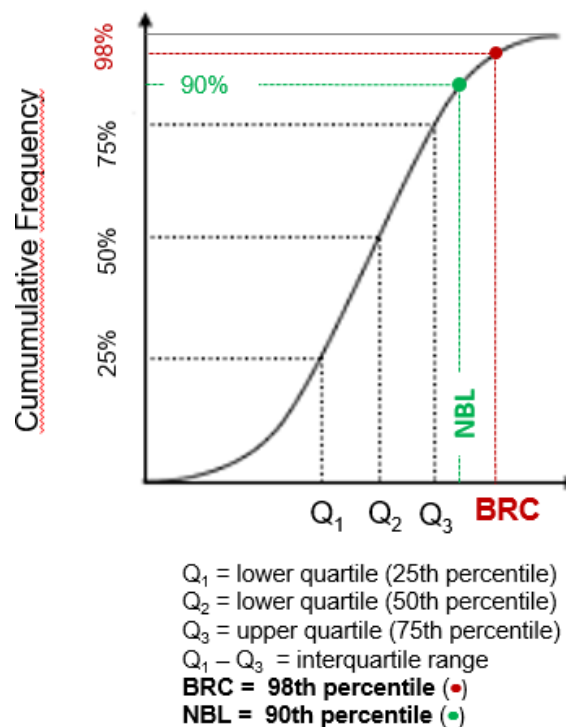


Figure 2. Position of Basal Reference Concentration, BRC (P_{98}) and Natural Background Level, NBL (P_{90}) in the Cumulative Frequency Curve, CFC



3 DATA PROCESSING METHODOLOGY

3.1 Data collection

The first step to reach the task *mapping groundwater characteristics for the management of aquifers naturally enriched in dissolved elements* was to set up an observation network of all participating members. Throughout these months, along 2020, different calls were made. The scope of the first requirement was to collect As data at the European level for the year 2016 from fourteen countries that participated. Some months later, for the second call and following, more information was requested, including fluoride concentrations and major chemistry. At this time, there is the participation of 17 countries that have provided data for As and sometimes also F, which is an important contribution when it comes to approaching the analysis of the distribution of these PTGTE for the first time with a Pan-European perspective.

Moreover, we have collected data from six case studies in Task 3.4 to analyse the distribution of As and/or F as *country study areas* (Austria, Denmark, Belgium, Serbia, Spain, and Sweden), and three cases of *local study areas* (from Austria (Carinthia region), France (Morvan granitoid), Serbia (Fruška gora), and Spain (Duero Basin)).

3.1.1 Questionnaire/Data Tables

During the first appeal, the required data were coordinates of the water sampling point and As concentration in µg/L. Although the result was very satisfying and promising, some questions required some adjustments, as a similar coordinate system, datum, statistical data, etc. which were taken into account for compilation of data collection in the second call of the database.

The base table was prepared to collect data for tasks 3.3 and 3.4. ("WP3_Task_3-3_3-4_NBL_data_compilation_table").

For participating countries in Task 3.4 it was required to contribute As and F concentrations in groundwater, and to provide the main statistical values (average, median, maximum, minimum and standard deviation) for the chosen trace elements and information for every water sample point. Further required parameters comprised physico-chemical parameters as electrical conductivity, at 20°C, pH and temperature (°C), as well as representative hydrochemical facies was (see Sheet **T3.4 All Countries** in "WP3_Task_3-3_3-4_NBL_data_compilation_table").

A		B		C		D		E		F		G		H		I		J		K		L		M		N		O		P		Q		R		S		T		U		V		W		X		Y																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																									
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Figure 4. Table header in the sheet **T3.4 Study areas**, belonging to *WP3_Task_3-3_3-4_NBL_data_compilation_table* questionnaire.

In the sheets *Data* and *Grid location* of “WP3_Task_3-3_3-4_NBL_data_compilation_table”, information is available to complete the requested data. In the first sheet of the table (sheet *Information*), participants are requested to contribute with more general information about some physical-chemical parameters and characteristics of the points of the observation network. Some of this information is common with Task 3.3.

The data collection followed the criteria listed below, which were disclosed in the second call for data collection.

3.1.2 Collection data: DATA TABLE

a) The selected time period for data is the range 2010-2016. If you are working with a representative year (preferably 2016), this should be included in this range or be very close to the years that define it. If this is not possible, in any case include data from a representative year or range of the last 20 years.

b) The coordinates system should be offered in two ways only: geographic coordinates or EEA1km grid (<https://www.eea.europa.eu/data-and-maps/data/eea-reference-grids>)

c) In relation with statistics for a year range, the average, max, min, median and stD will be offered.

d) If only one As measurement was taken from a specific water point during 2016, then this field provides the As concentration.

e) The detection limits will be expressed as “-µg/L” or as “-mg/L” (negative values)

f) For decimals we will use 'commas'.

g) More statistics details:

- If all As (µg/L) or F (mg/L) analyses are below the detection limit, then “-µg/L” or “-mg/L”, respectively, is given for all computed statistics.
- If there were different detection limits, the lowest one is provided in the minimum field, and the highest one is in both the maximum and average fields.
- If one of the As or F analyses was below the detection limit, then:
 - o “-µg/L” or “-mg/L”, respectively, is given for the minimum or the maximum (whatever corresponds).
 - o The average is calculated after substituting the “-µg/L” or “-mg/L” with half of the detection limit. Example: first sample is with As concentration “1 µg/L”, the second sample is “-0,02 µg/L”, thus the average = $(1 + 0,02 \cdot 0,5) / 2 = 0,505 \mu\text{g/L}$.
- Additional field provides the number of As or F analyses in the period. It could be relevant when assessing the computed statistics.

h) No cell will be empty in the table. When there was no recorded data the cell will contain this number “999999”.

i) USE. Please, include this added information in your table.



- Use
- Supply
- Irrigation
- Farm
- Industrial
- Piezometer
- Balneology
- Mineral water

j) The table format will be as Excel 97-2003

OTHER QUESTIONS

- Try to make the network as dense as possible. The density of the sampling network is important to be able to interpret the distribution of As and F in the geological environment and establish study areas.
- If interested you can offer a study area. It should have sufficient density of observation points with the concentration of As and F and the major chemistry and physico-chemical parameters.
- Although the delivery date is June 30, as soon as you have the data available, you can send it.
- Please contribute a sheet of paper on the geology of your country in the European context. If there is also a study area, add a small text with more precise details. Areas with higher concentrations of arsenic and fluorine deserve a more detailed analysis of the geology of the area and its surroundings. Be sure to consider fault structures, guidelines, fractures, etc., especially in sedimentary basins associated with FHR.

All samples (both those located with geographic coordinates or UTM and those referenced with the grid EEA (1km and 10 km) were referenced with geographic coordinates creating a single table.

3.1.3 Participating countries

A total of 17 countries and 18 organizations have participated providing their databases on dissolved As and/or F concentration in groundwaters, for task 3.4:

- | | |
|------------------------------|--|
| 1. Austria (As) | 10. Malta (As&F) |
| 2. Belgium (Flanders) (As&F) | 11. Poland (As&F) |
| 3. Bosnia Herzegovina (As&F) | 12. Portugal (As&F) |
| 4. Denmark (As&F) | 13. Romania (As&F) |
| 5. France (As&F) | 14. Serbia (As&F) |
| 6. Hungary (As) | 15. Slovenia (As&F) |
| 7. Iceland (As&F) | 16. Spain (ICGC, Catalonia (As))/IGME (As&F) |
| 8. Ireland (As) | 17. Sweden (As&F) |
| 9. Latvia (As&F) | |

At the Pan European scale, 39,002 data points for arsenic (As) in groundwater have been provided from seventeen participating countries. In relation to dissolved fluoride in



groundwater, the network consists in 50,532 data points, corresponding to a database (DB) provided by twelve countries. If mineral and thermal water data are included (information taken from Task 3.1), the arsenic data-points would be 38,458 and 51,117 the fluorine data-points.

These are average values corresponding to each cell in cases where the information has been provided using the grid EEA_1 km (Poland and Sweden) or EEA_10 km (Romania). For the information from Belgium, the mean values of the set of samples taken at different depths have been considered. Although the measurement values for Belgium (Flanders) have all been assigned to the Cenozoic (outcrop where geographically are located the sampling points), only the shallow measurement points are indeed Cenozoic, the deeper ones belong mostly to the Cenozoic but sometimes to the Mesozoic or Paleozoic. This also deserves another clarification: for arsenic, the higher values are measured in the Cenozoic, but for fluoride, the higher values are measured in the Paleozoic and Mesozoic.

For the rest of the countries the data-points represent the actual well-locations

The Table 1 offers the participation of different countries with As and F data in Task 3.4. The observation networks of each country have been grouped together to create an observation network at the Pan-European scale or level. Figures 5 and 6 show the observation nets for arsenic (As) and fluorine (F).

Table 1. Countries participating in task 3.4 with the corresponding particularities and the proposed case studies.

Country	Organization	Call 1 (As data)	Call 2 (As)	Call 2 (F)	Study areas		
1. Austria	GBA	X	X		X	Country	<i>Carinthia</i>
2. Belgium (Flanders)	VMM	X	X	X	X	Country (Flanders)	-
3. Bosnia Herzegovina	FZZG	X	X				
4. Denmark	GEUS	X	X	X	X	Country	-
5. France	BRGM	X	X	X	X	-	<i>Morvan</i>
6. Iceland	ISOR	-	X	X			
7. Ireland	GSI	Call 1					
8. Hungary	MBFSZ	-	Call 3	-			
8. Latvia	LEGMC	X	X	X			
9. Malta	MTI	X	-	Call 1			
10. Poland	PGI-PIG	X	X	X			
11. Portugal	LNEG	-	X	X			
12. Romania	IGR	X	X	-			
13. Serbia	GSS	X	X	-	X	Country	<i>Fruška Gora</i>
14. Slovenia	GEO-Zs	X	-	-			
15. Spain (including Catalonia, managed by ICGC)	IGME, ICGC	X	X	X	X	Country	<i>SE Duero Basin</i>
16. Sweden	SGU	X	X	X	X	Country	

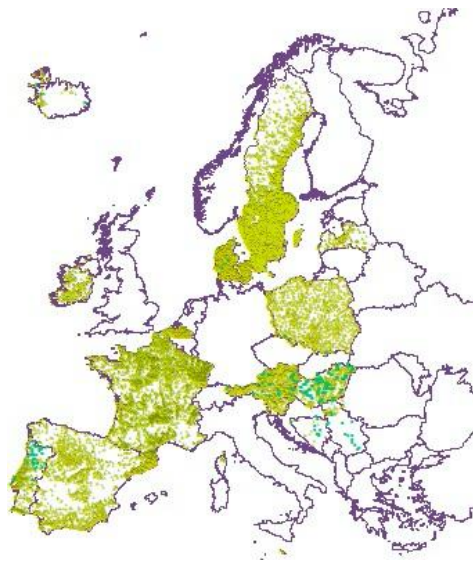


Figure 5. The distribution of points in the network of concentration of As in groundwater on a pan-European scale, with the participation of 17 countries (Austria, Belgium (Flanders), Bosnia- Herzegovina, Denmark, France, Iceland, Ireland, Hungary, Latvia, Malta, Poland, Portugal, Rumania, Serbia, Slovenia, Spain, Sweden). In yellow data points with arsenic concentration in groundwaters. In green-blue, mineral and thermal waters (Task 3.1).

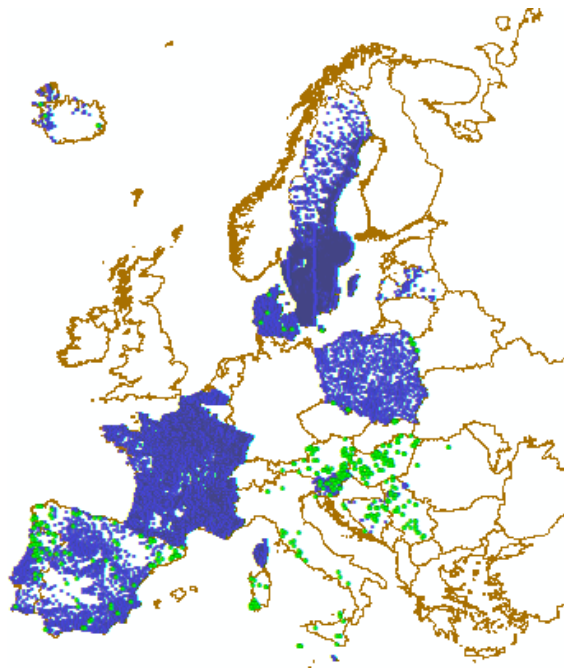


Figure 6. The distribution of points in the network of concentration of F in groundwater on a pan-European scale, with the participation of 10 countries (Bosnia-Herzegovina, Denmark, France, Iceland, Latvia, Malta, Poland, Portugal, Rumania, Serbia, Spain, Sweden). In blue, data points with fluoride concentration in groundwaters. In green, mineral and thermal waters (Task 3.1).

3.2 HOVER European geology

3.2.1 Summary European Geology

According to Ager (1975), Proterozoic movements, the various phases of the Caledonian orogeny and certain later events were clearly related to the Atlantic. The Variscan orogeny was the prelude to the Alpine and both related to the Mediterranean/Tethys. Most of the major lineaments of Europe, and many of the minor ones, are thought to be very ancient features. These in turn relate to the movement of crustal plates which periodically separated and brought together Europe, North America and Africa. Short-term episodes of plate convergence were



separated by long-term periods of crustal stability when particular types of sedimentary rocks, especially limestones and continental deposits, were laid down over remarkably large areas.

The European continent is part of the Eurasian continent and is separated from Asia by the late Paleozoic Uralian orogen. The European continent comprises two major sectors, Fennosarmatia in Eastern Europe with an Archean/Early Proterozoic basement and a Middle Proterozoic to Tertiary cover, and Central/Western/Southern Europe with Paleozoic orogens, which accreted since Silurian towards Fennosarmatia. Both sectors are separated by the **Caledonian thrust front** and the **Tornquist-Teisseyre fault** (TransEuropean suture zone), the later representing a wide zone of superposed fault-suture type structures (Neubauer, 2003).

The first emerged lands of Europe correspond to the Precambrian. These are the lands of the north and east of the continent. Since they emerged they have been functioning as erosion surfaces, so the shapes that we find in them are smooth and rounded. The materials that prevail are granites, gneisses and slates. To this group belong the regions of Scotland, the Scandinavian shield and the great Russian plain. These sets are associated with the Huronian Orogeny.

During the Caledonian Orogeny, at the beginning of the Paleozoic, the northern regions of Europe appeared. The northern lands emerged, from Ireland to Scandinavia, and the Scottish formations were rejuvenated. The reliefs of the Caledonian Orogeny were formed on very hard and deteriorated materials. These areas have been intensely affected by glacial morphogenesis down to a very low altitude. In fact, the fjords are glacial valleys flooded by the sea.

Most of the European continent appears in the Hercynian or Variscan Orogeny. The mountainous massifs arise from west to east (e.g. Hesperides Massif –Brittany, central France–, Bohemia or the Urals). Among these are shallow depressions that gradually fill in throughout the Mesozoic and Tertiary periods. The Sea of Tethys also appears: the great geosyncline with which the Alpine mountains will later be formed. The Variscan mountains became ancient massifs that were completely razed. In many places, the Alpine Orogeny rejuvenated this relief.

Throughout the Mesozoic, the entire complex acts as a large surface of erosion and the eroded materials accumulate near the large massifs. In this way the great European plains and the intramountain plains appear, over the sunken areas.

The Tethys marine geosyncline is also affected. Marine regressions and transgressions occur throughout the period. The most important ones take place at different levels of the Triassic, Jurassic and Cretaceous periods, during which a large amount of sediment accumulates. The dominant relief is the plain, with plateaus and mounds. In the Mesozoic we find large sedimentary assemblages, such as the London- Flanders-Paris basin, of marine facies and in which the materials are arranged concentrically. But, in addition, the interior graben areas are full of materials from continental facies, as is the case in the Sudetenland or the Bohemian massif. They are gently undulating regions. There are also graves of this type in the interior of the old massifs, but they were filled with sediments during the Tertiary, such as the Iberian plateaus. These sedimentary regions of the interior of the old massifs will be affected by the Alpine Orogeny that will give rise to cover folds.

During the Tertiary the Alpine Orogeny takes place, which in Europe reached its peak during the Miocene. During this orogeny, the materials accumulated in the geosyncline of the Tethys Sea are folded, but, in addition, the ancient Hercynian massifs are rejuvenated. The relief that presents, therefore, is the typical alpine relief of sharp ridges, mantles and changing folds, but also the relief of horst and graben typical of the fractured regions with raised and sunken blocks. During the Alpine Orogeny southern Europe emerged: Cantabrian Mountains, Pyrenees, Alps,

Carpathians and the Crimean peninsula in the north; as well as the Betic mountain range to Mallorca, the Apennines, the Dinaric Alps, the Balkans, Crete and Cyprus, to the south. This relief is organized around the much harder Hercynian shields.

During the Quaternary, the current relief was configured and the whole set began to act as an erosion surface in all climates. The traces of this retouch can be seen everywhere, since they have significantly modified the initial configuration, to the point of inverting the relief.

The most active periods, from the point of view of erosion, are those of reactivation, as opposed to those of biostasis. The arid periods modify the forms, especially in the south. Glaciations affect the entire continent, although more effectively to the north, during times of reactivation. It is at this moment when we find forms of accumulation and coating, hydro-eustatic, glacio-eustatic and isostatic phenomena. Ice ages have a very marked north-south incidence pattern.

According to Plant et al. (2003), like all continental masses, Europe currently comprises several blocks of the crust, which have been assembled over geological time (Figure 7).

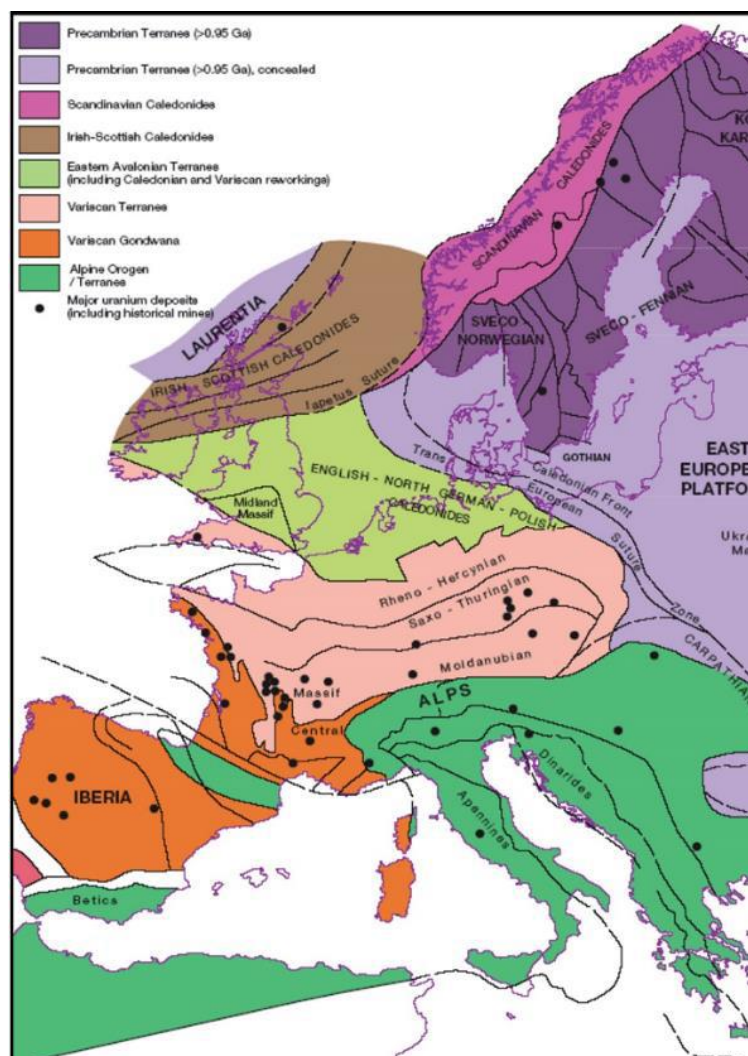


Figure 7. The 'terrane collage' of Precambrian and Phanerozoic Europe, a simplified sketch. Sutures and orogenic fronts are shown as bold lines, internal borders as thin or thin broken lines (by Plant et al. 2003).

The continental basement of Europe can be divided into two large, very distinct regions: (i) in the north and east a stable Precambrian craton known as the Eastern European Craton (CEE),



and (ii) in the south and west a mobile belt, formed by cortical blocks that have been successively incorporated into the old cratonic nucleus. The boundary between these two regions is marked by the NW-SE trending **Trans- European Suture Zone (TESZ)** (formerly known as the Trans-European Fault, Tornquist Line or Tornquist-Teisseyre Line), which stretches for approximately 2000 km. from the North Sea to the Dobrogea region of the Black Sea. The TESZ is obscured and hidden everywhere under the Mesozoic and Cenozoic sediments, but has been reasonably well defined as a broad NW-SE direction impact fault zone.

The boundaries between the main structural elements of the European continental elements are found in poorly defined places, partly as a result of a lack of data, and partly because they are hidden by younger rocks. Furthermore, metamorphic overprinting of some older orogenic areas has occurred during later orogenic cycles.

Large amounts of clastic sediments were deposited in many of the Permian basins and many of the depocenters were associated with pre-existing structural directions. On a European scale, one of the most important basin development sites was located along the TESZ (Figure 6), where geophysical data and drilling have identified deep NW-SE trending basins under powerful sequences of younger rocks. The early Permian basins along the TESZ also influenced the development of the hypersaline Late Permian Zechstein Sea, in which significant deposits of evaporites formed.

Some of the important Permian depocenters continued during the Triassic. Triassic rocks are associated with brackish continental seabeds, with shallow marine carbonates, sulfates, and halites. During the late Triassic, the clastic-evaporitic regime of the northwestern basin of Europe was synchronous with the repeated advancement of deltaic systems from Scandinavia and the EEC through the North Sea, Denmark, and the southern Baltic Sea areas.

During the Jurassic, the disintegration of the supercontinent Pangea began along the axis of the central Atlantic. During the middle and late Jurassic, new ocean basins were opened in the Mediterranean area, and Gondwana was separated from Laurasia. In Europe, the late Triassic and early Jurassic began with a great transgression of the Sea of Tethys and the establishment of a wide and open marine platform. The development of Europe during the early Cretaceous continued to be dominated by the extent of the crust, associated with the North Atlantic rift system, with little change in the structural framework and development of the basin. On a larger scale, tectonic activity increased in the Jurassic-Cretaceous transition.

Pre-Alpine basement rocks of Caledonian and Variscan age outcrop in scattered areas of the Alps, and are most abundant in central Europe. The Alps continue to be affected by a compressive stress regime associated with thickening of the crust.

The subsidence of the Neogene Pannonian Basin was associated with significant deformations during the Late Cenozoic, when large posterior arc basins were formed due to anomalous crust thinning and a high geothermal gradient.

Surface deposits cover most of Europe, from degraded soils and bedrock to sediments of fluvial, lake, glacial, aeolian, coastal, estuarine and swamp origin, which are believed to have been deposited during the last 2.4 Ma.

The Quaternary period was clearly a time of frequent and marked climatic oscillations, where the coldest periods exhibited mean annual air temperatures well below 0 °C. During the intermediate (interglacial) warm episodes, when the temperatures did not differ from current, the ice sheets retreated or disappeared, leaving characteristic depositional landforms and interglacial sediments.



European glacial advances generally extended beyond the Scandinavian shield. They were thick layers of ice that, as they expanded, enclosed large amounts of water so that the global sea level fell and land bridges appeared that united most of the mainland areas and the current islands in a single mass. In the heart of Pheno-Scandinavia, glacial erosion cut deep valleys and deposited thick, often complex streams interspersed with clay, boulders, sand and gravel, and windblown sand and dust (loess). As the ice sheets advanced, the main rivers were diverted, dammed to form lakes, river terraces were cut and new drainage basins were created.

Quaternary deposits cover much of the "lowlands" of Europe, covering mainly the geology of the bedrock. These deposits were partly created and certainly transported by glacio-fluvial and wind processes. The consequence of this complex genesis of erosion and deposition is that material from localized mineral sources is very likely to disperse in the direction of the resulting net transport, giving rise to elongated geochemical anomalies that extend considerable distances from the area of the fountain.

3.2.2 HOVER European geological reference map.

To know the relationship between the distribution of As and F concentration, and their indices associated with the concept of health, with geology on a European scale it was necessary to have a geological map of Europe as a reference. The map selected in its version for ArcGis was the one prepared by the Bundesanstalt für Geowissenschaften und Rohstoffe, BGR (Federal Institute for Geosciences and Natural Resources), whose purpose was and is harmonize the geological data across borders and to provide them to the general public. In late 2010 the One Geology-Europe portal went online, and since then it provides an harmonized geology at the scale 1:1.000.000. In cooperation with the Commission for the Geological Map of the World (CGMW) and UNESCO BGR published different geological maps of Europe. The geological information and the data which were needed for the mapping was collected from sources of geological surveys of Europe (EuroGeoSurvey) and other European research (BGR, https://www.whymap.org/EN/Themen/Sammlungen-Grundlagen/GG_geol_Info/Karten/International/Europa/europa_inhalt_en.html?nn=2032128, august 2020)

On this basis, a lithological and chronostratigraphic association has been made to simplify the European Geology. It is with this simplified version, the basis of which we will detail later, that the distribution of the trace elements selected have been analysed.

Igneous and metamorphic rocks were considered independent of the stratigraphic column and this differentiation was respected because it was understood that these rocks were the main primary sources of the trace elements As and F (Figure 8).

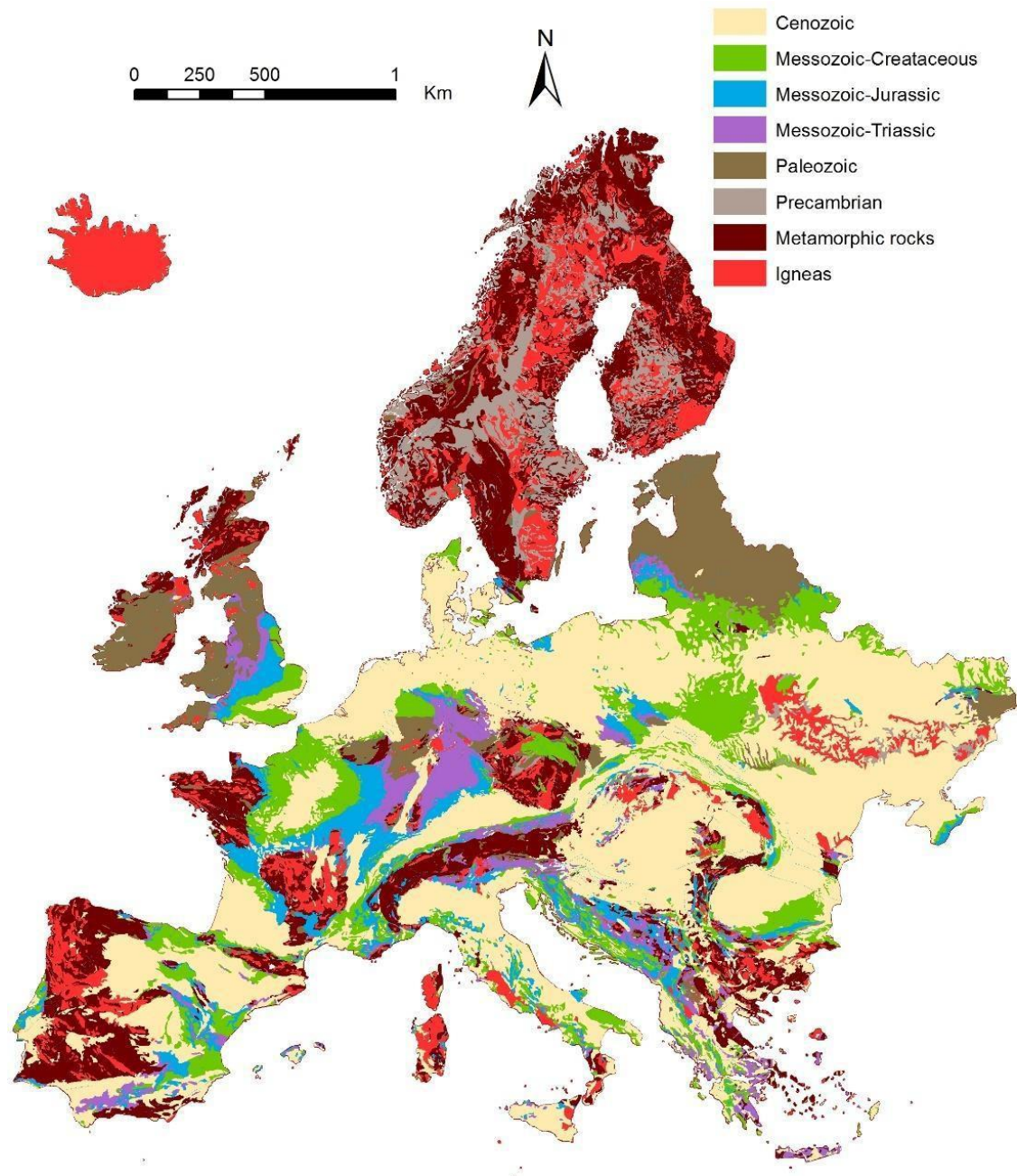


Figure 8. Simplified Geological map of Europe (according BGR, https://www.whymap.org/EN/Themen/Sammlungen-Grundlagen/GG_geol_Info/Karten/International/Europa/europa_inhalt_en.html?nn=2032128, august 2020) - Modified

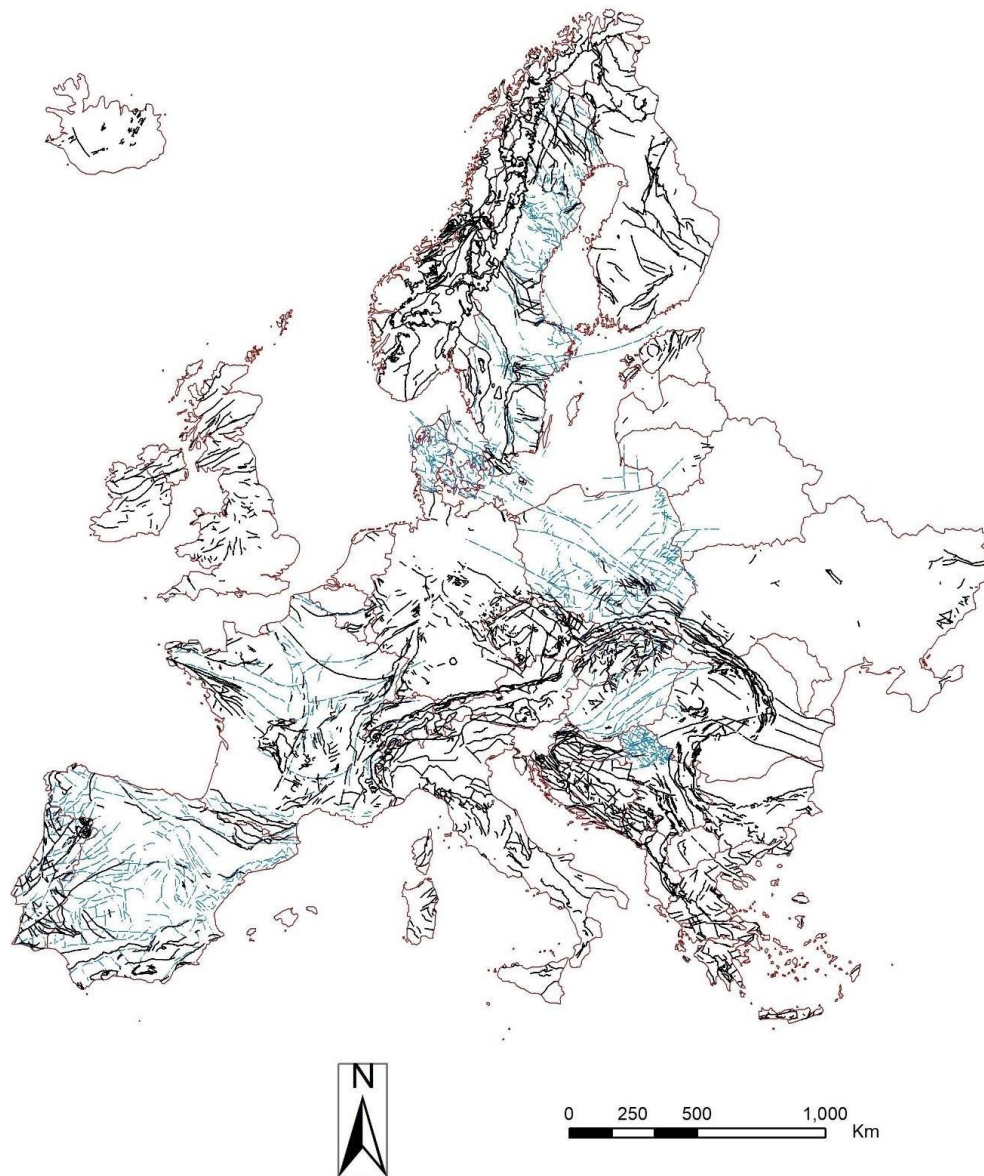


Figure 9. Tracing the fault lines (BRG, 2020, modified) and other faults according different research papers, technical reports, projects and maps (Debelmas, 1974; Arthaud andMatte, 1975; Marfil and de la Pena, 1987; Martínez-Catalán, 1990; Matte et al., 1990; BRGM-SGN, 1996; Clausen and Pedersen, 1999; Pharaoh, 1999; Wéber, 2002; Marović et al., 2002; Nielsen et al., 2003; DeVicente et al., 2004; Lagerbäck, and Sundh, 2008; Nielsen et al., 2010; Juhlin et al., 2010; Bergman et al., 2012; Thorsen, 2013; Małolepszy et al., 2015; Nielsen et al., 2015; Sušić et al.,2015; Barford et al., 2016; Briaïs et al., 2016; Hseinat and Hübscher, 2017; Békésia et al., 2018; Kufrasa et al., 2019; Baroň et al., 2019)

The stratigraphic column was simplified by grouping a whole series in the same colour until obtaining a geology that synthesized the main lithological features, respecting the chronostratigraphy. In this way, the Precambrian, Paleozoic, Mesozoic- Triassic, Mesozoic-Jurassic, Mesozoic-Cretaceous and Cenozoic (Tertiary and Quaternary) blocks were individualized. The three shapes of the faults were preserved, as well as the limits and extent of



the seawater mass/es. With this geological compendium, the geogenic anomalies of arsenic and fluorine in groundwater have been contrasted.

Interpreting the influence of fault structures on the distribution of As and F required a higher network density. With the aim of expanding this density, different technical and research works have been consulted (Debelmas, 1974; Arthaud and Matte, 1975; Marfil and de la Pena, 1987; Martínez-Catalán, 1990; Matte et al., 1990; BRGM - SGN, 1996; Clausen and Pedersen, 1999; Pharaoh, 1999; Wéber, 2002; Marović et al., 2002; Nielsen et al., 2003; De Vicente et al., 2004; Lagerbäck, and Sundh, 2008; Nielsen et al., 2010; Juhlin et al., 2010; Bergman et al., 2012; Thorsen, 2013; Małolepszy et al., 2015; Nielsen et al., 2015; Sušić et al., 2015; Barford et al., 2016; Briais et al., 2016; Hseinat and Hübscher, 2017; Békésia et al., 2018; Kufrasa et al., 2019; Baroň et al., 2019). The figures of these works have been georeferenced and added to the initial group of faults. Sometimes the type of layout was different (with a continuous line of the entire structure or with sections), but it coincided with a fault already present in the original map. The rule that has been followed has been: try to avoid obvious duplicates that could interfere in the spatial analysis, but at the same time avoid as much as possible to intervene in the original figure. Figure 9 shows tracing the fault lines according BRG (2020) and other faults.

3.3 Conceptual and statistical methods

The impacts of climate change on water resources depend not only on the inputs from the hydrological cycle, but also the way in which water resources are managed. In these cases, management becomes a determining factor of whether water resources are adequate and whether there is a deficit to meet society's demands. In this scenario, the role of groundwater resources is particularly relevant. Sustainable use of groundwater is key to achieving a minimum level of social wellbeing where surface water resources are deficient; however, the exploitation of groundwater resources requires strict controls if we wish to continue to assert that use of groundwater is a guarantee of good water quality. The framework of the WFD (2000/60/EC) and the daughter Groundwater Directive (2006/118/EC), recognize the need to adopt measures to support the quantitative and qualitative aspects of water bodies in order to ensure environmental sustainability, and guarantee access to water for human consumption through more and better water supply sources. The WFD (2000/60/EC) speaks of the need "to ensure.... the provision of the sufficient supply of good quality surface water and groundwater as needed for sustainable, balanced and equitable water use".

Trace elements, in general and, in particular, the PTGTEs are distributed in a non-homogeneous way on the earth's surface. The chemical quality of groundwater depends largely on them, even though they are in trace-level concentrations. In addition to the problems of scarce water resources, water quality problems have also been recognized due to the presence of high concentrations of PTGTEs.

On the objectives of the Task 3.4 is to elucidate the geological precepts that control HydroGeoToxicity by arsenic and fluoride concentration in the groundwater and in this way, provide a useful tool for planning and management of water resources in areas affected or potentially affected.

These results can be used as a tool in the planning and management of water resources in areas that exhibit water quality problems due to potentially hydrogeotoxic risk. If the results are satisfactory, the methodology used could be applied widely in other areas where similar problems have been identified and to any other geologically similar scenario elsewhere.



Methodologically speaking, the data for each country has been treated from two perspectives: statistically for knowing the basic statistical parameters (number of points or monitoring sites, maximum and minimum values, average, median and standard deviation) and for selecting Basal Reference Concentration (BRC) using the Cumulative Frequency Curves (CFC). Spatial methods have been applied to connect distribution of anomalous highest values with main geological factors, which could explain their distribution.

3.4 Spatial analysis methods

Geostatistics has been defined by G. Matheron as the application of probabilistic methods to regionalized variables (Matheron, 1963). At the difference of conventional statistics, whatever the complexity and irregularity of the real phenomenon, geostatistics search to discover a structure of spatial correlation. This account for the intuitive idea that closely separated points in space should be accordingly close in values.

Geostatistics is powerful for mapping and uncertainty quantification. What makes geostatistics powerful is its ability to characterize spatial variability through a consistent probabilistic model. Therefore, the predictions made using the spatial analysis methods are tailored to the intrinsic structure of the variable and not only to the sampling quantity or geometric pattern. This spatial structure is characterized by the variogram.

Kriging integrates different spatial methods applicable to diverse scenarios in which the spatial estimation of a regionalized variable is required. There are two groups of methods of estimation in Geostatistics: *parametric* and *non-parametric*. Although their theoretical bases are different, corresponding to parametric and nonparametric approaches, respectively, both lead to the local function estimation of spatial random variables. Both methods can be applied successfully in many cases.

In its simplest theoretical formulation, kriging is designed to estimate a variable Z at any point x_0 or its mean value over a domain. It is interpreted as a 'BLUE' method, i.e. the best linear unbiased estimator, this being a well-known characteristic explaining its wide acceptance in practical applications. Nevertheless, in certain situations the real problem is related not directly to estimating a variable Z at the point x_0 , $Z(x_0)$, annotated as $Z_k(x_0)$, but to the estimation of functions of $Z(x_0)$, which involves the spatial estimation of the conditional distribution function $\{Z(x_0)/z(x_i), i = 1, \dots, n\}$. A typical situation is observed in environmental sciences when the specialist looks for places where the contaminant concentration may exceed a given critical level, an 'alarm problem'; that is, whether $Z(x_0)$ exceeds a given threshold z_c .

The analysis of information has been carried out by mean geoprocessing tools of ArcGis, such as buffer, clip or intersect. By means of these procedures, it has been possible to establish the relationship between the geology and the faults with the concentration of As and F. The results of this stage of the HOVER project may allow the analysis of the potential risk of the appearance of elevated arsenic and fluoride values.

Buffer. Creates buffer polygons around input features to a specified distance.

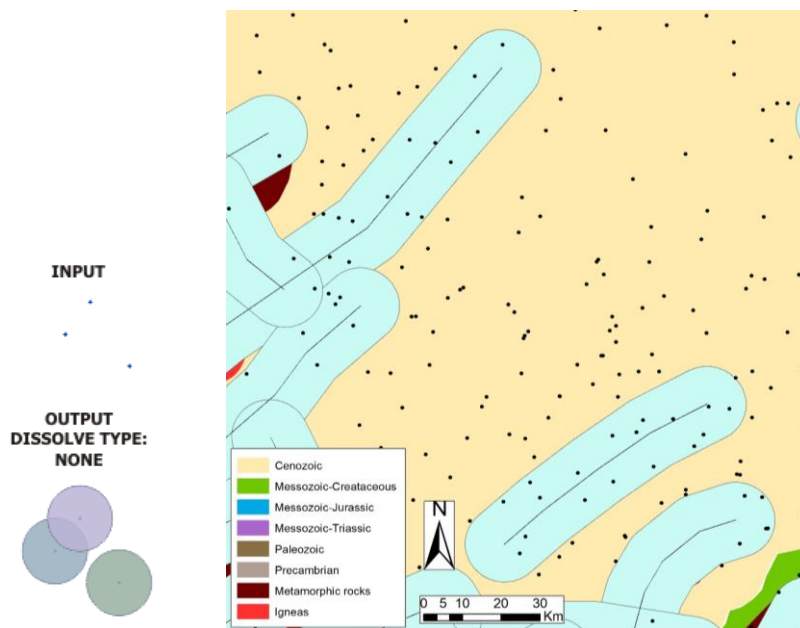


Figure 10. Representation of *Buffer* geoprocessing tool of ArcGis

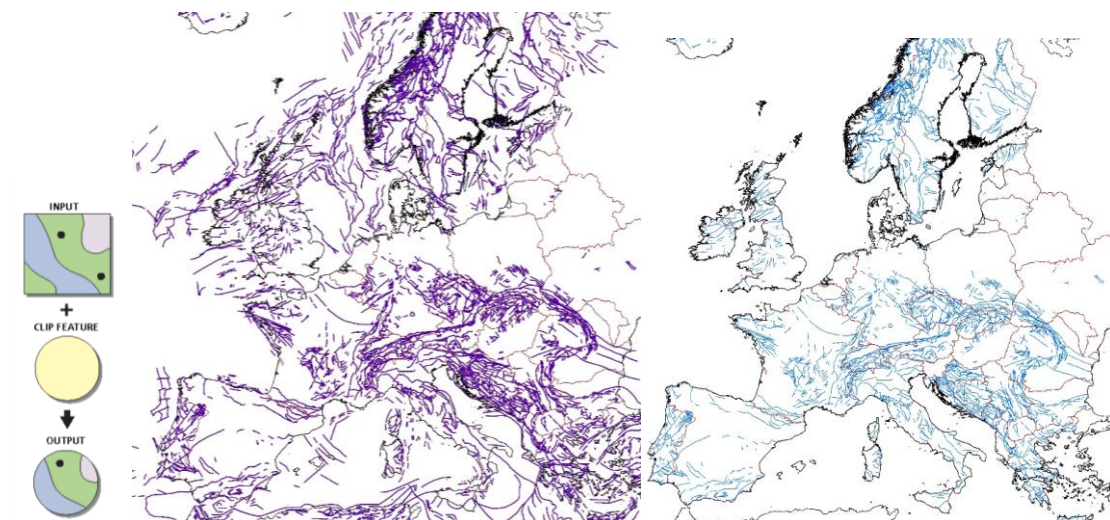


Figure 11. Representation of *Clip* geoprocessing tool of ArcGis

Clip. Extracts input features that overlay the clip features. Use this tool to cut out a piece of one feature class using one or more of the features in another feature class as a cookie cutter. This is particularly useful for creating a new feature class—also referred to as study area or area of interest (AOI)—that contains a geographic subset of the features in another, larger feature class.

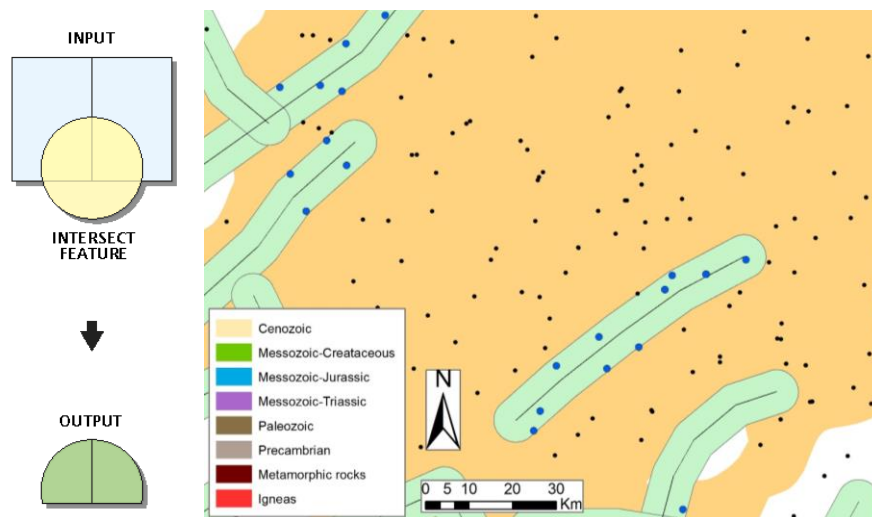


Figure 12. Representation of *Intersect* geoprocessing tool of ArcGis

Intersect. Computes a geometric intersection of the input features. Features or portions of features which overlap in all layers and/or feature classes will be written to the output feature class (Figure 12).

Union. Computes a geometric union of the input features. All features and their attributes will be written to the output feature class (Figure 13).

Merge. Combines multiple input datasets of the same data type into a single, new output dataset. This tool can combine point, line, or polygon feature classes or tables. Use the Append tool to combine input datasets with an existing dataset (Figure 14).

Dissolve. Aggregates features based on specified attributes (e.g. lithology) (Figure 15).

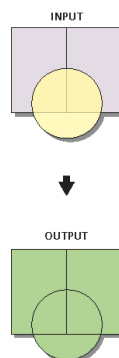


Figure 13. Representation of *Union* geoprocessing tool of ArcGis

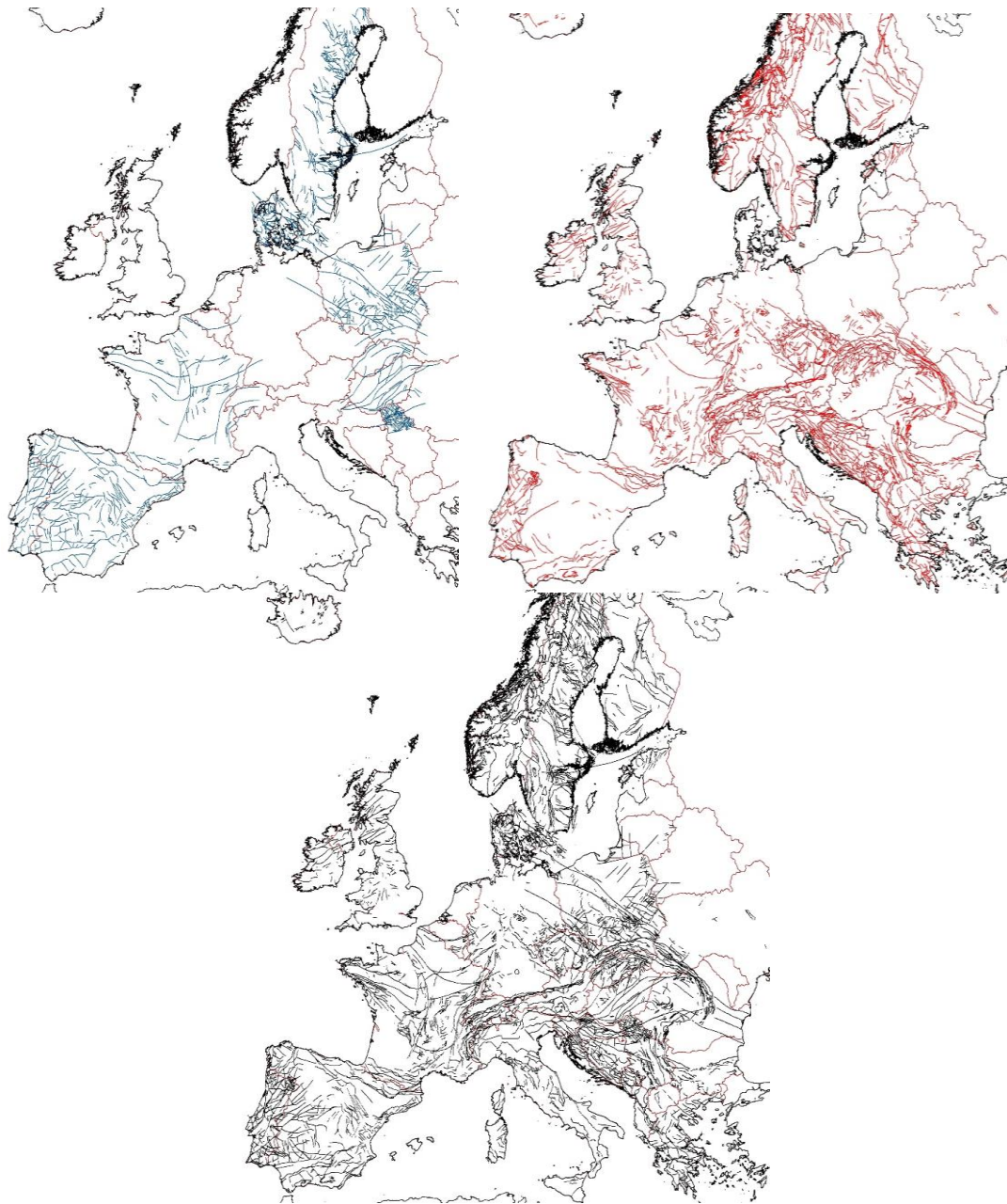


Figure 14. Representation of *Merge* geoprocessing tool of ArcGis

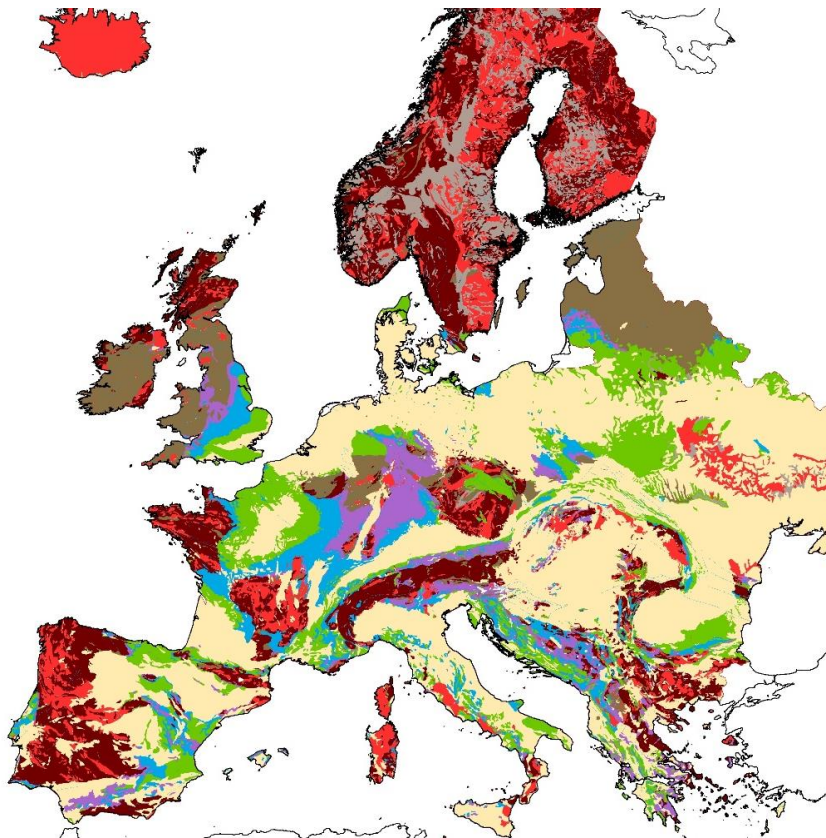
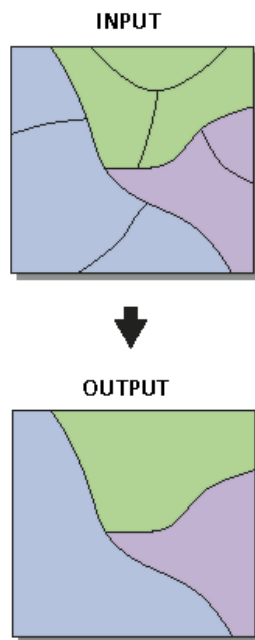


Figure 15. Representation of *Dissolve* geoprocessing tool of ArcGis

4 DATA COLLECTION

4.1 Overview of collected data

Information on the data provided by each participating geological survey is showed below.

As and F concentrations correspond to average values. This choice is based on the fact that it provides higher values than the median values. Average values are influenced by positive anomalies and, therefore, they are better help to recognize the association between high concentrations of As and/or F and geological factors (lithology and/or faults), one of the main purposes of this task.

4.2 Summary country databases

4.2.1 Austria

File As_DB: [2020_07_27_HOVER_WP3_3-4_results_Arsenic_FINAL_1+1.xlsx \(ANNEX 2\)](#)

Data provided by [D. Elster, GBA](#)

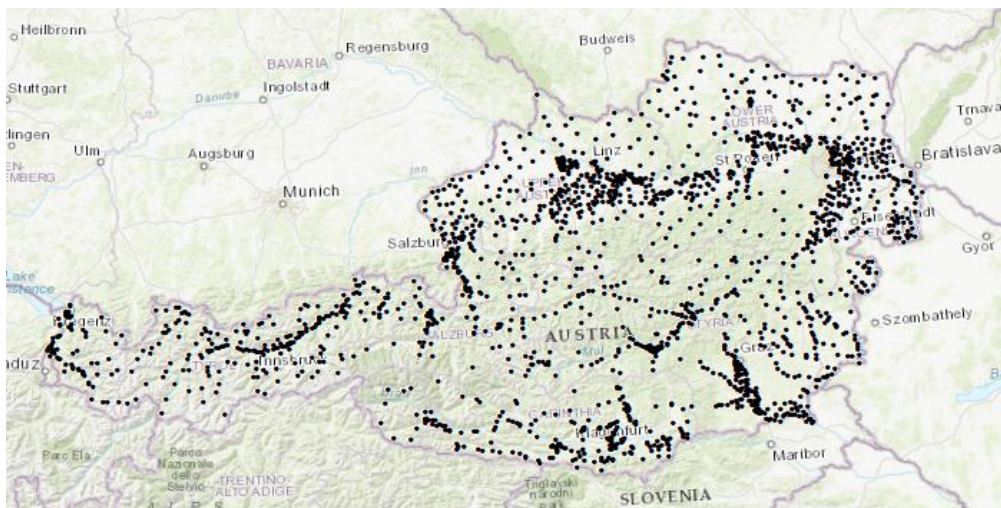


Figure 16. The date of arsenic concentration correspond to a period of 1997-2020, with 1787 monitoring sites (ms) derived from the Austrian Groundwater monitoring network ((WISA Wasserinformationssystem; see Gewässerzustandsüberwachungsverordnung, BGBl. II Nr. 479/06 i.d.g.F.) which can be accessed online: <https://wasser.umweltbundesamt.at/h2odb/index.xhtml>.

The dataset covers exclusively samples of surface near groundwater bodies.

Austria, with an extension of 83.879 km², offers a network of density of 0,021 ms/km² for arsenic concentration (Figure 16). The position of the water points has been offered using EEA reference gride of 1km.

Monitoring sites are constituted by springs, wells and boreholes.

In section 7, the relationship between As concentration and hydrochemistry in Austria will be discussed, both as a country study area and as a specific study area (Carinthia).

4.2.2 Belgium (Flanders)

File As&F_DB: [HOVER_WP3_GW_Flanders_def_all.xlsx](#)

Data provided by [G. Meeusen, VMM](#)

Base data comprises arsenic and fluoride concentration from 491 monitoring sites (ms) belonging to a time range between 2013-2017. Most of these points offer analysis at different depths, giving a total volume of 35.217 arsenic concentration data and 2.413 fluoride analysis.

The water points correspond totally to wells (boreholes) with a maximum depth of 566 m.

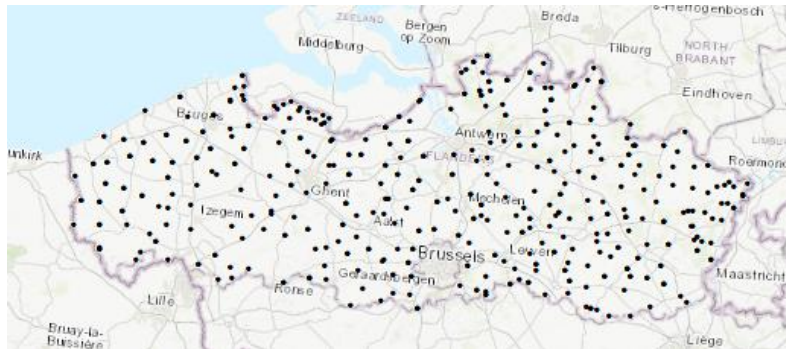


Figure 17. Simplified network for As and F concentrations in groundwaters of Flanders (Belgium). 2013-2017.

Belgium (Flanders), with an extension of 13.625 km², offers a network of 0,036 ms/km² of distribution of arsenic and fluoride concentration (Figure 17).

The position of the water points has been offered using latitude and longitude coordinates on the WGS84 reference ellipsoid (EPSG 4326).

In section 7 the relationship between As/F concentration and hydrochemistry in Belgium (Flanders) will be discussed as a country study area.

4.2.3 Bosnia-Herzegovina

File As_DB: [Task3.4_Table1a\(F\) - FZZG\(12188\).xlsx \(ANNEX 2\)](#)

Data provided by [F. Skopljak, FZZG](#)

Database comprises arsenic and fluoride concentration from 15 monitoring sites (ms). This information corresponds to the year 2011. The water points correspond mainly to springs to wells and water flow, all of them used for water supply.

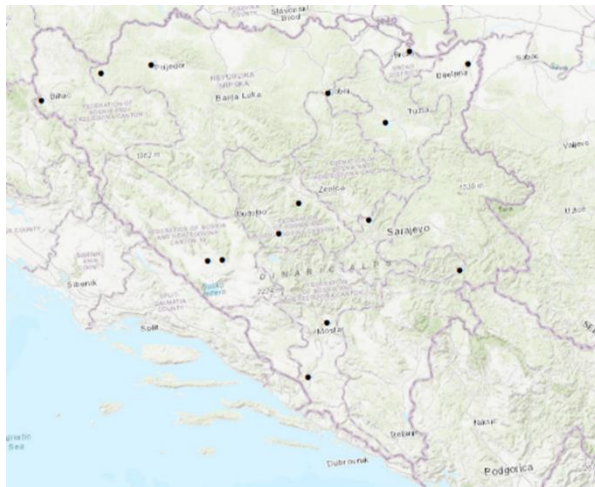


Figure 18. Network for As and F concentrations in groundwaters of Bosnia-Herzegovina. 2011.

Bosnia-Herzegovina has an extension of 51.197 km² and offers a network of 0,0003 ms/km² for arsenic and fluoride concentration (Figure 18).

The position of the water points were offered using UTM coordinates system (33 and 34 grid zones). UTM system was used for the representation of data in GIS Map.

4.2.4 Denmark

File As_DB: [WP34_dataset.xlsx \(ANNEX 2\)](#)

Data provided by [D. Voutchkova, B. Hansen and J. Schullehner, GEUS](#)

Provided base data comprises arsenic concentration from 6.245 ms and fluoride data from 6.248 ms. In both cases the data correspond to the range period of 2014-2018. Types of water points are boreholes used for supply. The maximum depth is 250 m.

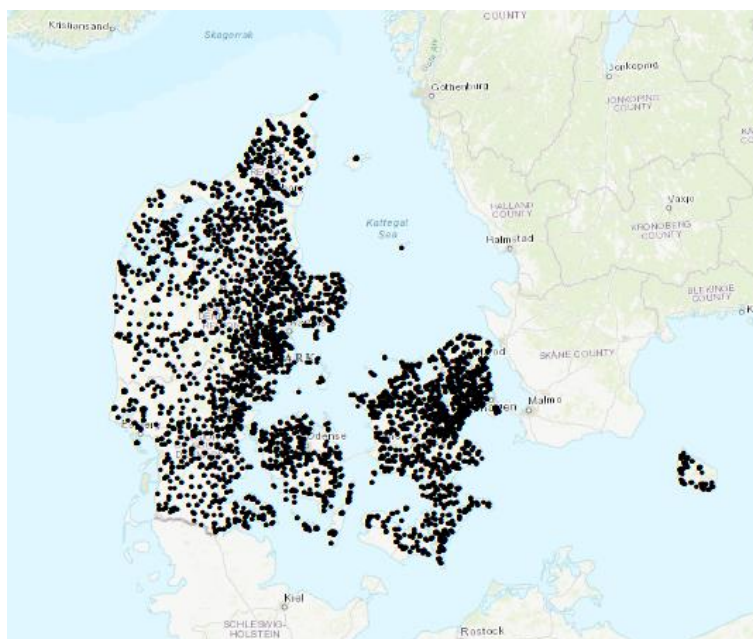


Figure 19. Network for As and F concentrations in groundwaters of Denmark.

2014-2018.

Denmark has an area of 42.933 km², thus offers a density network of 0,14 ms/km², for arsenic and fluoride concentration (Figure 19).

The position of the water points have been offered using UTM coordinates system (32 grid zone, EUREF89), and EEA_1km European grid with EORIGIN and NORIGIN. UTM system has been chosen for the representation of data in GIS geologivalbgr.

In section 7 the relationship between As/F concentration and hydrochemistry in Denmark will be discussed as a country study area.

4.2.5 France

File As_DB: [As_average_per_GWpoint_France_new.xlsx \(ANNEX 2\) \(first Call\): Arsenic](#)
[fluor_metropole_France.xlsx \(second Call\): Fluoride](#)

Data provided by [E. Malcuit \(As\)](#); [L. Gourcy \(F\)](#), BRGM

In the first call, As data were offered using the European Grid EEA 1km as a location system. The second call provided fluoride data from a larger observation network, using the geographic coordinate system. In order to unify both contributions, the arsenic data were referenced to a geographic coordinate system. As a result, from the union of both information, a network of 5.745 points with concentration of arsenic and fluoride, and a more extensive database of 20.218 monitoring sites with fluoride concentration.

The observation network is homogeneously distributed over the entire surface of France (643.801 km²), with a network density of 0,009 ms/km² for arsenic and fluoride, and 0,035 ms/km² for fluoride concentration (Figure 20).

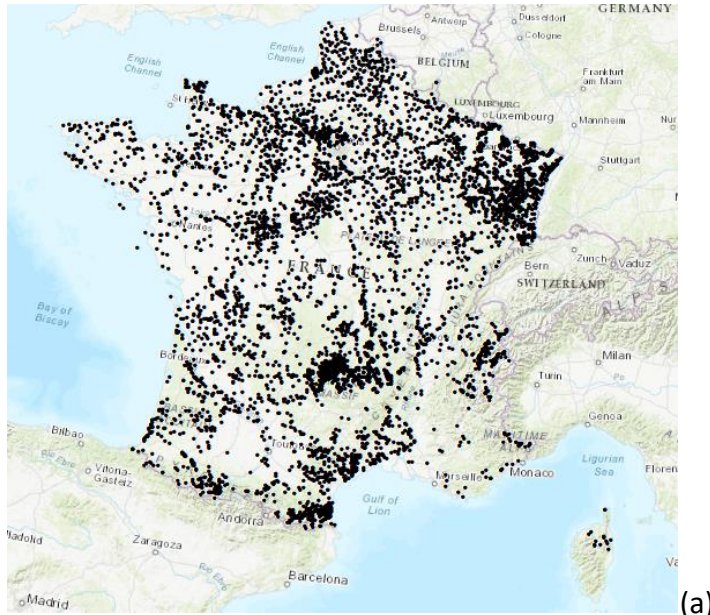
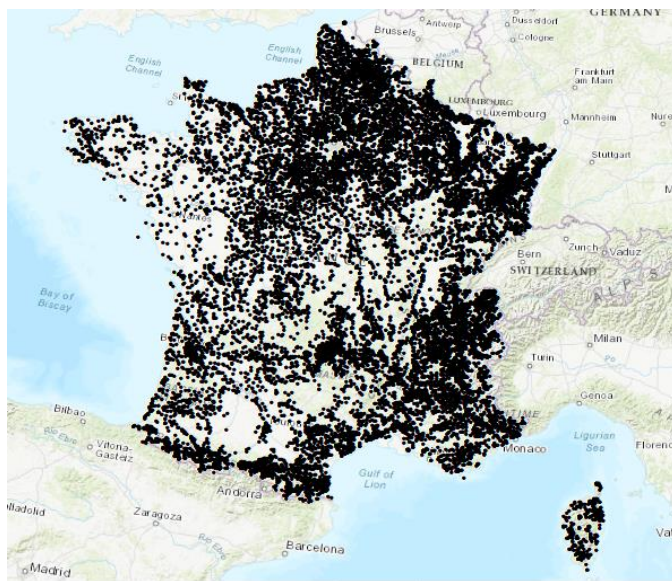


Figure 20.

(a) Network for As and F concentrations in groundwaters of France.



(b) Network for F concentrations in groundwaters of France.

(b)

In section 7, a more specific analysis will be exposed about a specific study area (Morvan Regional Natural Park).

4.2.6 Hungary

File As_DB: [WP3_Task_3_4_Arsenic_HU](#)

Data provided by [T. Szöcs, MBFSZ](#) with the permission of the General Directorate of Water Management (OVF)

Network provided comprises arsenic concentration from 673 monitoring sites (ms) belonging to 2016. Depths range 0-2476 m.

The surface of Hungary is 93030 km², which assumes a network density of 0,007 ms/km² for the distribution of arsenic concentration in Hungarian groundwater (Figure 21).

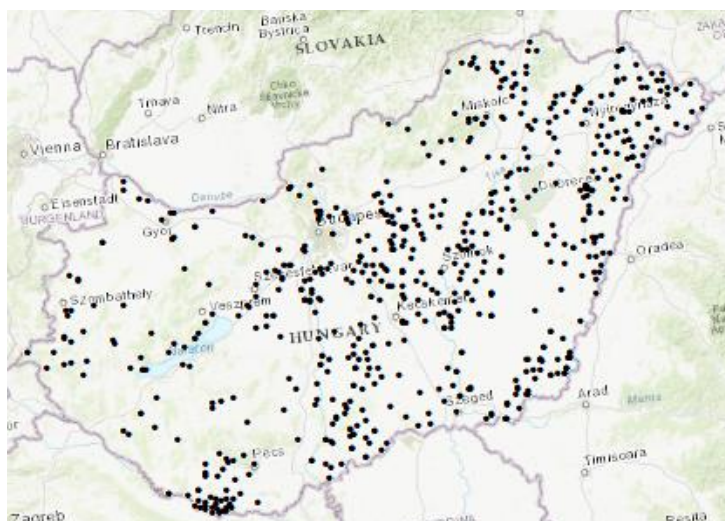


Figure 21. Network for As concentration in Hungarian groundwaters.

2016.

The position of the water points is offered using EEA REFERENCE GRID 1

4.2.7 Iceland

File As_DB: [WP3-As-ISOR.xls](#)

Data provided by [D. Þorbjörnsson, ISOR](#)

Base data comprises arsenic and fluoride concentration from 145 monitoring sites (ms). This information corresponds to the range of years 2002-2005. The water points correspond mainly to springs, boreholes and other discharge or abstraction points of groundwater, used for water supply, balneology and industrial purposes.

Iceland has an extension of 103.000 km² and offers a network of 0,0014 ms/km² for arsenic and fluoride concentration (Figure 22).

The position of the water points have been offered using a geographic coordinate system.

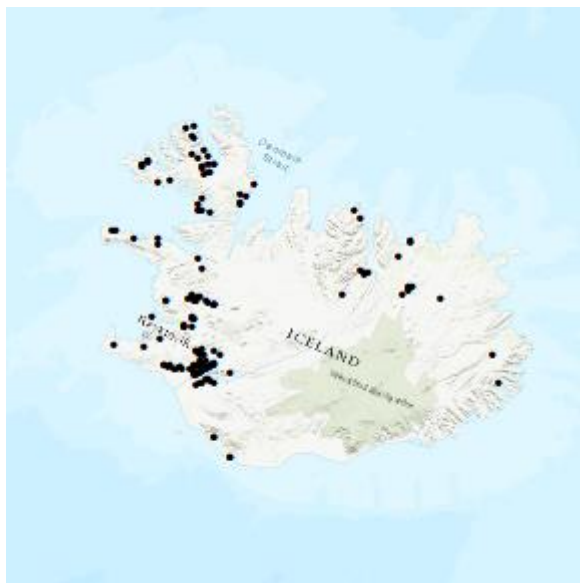


Figure 22. Network for As and F concentrations in groundwaters of Iceland.
2002-2005.

4.2.8 Ireland

File As_DB: [Ireland 2016 groundwater arsenic data.xlsx \(first Call\)](#)

Data provided by [K. Tedd, GSI](#)

Arsenic concentration network is formed by 268 ms, and the data correspond to 2016 . Ireland has an extension of 70.273 km², so that the density of the network is 0,04 ms/km² (Figure 23).

The position of the water points was offered using ie_point_TM65_Irish_Grid.

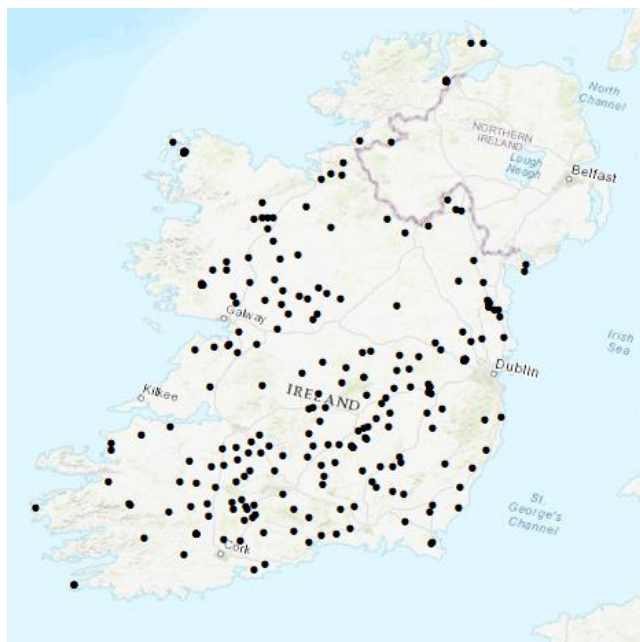


Figure 23. Irish network for As concentration in groundwaters.

2016.

4.2.9 Latvia

File As_DB: [WP3_Task_3-3_3-4_NBL_data_compilation_table_Latvia \(LEGMC\)II](#)

Data provided by [D. Borozdins, LVGMC](#)

Network provided comprises arsenic and fluoride concentration from 437 monitoring sites (ms) belonging to a time range between 2010-2016. Many of them are calcified as 'artesian well/borehole' with rehole with depths which range 1,6-455 m.

The surface of Latvia is 64.5895 km², which assumes a network density of 0,0007 ms/km² for the distribution of arsenic and fluoride concentration in Latvian groundwater (Figure 24).



Figure 24. Network for As concentration in Latvia groundwaters.

2010-2016.

The position of the water points has been offered using latitude and longitude coordinates on the WGS84 reference ellipsoid (EPSG 4326) and EEA REFERENCE GRID 1 km.

4.2.10 Malta

File As_DB: [Arsenic from your CSV source WGS84 utm zone 33N.xlsx](#)

Data provided by H. Debattista, MTI

Base data comprises arsenic and fluoride concentration from 36 and 39 monitoring sites (ms), respectively. This information corresponds to the period 1988-2006. The water points network is formed of mainly boreholes, with a maximum depth of 240 m.



Figure 25. Network for As and F concentration in Maltese groundwater network.

1998-2016.

Malta has an extension of 316 km² and offers a network of 0,123 ms/km² for arsenic and fluoride concentration (Figure 25).

The position of the water points have been offered using UTM_ETRS89_33 Zone

4.2.11 Poland

File As_DB: [WP3_Task_3-3_3-4_NBL_data_compilation_table_Latvia \(LEGMC\)II](#)

Data provided by [A. Felter](#), [J. Cabalska](#), [A. Mikożajczyk](#), [PGI](#)

(Works were co-financed by the Polish Ministry of Science and Higher Education)

Base data comprises arsenic and fluoride concentration from 1504 monitoring sites (ms) corresponding to the period 2010-2016. Since the EEA1km grid has been used as a location reference, some points coincide in the same cell. In these cases, the mean concentration of As and F has been calculated for each cell, so that each coordinate point corresponds to a certain concentration of As or F.

The water points correspond mainly to boreholes, but also springs and wells, most of them used for supply. The maximum depth is 750 m.

Poland has an extension of 312.679 km² and offers a network density of 0,05 ms/km² for arsenic and fluoride concentration (Figure 26).

The position of the water points were offered using EEA Reference Grid 1 km, with EFORIGIN_ETRS89 and NOFORIGIN_ETRS89 coordinates.

Scientific work is co-funded by the Geological Surveys and national funds allocated for science within the period 2018-2021.

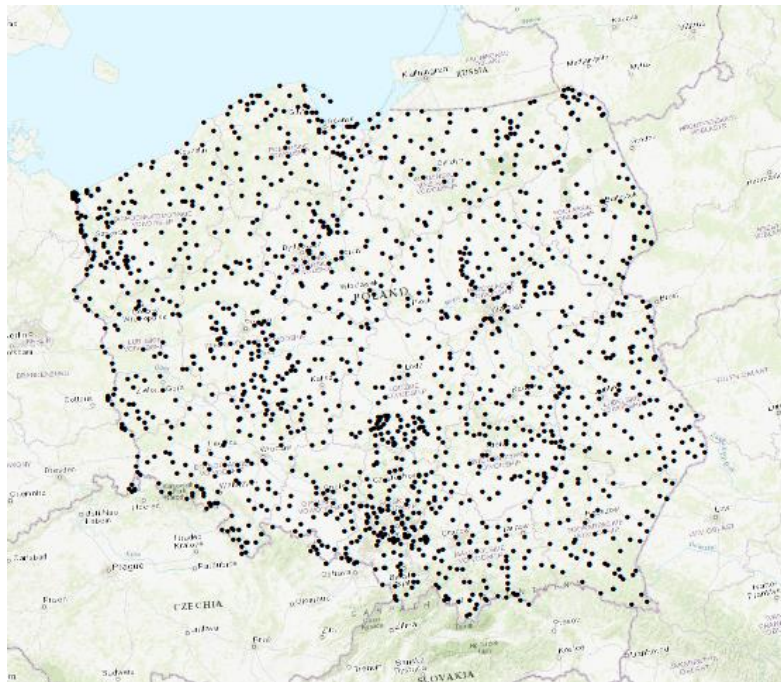


Figure 26. Network for As and F concentration in Polish groundwaters.

2010-2016.

4.2.12 Portugal

File As_DB: [WP3_Task3-4_NBL_data_compilation_table_FINAL_PT.xlsx](#)

Data provided by [A. Pereira, J. Sampaio, LNEG](#)

(C. Meireles is the first author of the “Overview Portugal Geology: Annex II)

Provided base data comprises arsenic concentration from 545 ms and fluoride data from 512 ms. In both cases the data correspond to the range period of 2001-2019. Types of water points are mainly boreholes, which reach a maximum depth of 422 m.

Portugal has an extension of 92,212 km², thus offers a density network of 0,006 ms/km², for arsenic and fluoride concentration (Figure 27).

The position of the water points have been offered using EEA REFERENCE GRID 1 km (with ETRS89 coordinates).

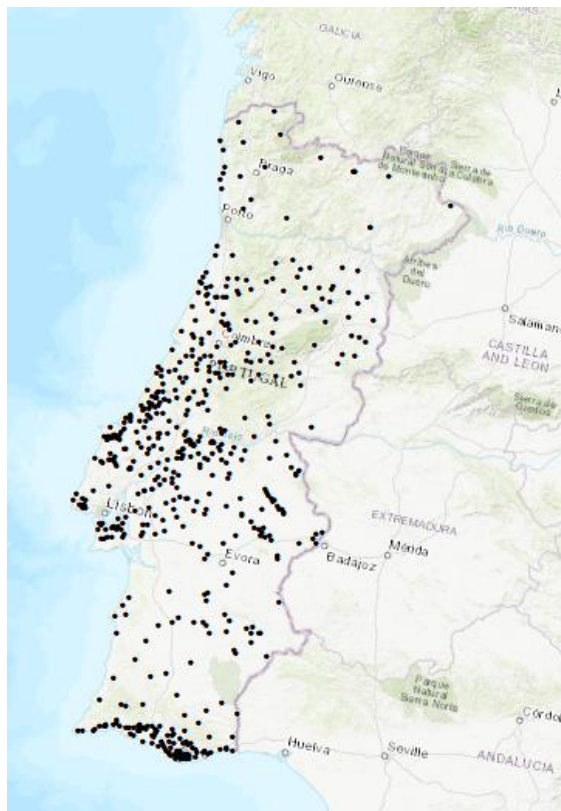


Figure 27. Network for As and F concentration in Portuguese groundwaters.

2001-2019.

4.2.13 Romania

File As_DB: [RAPORT_Raport \(Autosaved\).xlsx](#)

Data provided by [D. Perşa, IGR](#)

Base data comprises arsenic concentration from 24 monitoring sites (ms) and fluoride concentration from 16 ms. The data cover the period 2011-2016.

The water points correspond mainly to boreholes for supply, which maximum depth is of 750 m. Water points are located with EEA Reference Grid 1 km (Figure 28).

Romania has an extension of 238,397 km² and offers a network density of 0,0001 ms/km² for arsenic and fluoride concentration.



Figure 28. Network for As and F concentration in Romanian groundwaters network.

2011-2016.

4.2.14 Serbia

File As_DB: [WP3_Task_3-3_3-4_NBL_data_compilation_table_GSS.xlsx](#) [Task3.4_Table1a\(As\)\(Vojvodina\).xlsx](#)

Data provided by: [T. Petrović, GSS](#)

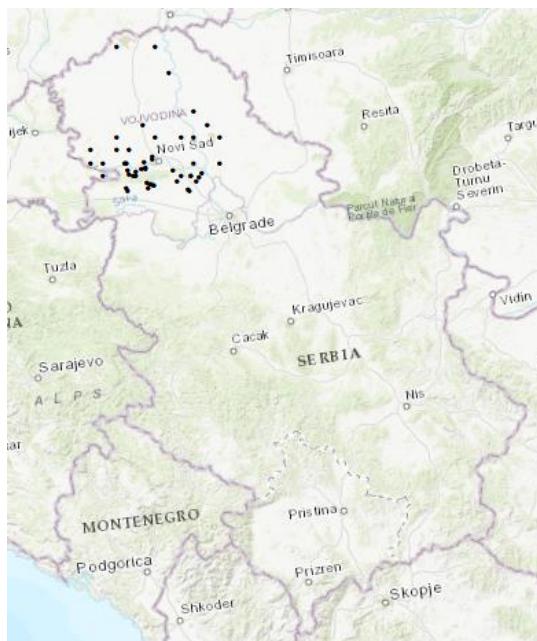


Figure 29. Network for As and F concentration Serbia (including Vojvodina province for As information).

2009-2017 (2008-2009, Vojvodina).

Network comprises provided arsenic concentration from 33 monitoring sites (ms) for As and F concentrations, belonging to a time range between 2009-2017. Most of the water points are classified as 'artesian well/borehole' and are used for supply. The maximum depth reaches 310 m. The DB includes also information from Vojvodina province.

The surface of Serbia is 88,361 km², which assumes a network density of 0,0007 ms/km² for the distribution of arsenic concentration in Serbian groundwater network, and 0,0004 for fluoride concentration (Figure 29).

The position of the water points have been located using latitude and longitude coordinates on the WGS84 reference ellipsoid (EPSG 4326) and EEA REFERENCE GRID 1 km.

In section 7.2.2 the relationship between As/F concentration and hydrochemistry in Serbia will be discussed as a country study area and Fruška Gora as an specific study area.

4.2.15 Slovenia

File As_DB: [Task 3.4 Table 1a \(As\)_GeoSZ_Slovenia.xlsx](#)

Data provided by [N. Rman, GEO-ZS](#)

Arsenic concentration network is formed by 203 monitoring sites, and the data correspond to the period 2007-2019. The water points correspond mainly to springs, capture springs, automatic measuring stations, pumping stations, boreholes, and private wells. The maximum depth is 200 m. In addition to the groundwater network, geothermal water well points are incorporated into the network (Figure 30).

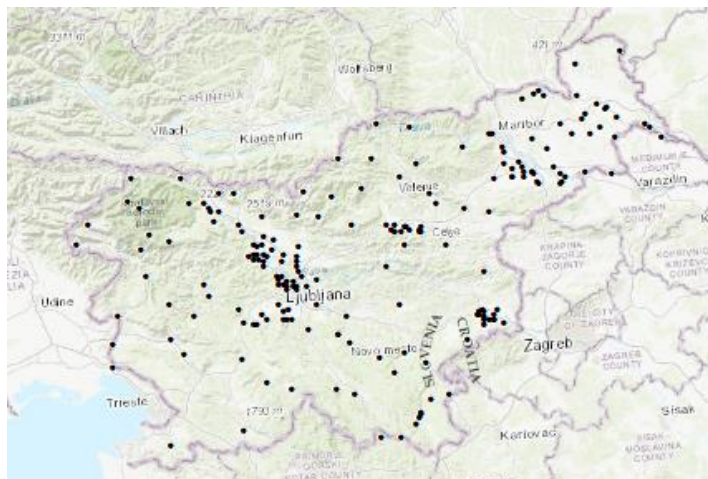


Figure 30. Network for As and F concentration in Slovenia.

2007-2019

Slovenia has an extension of 20,271km², so that the density of the network is 0.011 ms/km² (Figure 23). The position of the water points was offered using WGS_1984_UTM_Zone_33N .

4.2.16 Spain

File As_DB: [WP3_Task_3-4_Data_compilation_table_Spain.xlsx](#)

[WP3_Task_3-3_3-4_NBL_data_compilation_table_FINAL_ICGC.xlsx](#)

Data provided by [E. Giménez-Forcada, IGME](#) / [G. Arnó, ICGC](#)

The data for peninsular Spain were provided by the IGME and the ICGC (Catalonia). Mineral and thermal water data have been incorporated into this database as support for the interpretation of the data of As and F. It is a network made up of springs, wells (<30 m), boreholes and piezometers. As and F concentration data correspond to the period 2010-2016. The network of As concentration in groundwater is made up of 3005 monitoring sites. The data from the fluorine concentration network covers all of mainland Spain, except Catalonia, and is made up of 1838 control points.

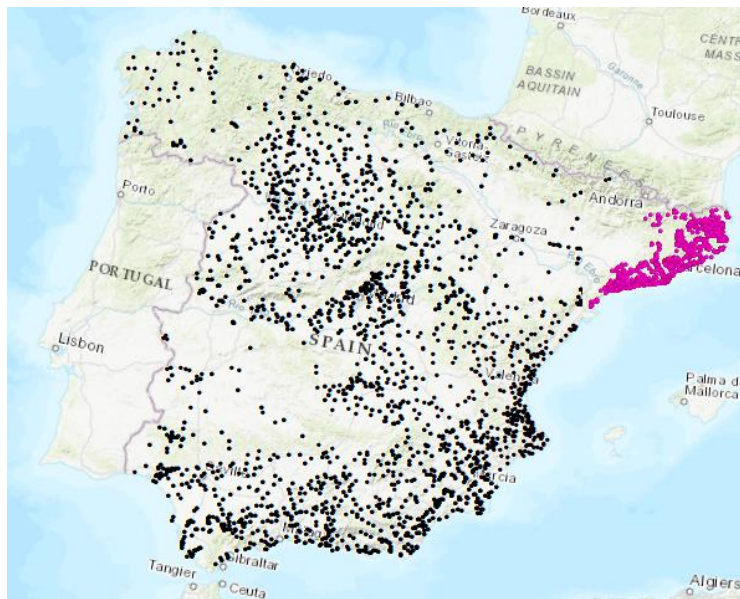


Figure 31.

Network for As and/or F concentration in Spanish groundwater network.

2010-2016.

In fuchsia, network for As concentration provided by ICGC (Catalonia).

Only the territory of mainland Spain, has been analysed. The Canary Islands or the Balearic Islands have not been included in the present study.

The coordinate system for the location of the points of the observation network has been with GC_WGS84 (IGME) and GC_WGS84 & EEA REFERENCE GRID 1 km (ICGC).

Given that the surface of mainland Spain is 494,011 km², the density of network has an average of 0.005 ms/km² (Figure 31).

In section 7 the relationship between As/F concentration and hydrochemistry in Spain will be discussed, both as a country study area and as a specific study area (SE Duero Basin).

4.2.17 Sweden

File As_DB: [WP3_Task_3-3_3-4_NBL_data_compilation_table_FINAL_SWEDEN.xlsx](#)

Data provided by [L. Rosenqvist, SGU](#)

Provided base data comprises arsenic concentration from 26042 (17083 values for every cell), and fluoride data from 36281 F ms (17083 values for every cell from grid EEA1km). In all cases the data correspond to the range period of 2009-2018. Types of water points are springs, wells (<30 m) and boreholes used for supply.

Sweden has an extension of 450295 km², thus offers a density network of 0,06 ms/km² for As and 0,08 for fluoride concentration (Figure 32).

The position of the water points have been offered using EEA 1km European grid with EORIGIN and NORIGIN. When there was more than one point in a cell, it was decided to calculate the average of the concentration values of As and F. In this way, each EORIGIN NORIGIN location is associated with a single concentration value.



Figure 32. Network for As and F concentration in Sweden.

2009-2018

In section 7 the relationship between As/F concentration and hydrochemistry in Sweden will be discussed as a country study area.

In total, a Pan-European area of 3,351,145 km² has been studied in relation to the distribution of As and F concentrations. The network is formed by 81,272 monitoring sites of As concentration, and 69,815 water points with fluoride concentrations. To these grids correspond a density of 0.024 ms / km² for As and 0.021 ms / km² for fluoride, as is shown in Table 2, which includes a summary of the information provided by the different participants.



COUNTRY	File	Data provided by	Geological survey	Location	As/F Data	Type	Depth max (m)	Period	As ms	F ms	Surface km²	As density ms/km²	F density ms/km²
Austria	2020_08_18_HOVER_WP3_3-4_results_Arsenic_FINAL	D. Elster	GBA	EEA REFERENCE GRID 1 km	As	Springs, wells (<30 m) and boreholes	127	1997-2020	1787	-	83879	0.02	-
Belgium (Flanders)	HOVER_WP3_GW_Flanders_def_all.xlsx	G. Meusen	VMM	GC_WGS84	As&F	Wells	566	2013-2017	35217	2413	13625	2.6	0.2
Bosnia-Herzegovina	Task3.4_Table1a(f) - FZG12188).xlsx (ANNEX 2)	F. Skopljak	FZG	UTM 33Q34 Zone)	As&F	Springs and wells	-	2011	15	15	51197	0.0003	0.0003
Denmark	WP34_dataset.xlsx (ANNEX 2)	D. Voutchkova	GEUS	EEA REFERENCE GRID 1 km (with EORGIN and NORGIN)	As&F	Borehole & Supply	250	2014-2018	6245	6248	42933	0.1	0.1
France	As_aveage_per_GWpoint_France_new.xlsx (ANNEX 2) (first Coll) & fluor_metropole_France.xlsx (second Coll); Floride	E. Maréchal, L. Gourry	BRGM	GC_WGS84 & EEA REFERENCE GRID 1 km	As&F	-	-	-	5745	20218	643801	0.01	0.03
Iceland	WP3-As-ISOR.xls	D. Þorjónsson	ISOR	GC_WGS84	As&F	Springs, boreholes and others & supply, balineology and industrial purposes	-	2002-2005	145	145	103000	0.001	0.001
Ireland	Ireland 2016 groundwater arsenic data.xlsx (first Coll)	K. Todd	GSI	ie_point_TMS6 Irish Grid	As	-	-	2016	268	-	70273	0.004	-
Hungary	WP3_Task_3-4_Arsenic_HU	T. Szűcs	MBFSZ	EEA REFERENCE GRID 1 km	As	Springs and wells	2475.6	2016	673	-	93030	0.007	-
Latvia	WP3_Task_3-3_3-4_NBL_data_compilation_table_Latvia (LEGOMC)II	D. Borodians	LIVGMC	GC_WGS84	As&F	Artesian well/borehole	455	2015-2016	437	437	645895	0.001	0.001
Malta	Arsenic from your CSV source WGS84 utm zone 33N.xlsx	H. Debonatista	MTI	UTM_ETRS89_33 Zone	As&F	Boreholes	240	1988-2006	36	39	316	0.1	0.1
Poland	WP3_Task_3-3_3-4_NBL_data_compilation_table_Latvia (LEGOMC)II	A. Felter	PGI	UTM EUREF89_32 Zone & EEA REFERENCE GRID 1 km (with EORGIN and NORGIN)	As&F	Springs, wells (<30 m) and borehole	750	2010-2016	1504	1504	312679	0.005	0.005
Portugal	WP3_Task3-4_NBL_data_compilation_table_FINAL_PT.xlsx	A.P. Pereira	LNEG	EEA REFERENCE GRID 1 km (with ETRS89 coordinates)	As&F	Boreholes overall	422	2001-2019	545	512	92212	0.006	0.006
Romania	RAPORT_Raport (Autosaved).xlsx	D. Persa	IGR	EEA REFERENCE GRID 1 km	As&F	Boreholes & Supply	240	2011-2016	24	16	238397	0.0001	0.0001
Serbia	WP3_Task_3-3_3-4_NBL_data_compilation_table_GSS.xlsx	T. Petrović	GSS	GC_WGS84 & EEA REFERENCE GRID 1 km	As&F	Artesian well/borehole & supply	310	2009-2017 (+27 Vojvodina)	33	33	88361	0.0007	0.0004
Slovenia	Task 3.4 Table 1a (As)_GeoSZ_Slovenia.xlsx	N. Rman	GEOTZS	WGS_1984_UTM_Zone_33N	As	Springs, capture springs, automatic measuring stations, pumping stations, boreholes & private wells	200	2007-2019	223	-	20271	0.011	-
Spain	WP3_Task_3-4_Data_compilation_table_Spain.xlsx	WP3_Task_3- E. Giner-Ferrada	IGME	GC_WGS84	As&F	Springs, wells (<30 m) and boreholes & parameters	-	2010-2016	3007	1954	494011	0.006	0.004
	3_3-4_NBL_data_compilation_table_FINAL_GCC.xlsx	G. Arno	IGCC	GC_WGS84 & EEA REFERENCE GRID 1 km	As	-	-	-	-	-	-	-	-
Sweden	WP3_Task_3-3_3-4_NBL_data_compilation_table_FINAL_SWEDEV.xlsx	L. Rosqvist	SGU	EEA REFERENCE GRID 1 km	As&F	Springs, wells (<30 m) and boreholes & Supply	-	2009-2018	26042	36281	450295	0.06	0.08
Europe									81300	69815	3444175	0.024	0.020

Table 2. Summary of the data provided by the participating geological services for Task 3.4. They are exposed together with data at Pan-European level: study area, points and network density.



5 RESULTS AND DISCUSSION

5.1 Main statistics

The data have been treated statistically to know the basic statistical values of each database provided by each organization. Tables 3 and 4 collect the summary of the data statistics for each country regarding to As and F concentration in groundwater.

Table 3. Summary of the data statistics for each country participating in the observation of As concentration in groundwater.

	Data	Max	Average	Median	Standard Dev.
	ms	µg/L	µg/L	µg/L	µg/L
AUSTRIA	1787	85.8	1.1	0.1	4.8
BELGIUM (FLANDERS)	491	1295.4	7.5	2.3	59.4
BOSNIA-HERZEGOVINA	15	4.5	0.6	0.2	1.2
DENMARK	6245	68.0	2.2	0.8	3.9
FRANCE	6009	272.9	2.9	1.0	8.2
HUNGARY	673	168.0	13.0	5.9	19.8
ICELAND	145	35.4	3.2	1.1	5.1
IRELAND	796	110.0	1.7	0.5	7.8
LATVIA	398	10.3	1.5	1.0	2.0
MALTA	40	15.8	2.5	0.9	12.4
POLAND	1491	539.4	2.8	1.0	17.6
PORTUGAL	545	56.0	3.2	1.5	5.1
ROMANIA	24	87.0	29.8	22.1	23.9
SERBIA	52	250.0	27.3	8.0	50.0
SLOVENIA	203	59.0	0.9	0.5	4.4
SPAIN	3005	353.2	4.3	1.8	15.1
SWEDEN	17083	1000.0	1.1	0.3	10.1

Sweden, Denmark, France, Spain, Austria and Poland (in this order by data supplied) provided databases for As concentrations that exceed a thousand observationpoints. The contribution of Belgium (Flanders) should also be considered in this group, due to its extensive database, although many of them are at different depths from the same observation point and this apparently limits the number of points.

The observation network for As concentrations is made up of 39,002 site points of groundwater, corresponding to seventeen countries.



Table 4. Summary of the data statistics for each country participating in the observation of F concentration in groundwater. Values of 0.0 (values with only one decimal place) are understood to be equivalent to <DL.

	Data	Max	Average	Median	Standard Dev.
	ms	mg/L	mg/L	mg/L	mg/L
BELGIUM (FLANDERS)	491	10.2	1.1	0.3	1.7
BOSNIA-HERZEGOVINA	15	0.4	0.1	0.0	0.1
DENMARK	6246	6.7	0.3	0.2	0.4
FRANCE	20443	5.6	0.2	0.1	0.4
ICELAND	145	14.2	1.2	0.4	2.0
LATVIA	185	14.8	0.3	0.2	1.1
MALTA	40	15.8	3.5	2.2	3.4
POLAND	1504	29.2	0.3	0.1	0.7
PORTUGAL	512	8.9	0.2	0.2	0.5
ROMANIA	16	1.0	0.2	0.2	0.2
SERBIA	33	0.9	0.2	0.2	0.2
SLOVENIA	203	0.2	0.1	0.1	0.0
SPAIN	1838	16.0	0.7	0.5	0.8
SWEDEN	17083	16.0	0.8	0.5	0.8

France, Sweden, Denmark, Spain and Poland (in this order by the data provided) have supplied database for F concentrations that exceed a thousand observation points.

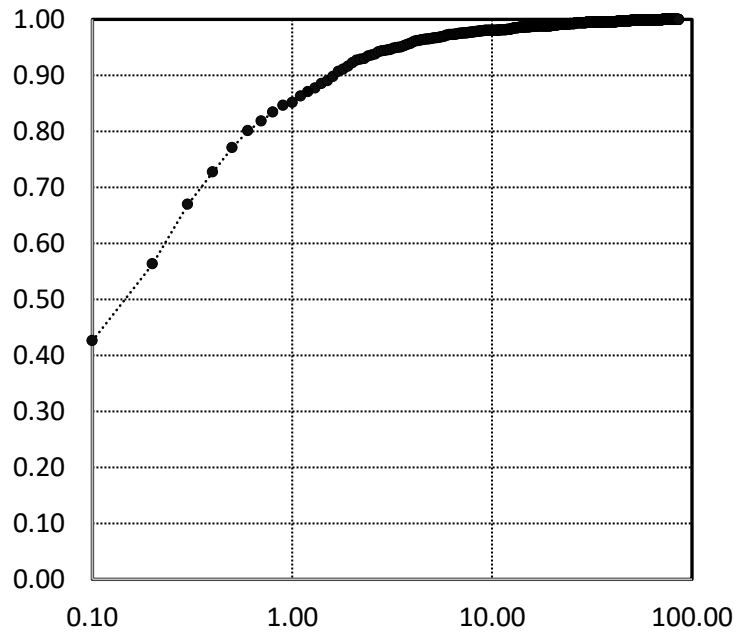
The F network is made up of 50,531 site points corresponding to fourteen countries.

Choice of Basal Reference Concentration, BRC

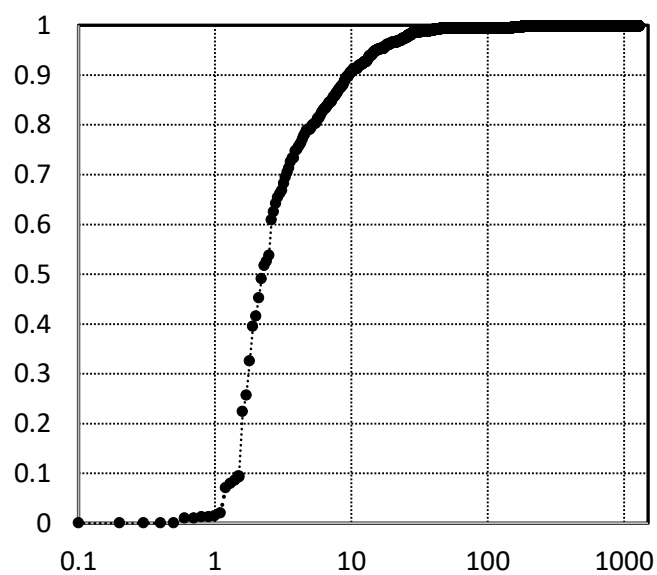
The following figures show the **Cumulative Frequency Curves (CFC)** of the countries with a higher density of the observation network and a greater number of points. In the other cases, the results are not conducive to determine the most suitable percentile to represent the Basal Reference Concentration (BRC) for As and F, respectively selecting to represent the data on a logarithmic scale in abscissa (Edmunds et al., 2003).

The figure 33 (a-m) shows the CFC for **arsenic** concentration distribution for Austria, Belgium (Flanders), Denmark, France, Iceland, Latvia, Poland, Portugal, Spain, and Sweden. The database provided by Bosnia-Herzegovina, Malta, Romania and Serbia are not sufficient to draw a meaningful CFC.

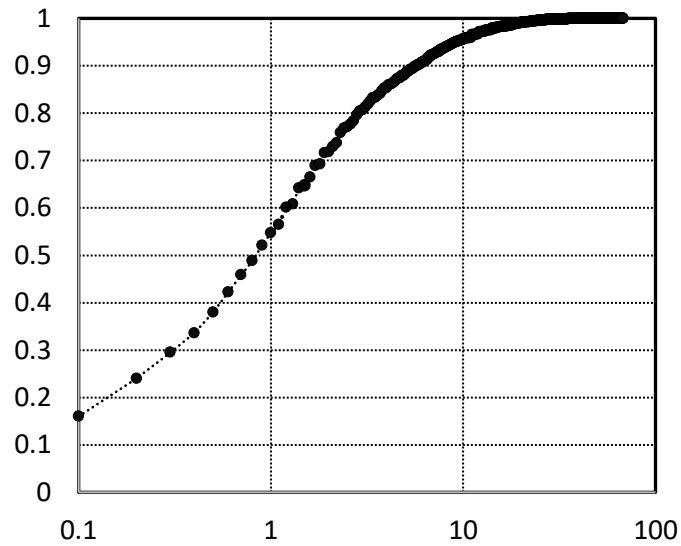
Cumulative Frequency Curve
AUSTRIA - As $\mu\text{g/L}$



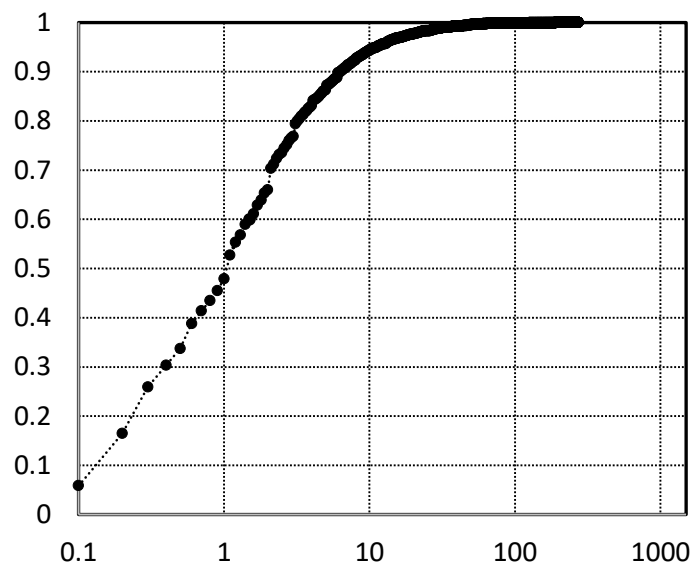
Cumulative Frequency Curve
BELGIUM (FLANDERS) - As $\mu\text{g/L}$



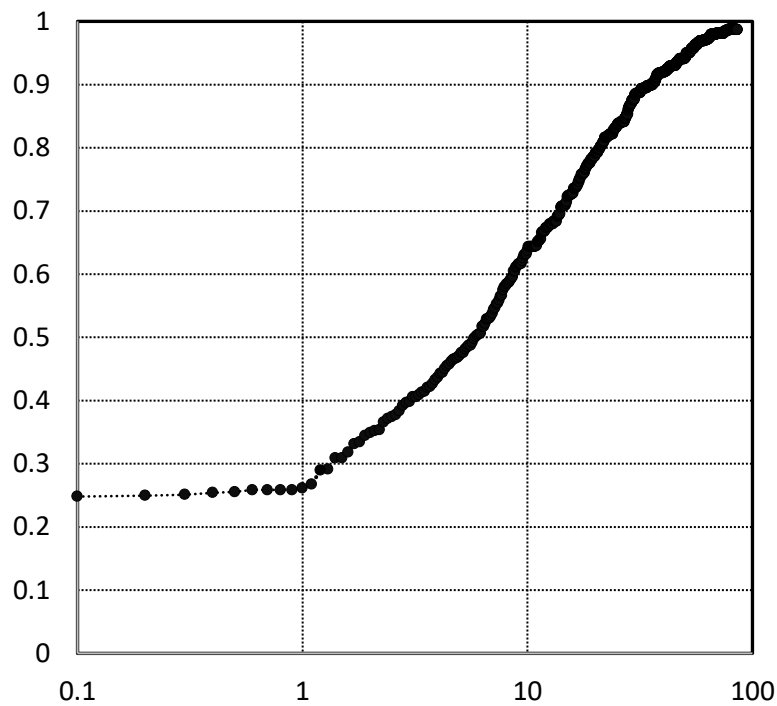
Cumulative Frequency Curve
DENMARK - As $\mu\text{g/L}$



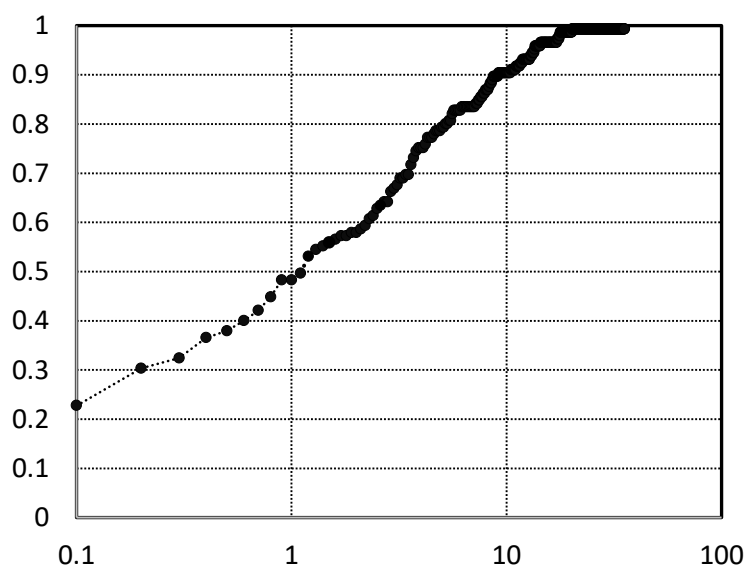
Cumulative Frequency Curve
FRANCE - As $\mu\text{g/L}$



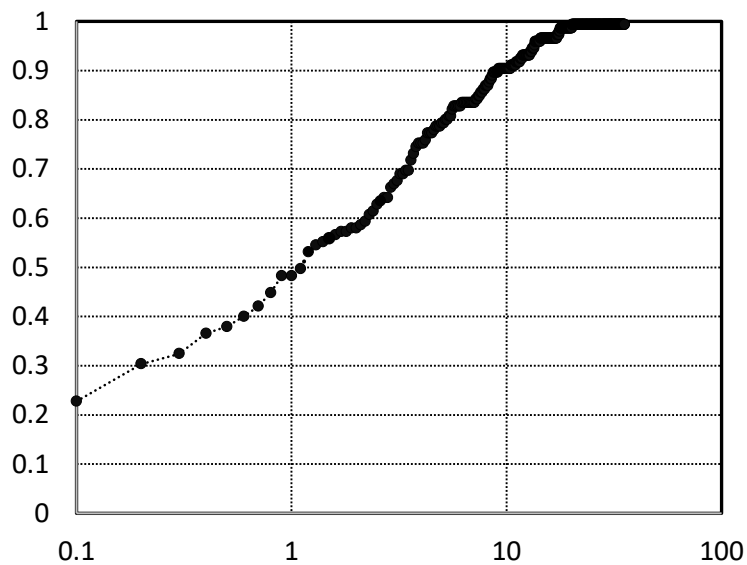
Cumulative Frequency Curve
HUNGARY - As $\mu\text{g/L}$



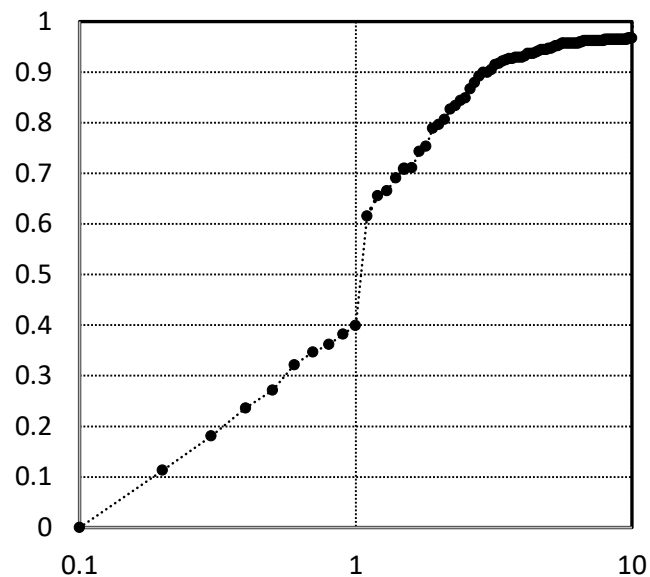
Cumulative Frequency Curve
ICELAND - As $\mu\text{g/L}$



Cumulative Frequency Curve
IRELAND - As $\mu\text{g/L}$

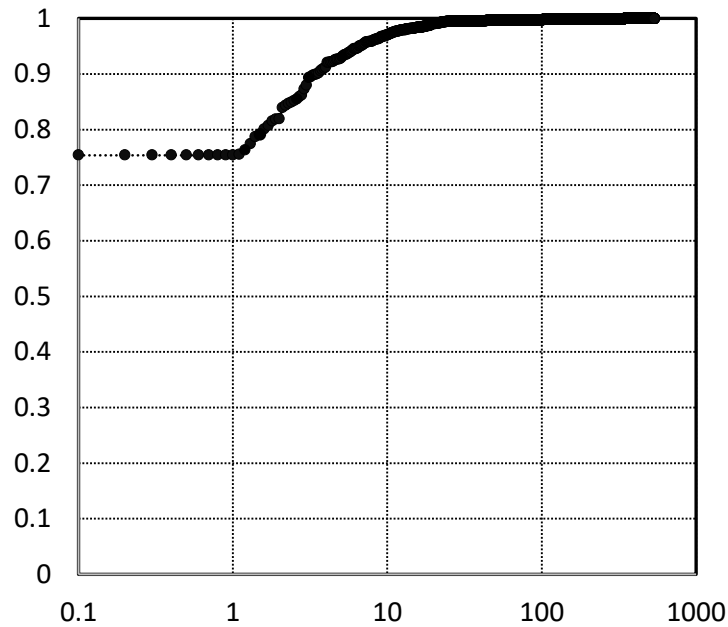


Cumulative Frequency Curve
LATVIA - As $\mu\text{g/L}$

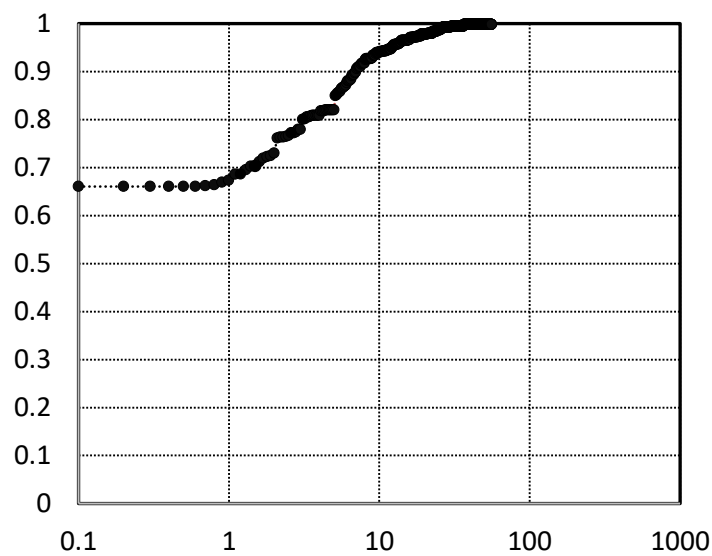




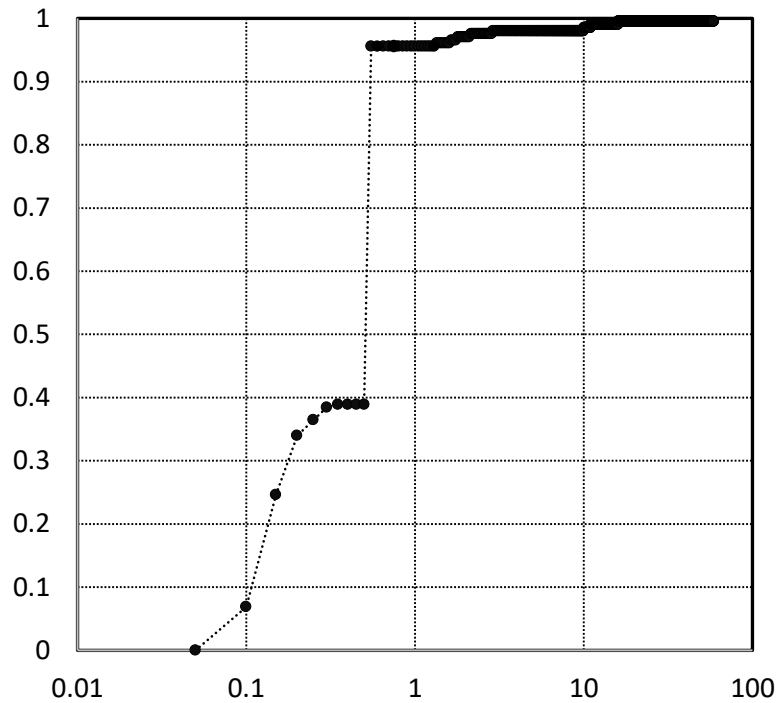
Cumulative Frequency Curve
POLAND - As $\mu\text{g/L}$



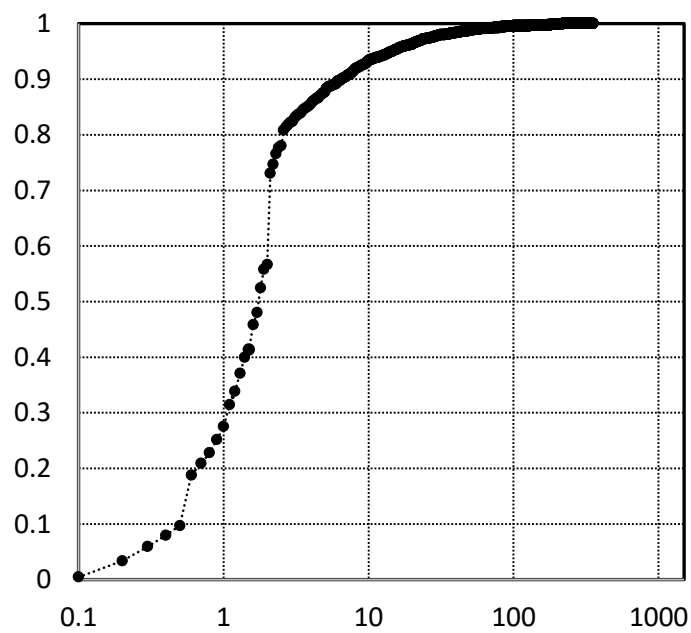
Cumulative Frequency Curve
PORTUGAL - As $\mu\text{g/L}$



Cumulative Frequency Curve
SLOVENIA - As $\mu\text{g/L}$



Cumulative Frequency Curve
SPAIN - As $\mu\text{g/L}$



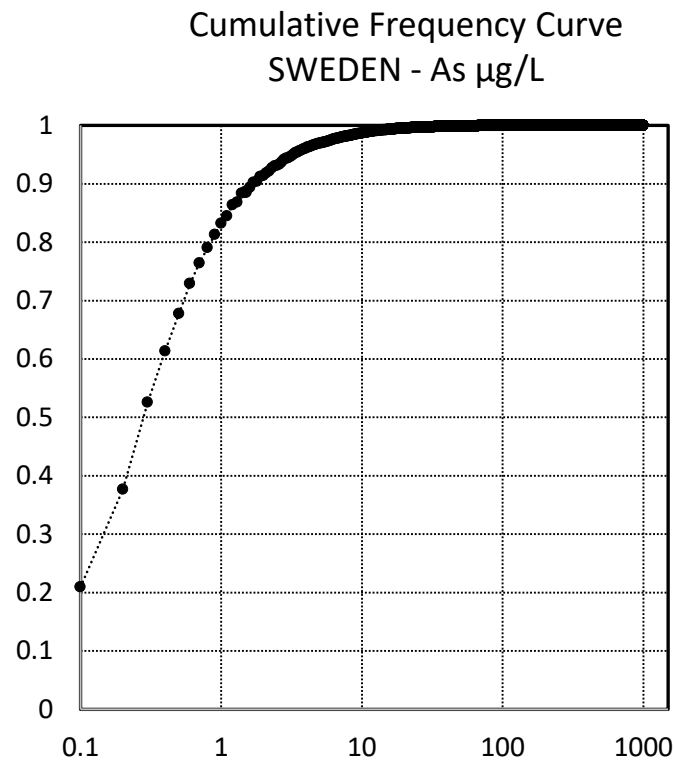
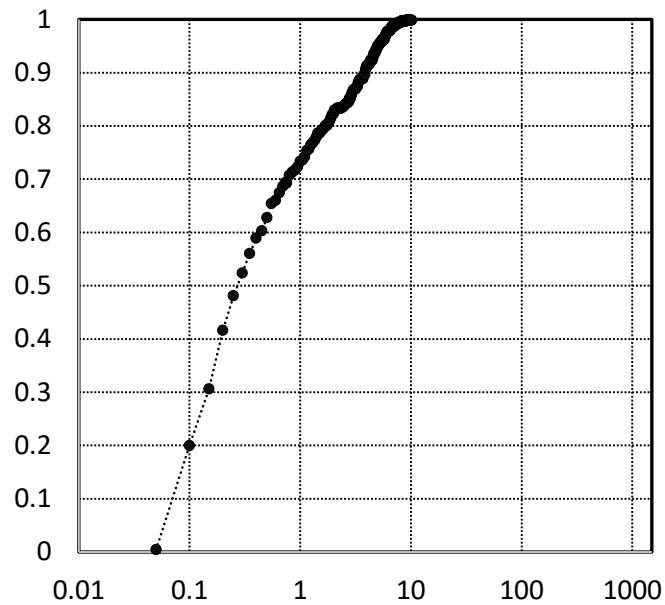


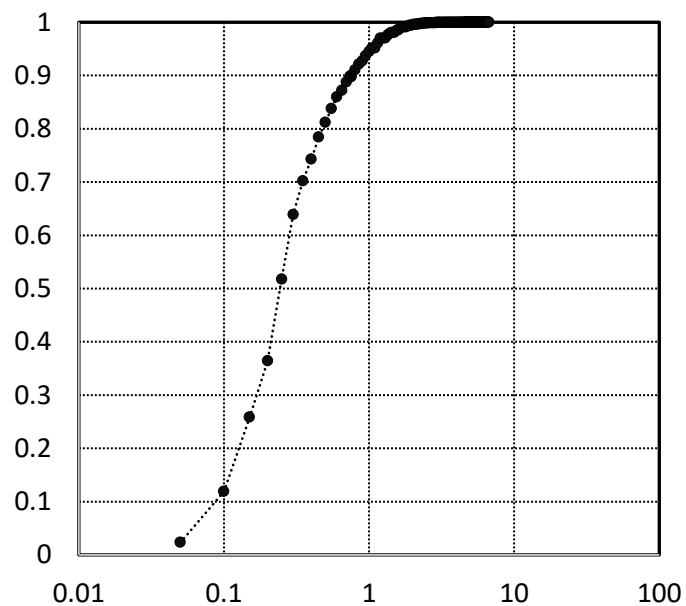
Figure 33. Cumulative frequency curves (CFC) for As in each country: Austria, Belgium (Flanders), Denmark, France, Hungary, Iceland; Latvia, Poland, Portugal, Slovenia, Spain, and Sweden.

The CFCs for **fluoride** concentration calculated for Europe (only following countries), Belgium (Flanders), Denmark, France, Iceland, Latvia, Poland, Portugal, Slovenia, Spain, and Sweden are shown in Figure 34 (a-j).

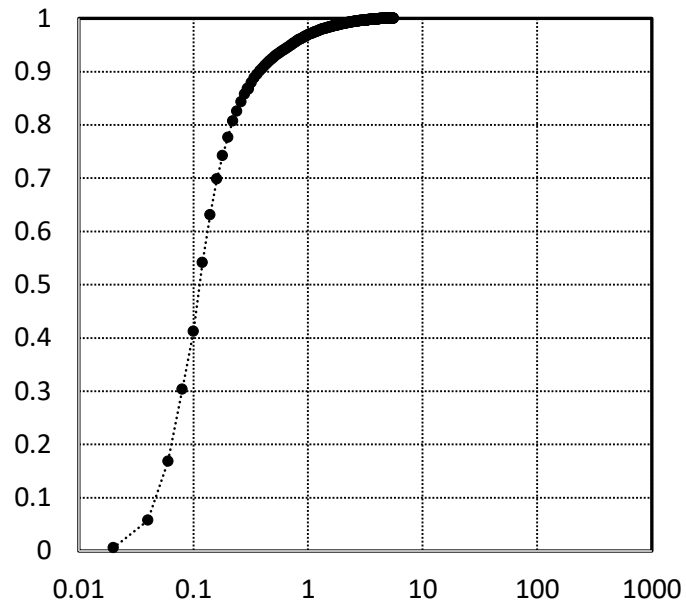
Cumulative Frequency Curve
BELGIUM (FLANDERS) - F mg/L



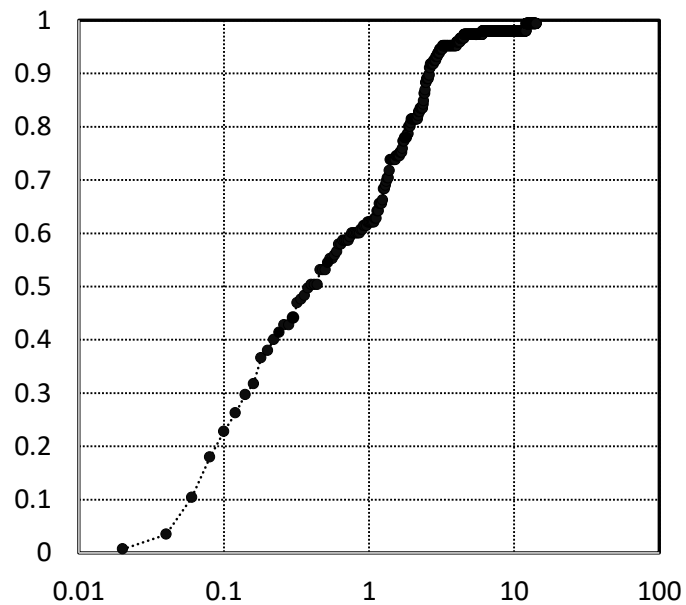
Cumulative Frequency Curve
DENMARK - F mg/L



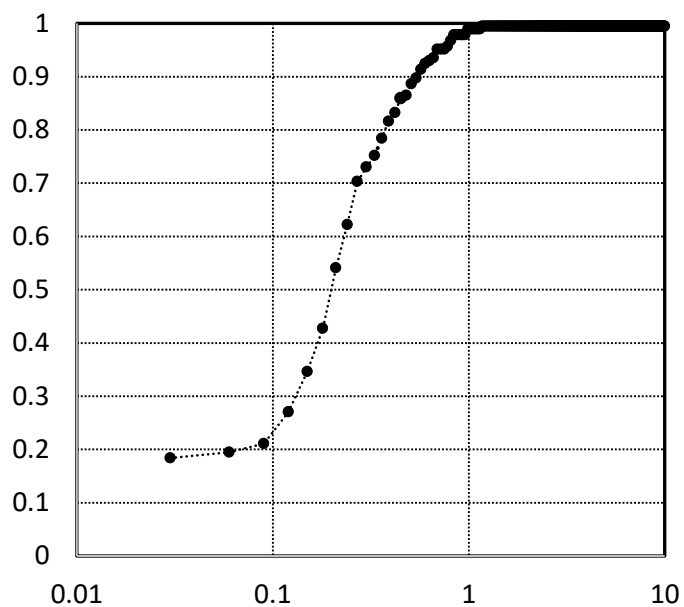
Cumulative Frequency Curve
FRANCE - F mg/L



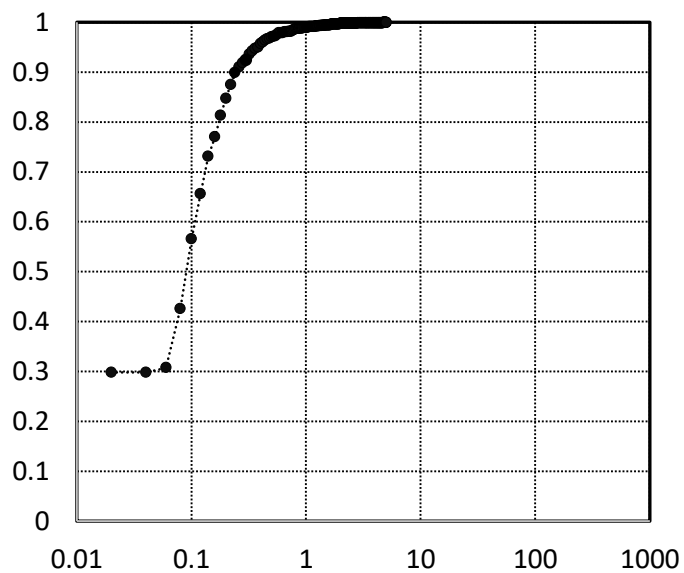
Cumulative Frequency Curve
ICELAND - F mg/L



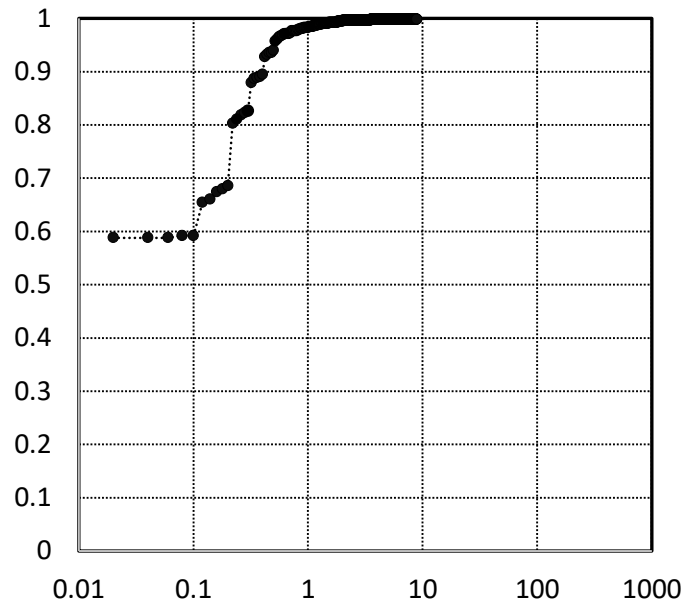
Cumulative Frequency Curve
LATVIA - F mg/L



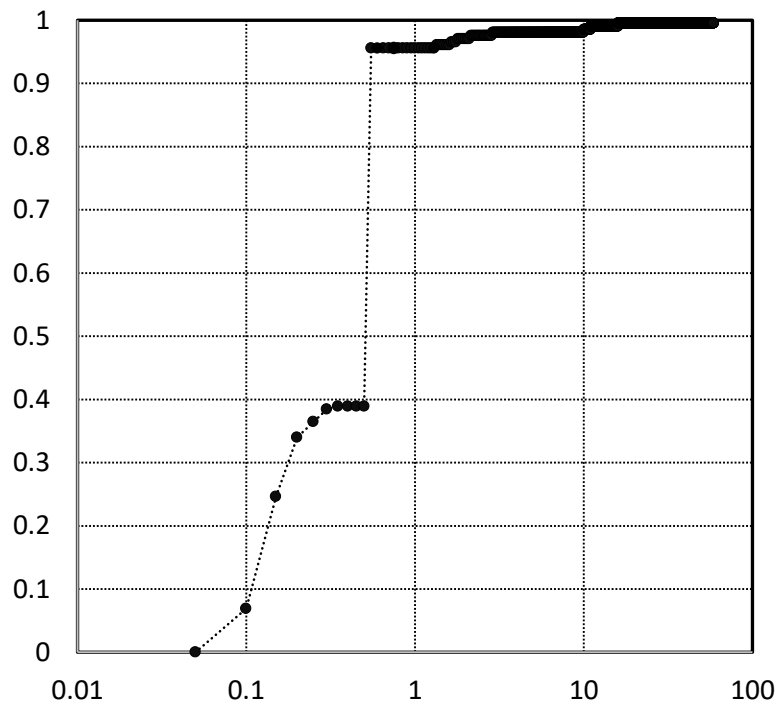
Cumulative Frequency Curve
POLAND - F mg/L



Cumulative Frequency Curve
PORTUGAL - F mg/L



Cumulative Frequency Curve
SLOVENIA - F mg/L



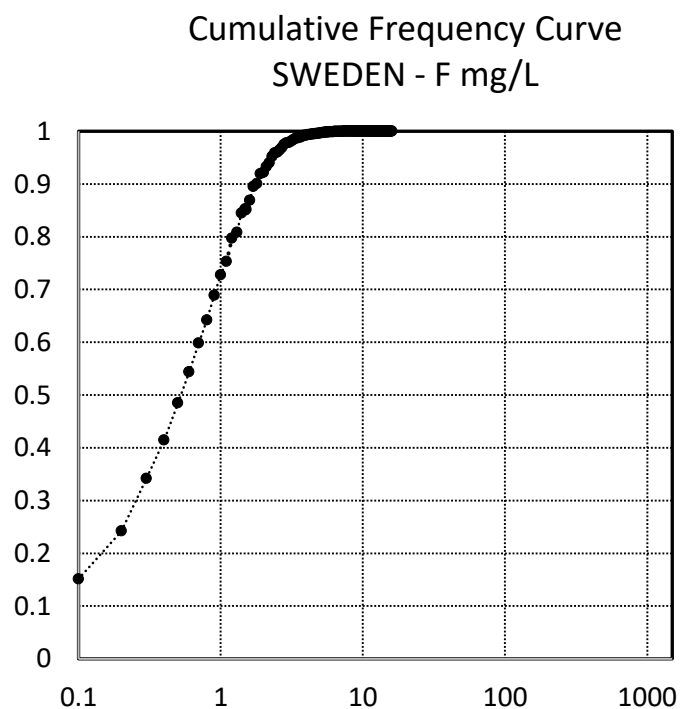
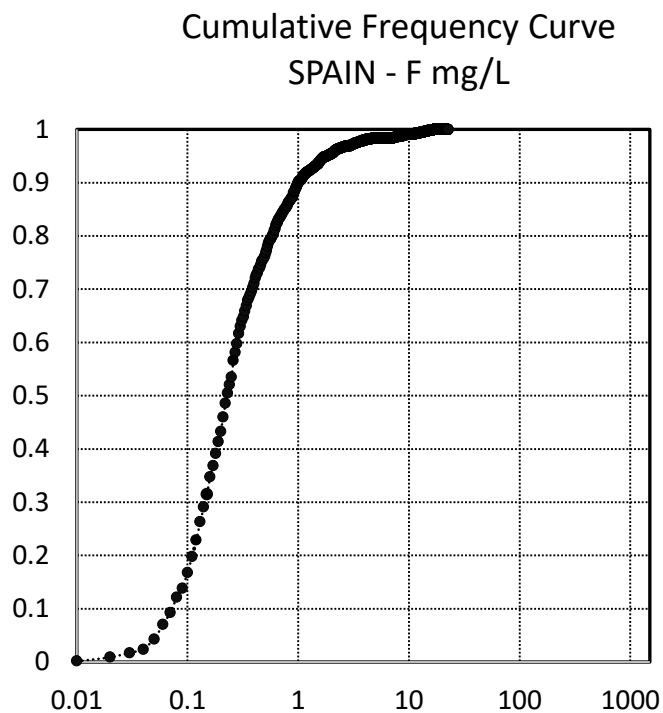


Figure 34. Cumulative Frequency Curves (CFC) for F in each country: Europe, Belgium (Flanders), Denmark, France, Iceland; Latvia, Poland, Portugal, Slovenia, Spain, and Sweden.

In almost all cases, BRC (P_{98}) represents the value from which there was a net change in the slope, marking a sustained change in trend until reaching the maximum concentrations. As

previously commented, this value, therefore, has been chosen as a reference, and the distribution of values above this threshold should be considered as significant maximum anomalies of As and / or F which create a geographic distribution pattern called to be interpreted in regional and Pan-European geological environment.

As previously mentioned, the concentration of As and F corresponding to P₉₈ is expressed as Basal Reference Concentration (BRC). In the database analysed, among all the percentiles, P₉₈ was the one that most frequently marked the change in slope towards the highest values of the series, therefore this value has been chosen as reference for the Basal Reference Concentration (BRC).

The **Basal Reference Concentration, BRC for As is 15 µg/L** (Figure 35), and **2.3 mg/L for F** (Figure 36). For comparison purposes, the Natural Background Level, NBL (P₉₀, established in T3.3.) for As is 4 µg/L, and 1.2 mg/L for F; both below the respective value of HGT =1 (10 µg/L for As and 1.5 mg/L for F). The Natural Background Level, NBL (P₉₀, established in T3.3.) is **4 µg/L** for As and **1.2 mg/L** for F, both below the respective value of HGT =1 (10 µg/L for As and 1.5 mg/L for F).

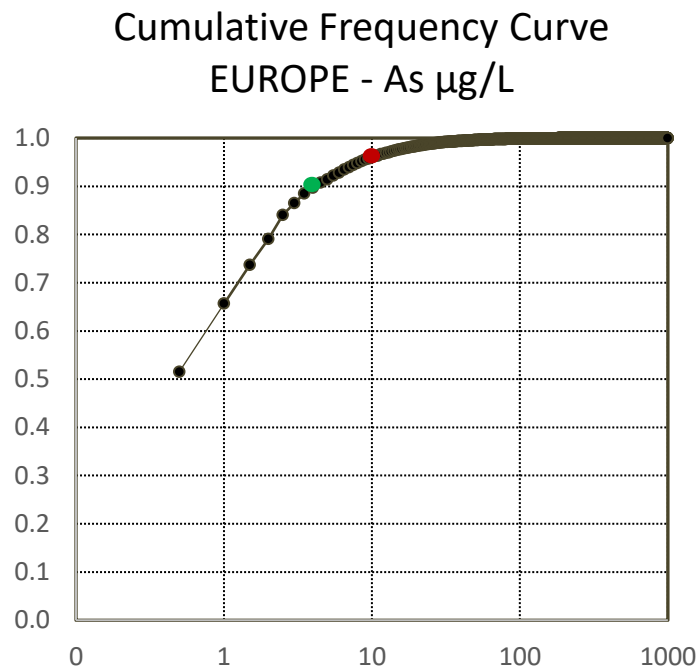


Figure 35. Cumulative Frequency curve for all As data at Pan-European level.
The P₉₈ (BRC) correspond to 15 µg/L.

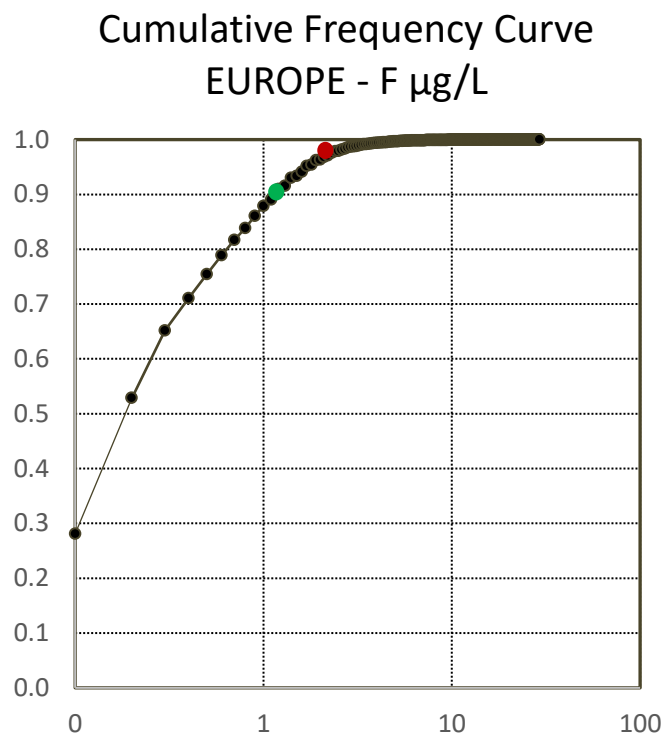


Figure 36. Cumulative Frequency curve for all F data at Pan-European level.
The P_{98} (BRC) correspond to 2.3 mg/L.

5.2 As and F evolution vs. European hydrochemistry (HFE-Diagram)

Among the hydrochemical diagrams representing the chemistry of groundwater, was chosen the Hydrochemical Facies Evolution Diagram (HFE Diagram) to represent all major chemistry of the samples (when available). Although this diagram was introduced as a diagnostic element in marine intrusion studies (Giménez-Forcada 2010; Giménez-Forcada, 2014; Giménez-Forcada & Sánchez, 2015), it can be applied to general cases such as other hydrochemical diagrams (see Giménez-Forcada et al., 2017a).

The advantage it offers compared to other more popular diagrams, is that the water samples are represented as a clear hydrochemical facies, not amalgamated, and that their representation marks evolutionary lines associated with different point processes, in addition to being able to represent all the major chemistry together with all the minor/trace elements or parameters in a same diagram (Giménez-Forcada, 2018).

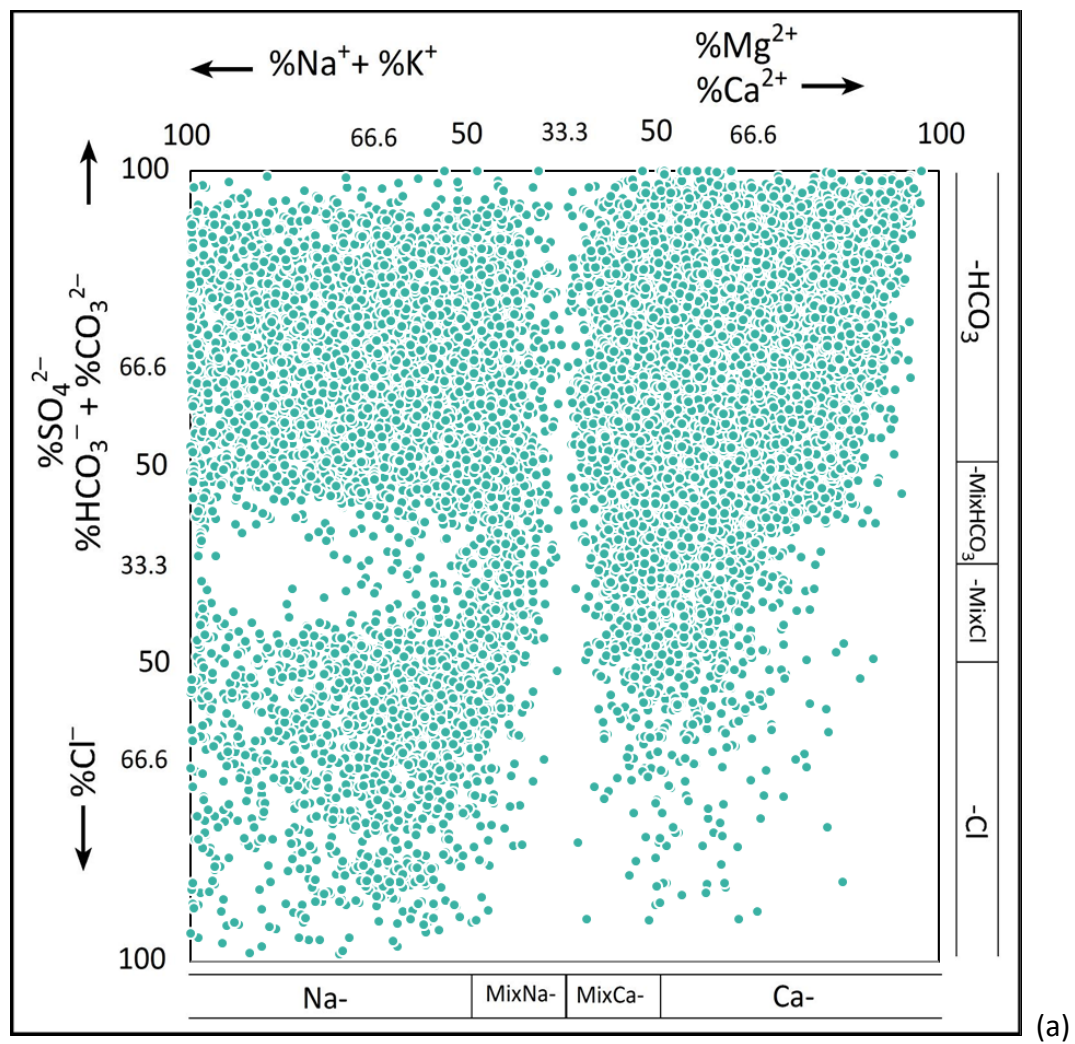


Figure 37. HFE-Diagram for representative hydrochemistry at Pan-European level (water samples from Austria, Belgium, Denmark, Serbia, Spain and Sweden).

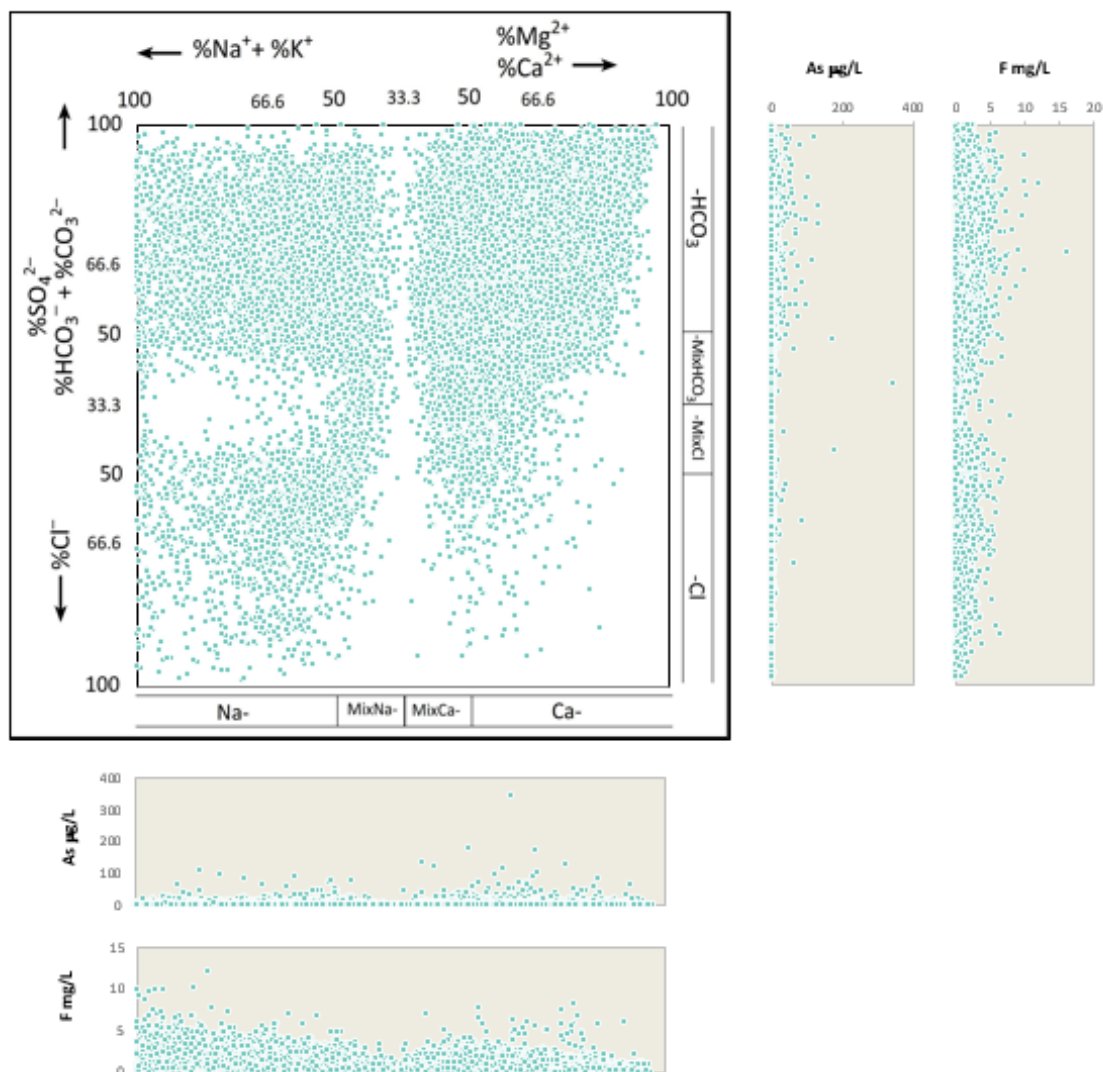


Figure 38. HFE Diagram illustrating the evolution of the concentration of As and F in relation to the general hydrochemistry at Pan-European scale (water samples from Austria, Belgium (Flanders), Denmark, Serbia, Spain, Sweden).

In figure 37, the HFE Diagram illustrates the general hydrochemistry on a pan-European scale (Austria, Belgium (Flanders), Denmark, Serbia, Spain, Sweden), together with the evolution of the concentration of As and F with respect to the percentage of cations and anions (Figure 38). In section 7 of this report, the diagram for each of these countries will be presented as *country study areas*.

Samples with **As concentrations above 10 µg/L (711 sp)**, belong to **CaHCO₃ (52%)** or **NaHCO₃ facies (36%)**. Only 9% are waters of chlorinated facies (NaCl (7%) or CaCl).



(2%)) (Table 5). For waters with F concentration >1.5 mg/L (2725 swp), the predominant HF are NaHCO₃ (51%) and CaHCO₃ (37%), followed by NaCl and CaCl (with 7% and 1%, respectively) (Table 6).

Table 5. Percentage of hydrochemical facies with F concentrations >10 µg/L (HGT_{As} =1)

Hydrochemical Facies	Percentage
CaHCO ₃	52%
NaHCO ₃	36%
CaCl	2%
NaCl	7%
Others (SO ₄ , Mg)	3%

Table 6. Percentage of hydrochemical facies with F concentrations >1.5 mg/L (HGT_F =1)

Hydrochemical Facies	Percentage
NaHCO ₃	51%
CaHCO ₃	37%
CaCl	1%
NaCl	10%
Others (SO ₄ , Mg)	1%

The highest arsenic concentrations (>50 µg/L) are found in the main hydrochemical facies CaHCO₃ and NaHCO₃, predominantly. The CaCl and NaCl facies have a very low representation. For highest fluoride concentrations (5 mg/L) is similar, except that the main facies are at reversed order, and the most representative hydrochemical facies (HF) is NaHCO₃.

Tables 5 and 6 summarizes which HF are associated with the highest concentrations of As and F at the Pan-European level (information extracted from major chemical water samples from Austria, Belgium, Denmark, Spain and Sweden).

5.3 Hydrogeotoxicity (HGT) and Basal Reference Concentration (BRC) at European scale

5.3.1 Hydrogeotoxicity by As and F: HGT_{As} and HGT_F

For the weighting of arsenic concentrations from the health perspective (or HGT_{As}) the reference guide level for drinking water has been chosen according to European legislation and the World Health Organization, which set a value of 10 µg/L. With this concentration are 4% of the samples from the observation network on a pan-Europeanscale.



Table 7. Summary of the distribution of the 4% of the samples exceeding the 10 µg/L arsenic concentration in groundwater. The number of samples and their corresponding percentage for Denmark, if the threshold of 5 µg/L of As is considered, is indicated in parentheses. Also the total of samples, if Danish waters with As > 5 µg/L are included, is indicated in the total in parentheses.

Country	N. Samples	
	As >10 µg/L	%
Austria	36	2 %
Belgium	51	3 %
Denmark	299 (812)	18 (37) %
France	356	22 %
Hungary	256	16 %
Iceland	14	1 %
Ireland	21	1 %
Latvia	14	1 %
Poland	48	3 %
Portugal	34	2 %
Romania	23	1 %
Serbia	26	2 %
Slovenia	4	0.2 %
Spain	219	13 %
Sweden	247	15 %
TOTAL	1349 (2161)	100 %

For arsenic, and in the case of Denmark, the number of samples that exceeds the arsenic concentration limit for the Danish laws (5 µg/L) are also indicated (in parentheses).

For dissolved fluoride in groundwater, the threshold established by WHO for drinkable water is 1.5 mg/L (HGT_F=1)

Table 8. Summary of the distribution of the 7% of the samples exceeding the 1.5 mg/L fluoride concentration in groundwater.

Country	N. Samples	
	F >1.5 mg/L	%
Belgium	105	3 %
Denmark	125	4 %
France	470	14 %
Iceland	38	1 %
Latvia	1	0.03 %
Poland	10	0.3 %
Portugal	5	0.1 %
Spain	86	2 %
Sweden	2612	76 %
TOTAL	3452	100 %

Tables 7 and 8 show the number of points for each country with values above the limit for drinkable water for As and F, respectively.

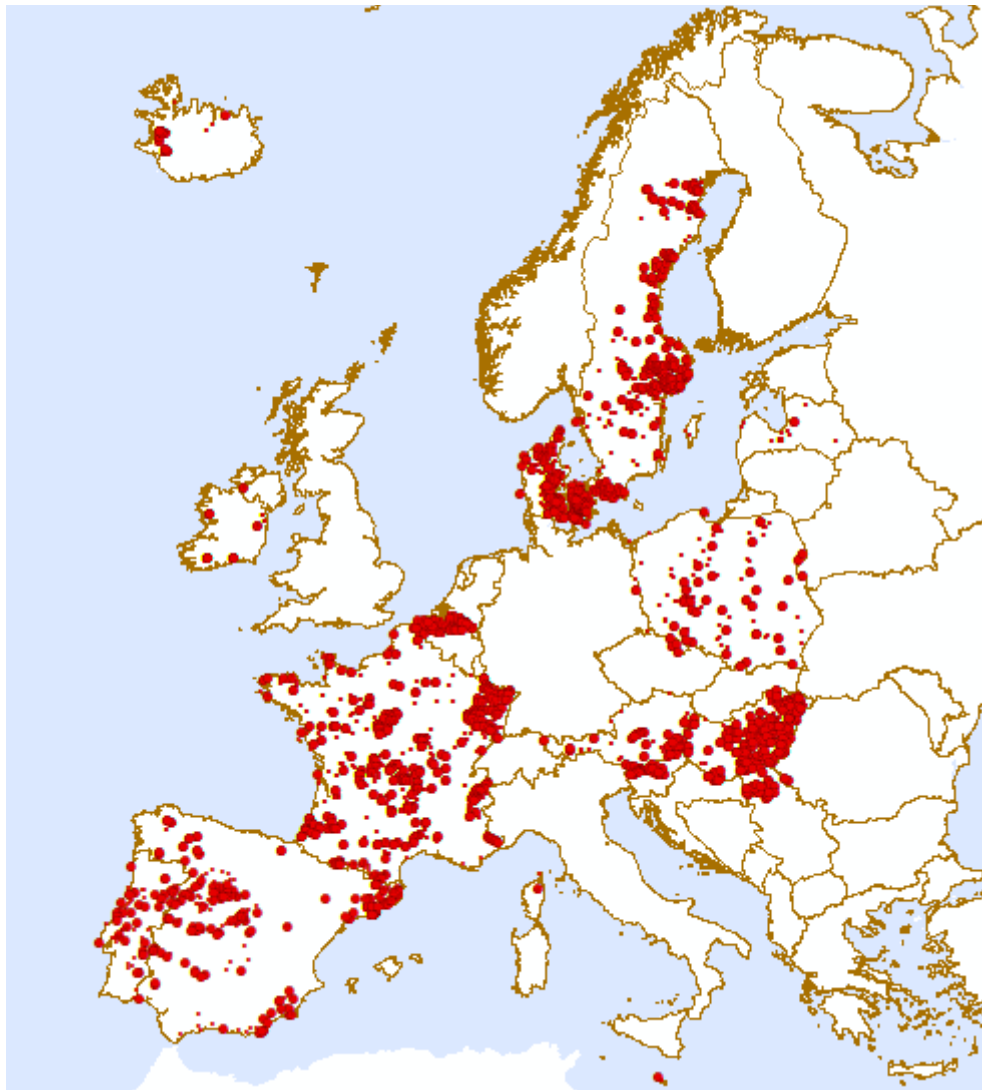


Figure 39. Distribution of $HGT_{As} \geq 1$ (big red points) and $HGT_{As} \geq 0.5$ ($HGT \geq 1$ for Denmark) (small red points) at Pan-Europe scale. The maximum density of highest values of HGT_{As} occurs in Pannonian basin, Belgium (Flanders), Denmark and some sectors in France, Sweden, Spain and Poland.

Figure 39 gives the distribution of water samples with As concentration $\geq 10 \mu\text{g/L}$ ($HGT_{As} \geq 1$) for the seventeen participating countries.

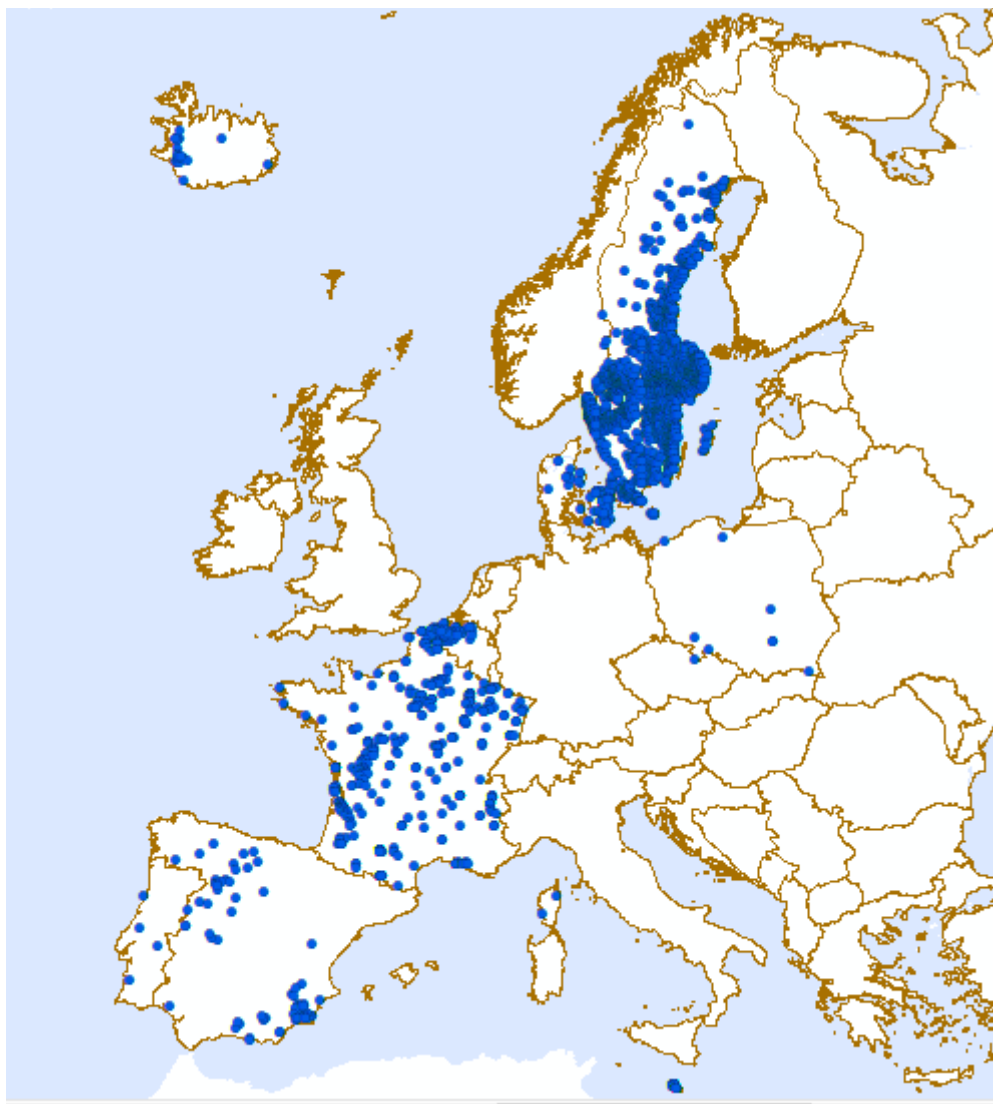


Figure 40. Distribution of $HGT_F \geq 1$ at Pan-Europe scale.

Figure 40 shows the distribution of water samples with a F concentration ≥ 1.5 mg/L ($HGT_F \geq 1$) for the twelve participating countries in F network. The density of the network is maximum in Sweden and France.

5.3.2 *Hydrogeotoxicity (HGT) vs. Basal Reference Concentration (BRC)*

One of the characteristics of the trace element distribution is that it is uneven and apparently without a regulatory pattern; this is especially true for arsenic, the geographical distribution of which is often described as 'patchy'.

Although the processes that regulate the water-rock interaction in the study area are usually known, many times the rules of their geographical distribution remain to be explained on broader scale (regional and Pan-European).

Discarding the anthropic or anthropic factors (many times of a specific nature when it comes to high concentrations or dispersed but in this case with concentrations around average values), it



is important to focus on the highest concentrations of trace elements and relate them with natural environment. In many cases, they are the ones that lead to identifying the most important geological factors that are behind the pattern that we are trying to decipher. With this premise and based on studies on the distribution of As in the south of the Duero Basin (Giménez-Forcada et al., 2017a; Giménez-Forcada et al., 2017b) it was important to identify the concentration from which the highest geogenic anomalies must be interpreted.

As already mentioned in previous sections and can be extracted from Table 3, the datasets differ highly among participating countries (e.g. in Austria surface near groundwaters and commonly no deep groundwaters).

Table 9. Main values relates in relation to BRC_{As} (P_{98}) and HGT_{As} .

	As $\mu\text{g/L}$ Max. value	Maximum HGT_{As}	% Samples with $HGT_{As} > 1$	As = 10 $\mu\text{g/L}$ $HGT_{As} = 1$	P_{98} (BRC) As $\mu\text{g/L}$
AUSTRIA	86	9	2%	P98	10
BELGIUM (FLANDERS)	1295	130	9%	P90	28
BOSNIA-HERZEGOVINA	5	0.5	-	P87	2
DENMARK ¹	68	7 (14)	4% (12%)	P95 (P88)	15
FRANCE	273	27	6%	P94	22
HUNGARY	168	17	36%	P64	69
ICELAND	35	4	10%	P90	18
IRELAND	35	4	10%	P90	18
LATVIA	10	1	3%	P96	10
POLAND	539	54	3%	P97	13
PORTUGAL	56	6	6%	P94	23
SERBIA	250	25	-	P50	233
SLOVENIA	59	6	2%	P98	10
SPAIN	353	35	7%	P93	31
SWEDEN	1000	100	1%	P98	10

¹ DENMARK. In parenthesis data according Danish legislation for As in drinking water (5 $\mu\text{g/L}$)



Table 10. Main values relates in relation to BRC_F (P_{98}) and HGT_F .

	F mg/L Max. value	Maximum HGT_F	% Samples with HGT_F>1	F = 1.5 mg/L HGT_F=1	P₉₈ (BRC) F mg/L
BELGIUM (FLANDERS)	10	7	0	P78	7
DENMARK	7	4	2%	P98	1.5
FRANCE	6	4	2%	P98	2
ICELAND	14	9	27%	P73	12
LATVIA	15	10	1%	P99	<1.5
POLAND	5	3	1%	P99	<1.5
PORTUGAL	9	6	1%	P99	<1.5
SPAIN	23	15	7%	P93	4
SWEDEN	16	11	15%	P85	3

5.3.3 Relationship between HGT_{As} and HGT_F , and BRC_{As} and BRC_F with lithology at Pan-European scale

Water-rock interaction processes are one of the factors that regulates the concentration of trace elements in groundwater and the impact of these processes can be analyzed both punctually or locally and on a regional or Pan-European scale, as shown below.

In figures 41 and 42, the distribution of HGT_{As} and HGT_F in groundwaters is compared with different lithology (type of rocks (metamorphic and igneous rocks) and chronostratigraphic levels) using SIG (ArcGis). Only for samples $HGT_{As} \geq 1$ and $HGT_F \geq 1$ (threshold for As in drinking water is established in 10 µg/L, and is 5 µg/L in Denmark).

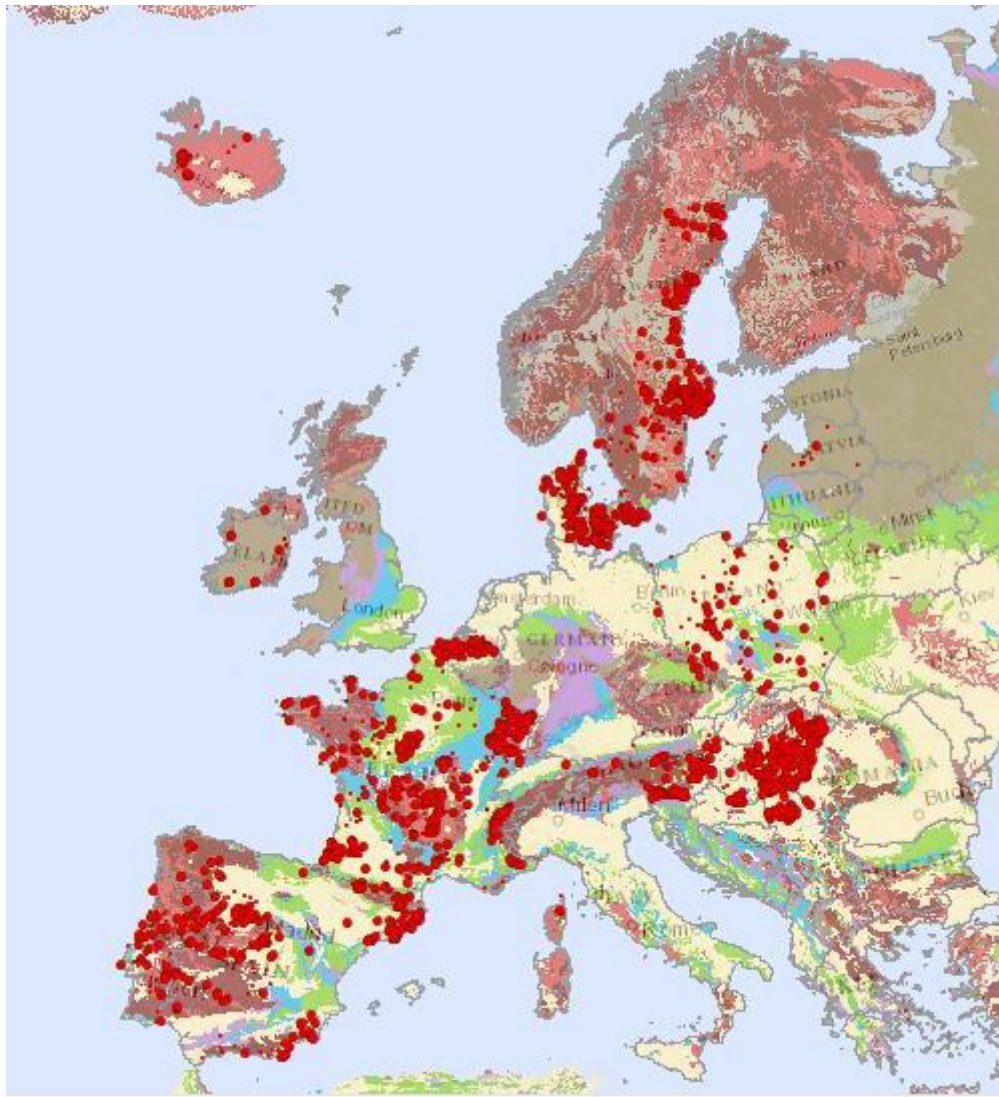


Figure 41. $HGT_{As} \geq 1$ distribution in groundwaters at Pan-European scale. The data correspond to seventeen countries: Austria, Belgium (Flanders), Bosnia-Herzegovina, Denmark, France, Hungary, Iceland, Ireland, Latvia, Malta, Romania, Polonia, Portugal, Serbia, Slovenia, Spain and Sweden). Symbols: small red points $HGT_{As} \geq 0.5$; big red points $HGT_{As} \geq 1$.

Groundwaters with $HGT_{As} \geq 1$ (and $HGT_{As} \geq 0.5$ for Denmark) are identified mainly in Hungary, Belgium, Denmark, Sweden, France, Portugal, Spain, Austria, Poland, Serbia, Ireland, and Iceland (Figure 35). Many of these anomalies appear in mountainous reliefs made up of endogenous rocks, but overall are identified in big Cenozoic depression areas. Locally, $HGT_{As} \geq 1$ is also associated to Triassic rocks (France).

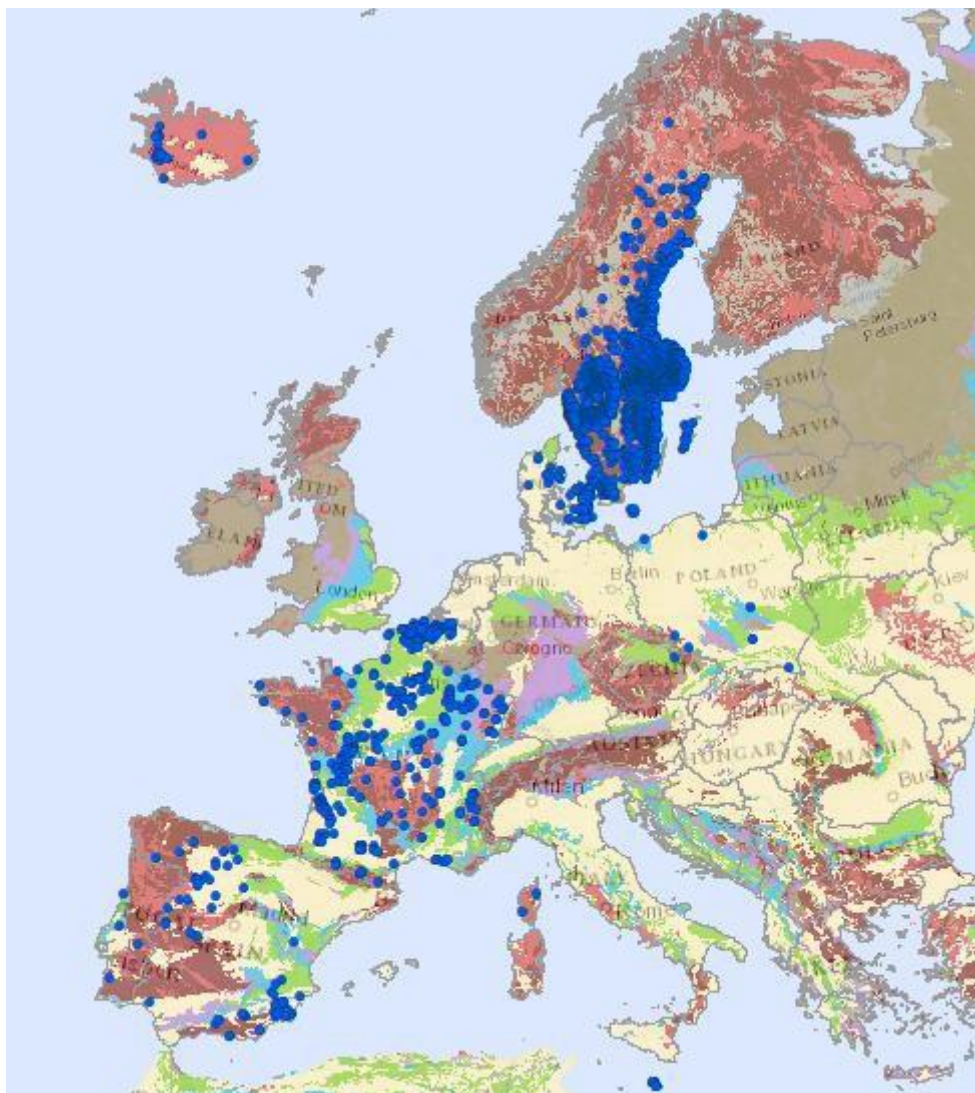


Figure 42. $HGT_F \geq 1$ distribution in groundwaters at Pan-European scale. The data correspond to twelve countries: Belgium (Flanders), Denmark, France, Iceland, Latvia, Malta, Poland, Portugal, Serbia, Slovenia, Spain and Sweden). Symbols: blue points $HGT_F \geq 1$.

The observation network of F (Figures 41 and 42) is larger than that of As (more points) but includes a smaller number of countries. Values of $HGT_F \geq 1$ occur in Sweden, France, and Belgium, but also (to a lesser extent), in Denmark, Spain, Iceland, and Malta. Most of them are located around relevant ancient massifs but also associated with Mesozoic carbonated outcrops. There are also relevant values in some Cenozoic basins next to the oldest mountain massifs with endogenous rocks outcrops.

The other index to consider is the BRC values for each trace element (As and F). In this case, data from mineral and thermal waters are included because what is intended with this index is to identify the pattern of the maximum anomalies (P_{98}) and their relationship with the lithology of the geological materials that emerge.

Figures 43 and 44 plot the distribution of As and F concentration values that exceed the respective BRC: 18 $\mu\text{g/L}$ for As and 2.3 mg/L for F on the simplified geological map.

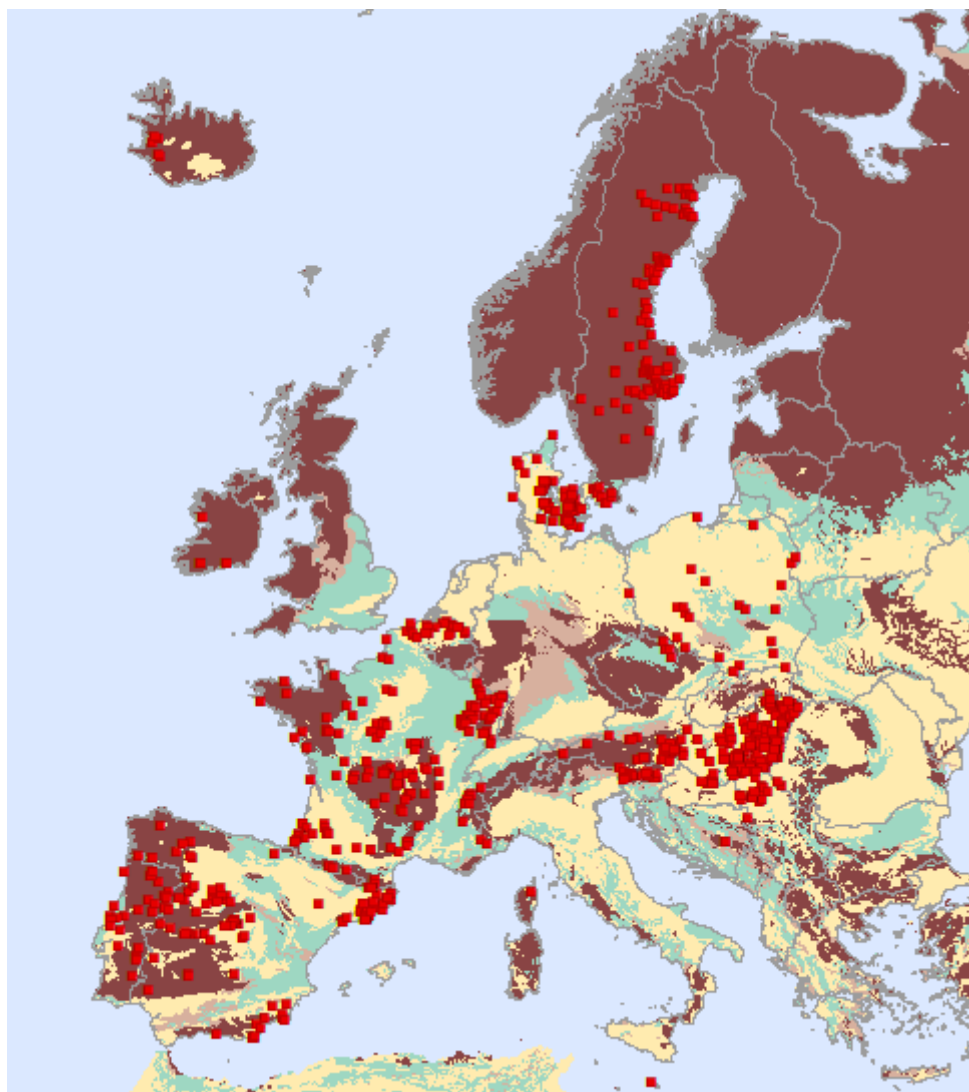


Figure 43. Map with the distribution of As values $\geq 15 \mu\text{g/L}$ (P_{98}), associated with a HGT_{As} of 1.5, in relation to the lithology and chronostratigraphic levels of the simplified European geological map. **Legend:** dark brown (1) European ancient Massifs, EAM (it includes Precambrian, Paleozoic, Igneous and Metamorphic rocks), purple (2) Mesozoic-Triassic; aquamarine (3) Mesozoic-Carbonated rocks (Mesozoic-Jurassic and Mesozoic-Cretaceous); light yellow (4) Cenozoic.

To simplify the analysis, European geology has been simplified, leaving only 4 units: (1) European ancient Massifs, EAM (it includes Precambrian, Paleozoic, Igneous and Metamorphic rocks), (2) Mesozoic-Triassic; (3) Mesozoic-Carbonated rocks (Mesozoic-Jurassic and Mesozoic-Cretaceous); (4) Cenozoic. Fault structures are not represented in these maps.

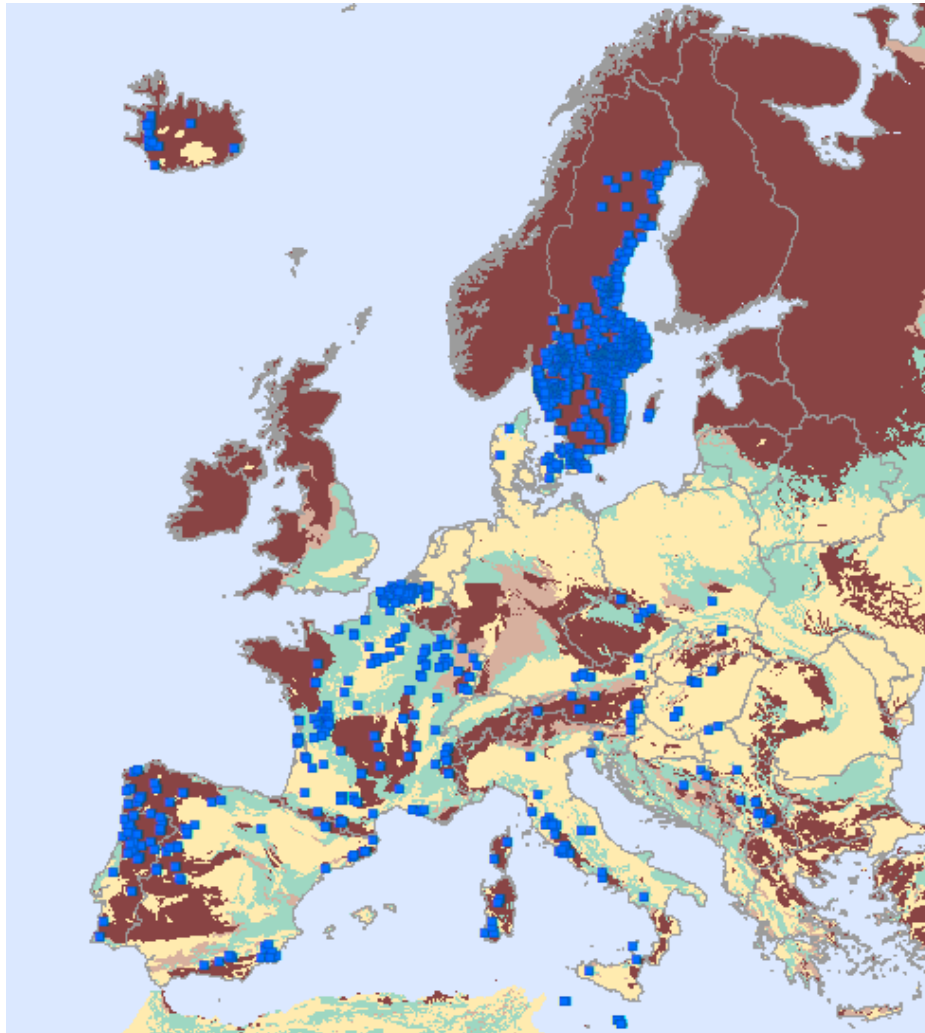


Figure 44. Map with the distribution of F values ≥ 2.3 mg/L (P_{98}), associated with a HGT_F of 1.5, in relation to the lithology and chronostratigraphic levels of the simplified European geological map. **Legend:** dark brown (1) European ancient Massifs, EAM (it includes Precambrian, Paleozoic, Igneous and Metamorphic rocks), purple (2) Mesozoic-Triassic; aquamarine (3) Mesozoic- Carbonated rocks (Mesozoic-Jurassic and Mesozoic-Cretaceous); light yellow (4) Cenozoic.

The maximum concentration values have been selected, as symbolized by the BCR, and each point has been geographically related to the geological material on which it is located. The results are shown in the Tables 11 and 12 which collect the analysis about the interactions between the four lithological groups and the BRC index (BRC_{As} and BRC_F values), and countries associated.



Table 11. (a) Summary about the intersection of As concentration $>15 \mu\text{g/L}$ ($\geq P_{98}$) with igneous and metamorphic rocks and different chronostratigraphic units (Precambrian, Paleozoic, Mesozoic-Triassic, Mesozoic-Jurassic, Mesozoic-Cretaceous, and Cenozoic. (b) Distribution by countries. (c) Summary.

Unit/Rock	N.	% Samples	Min As $\mu\text{g/L}$	Max As $\mu\text{g/L}$	Average As $\mu\text{g/L}$	Median As $\mu\text{g/L}$	Countries	(a)
Cenozoic	581	59	15	1295	39	23	Hungary, Denmark, Spain, Poland, Belgium, France, Portugal, Romania, Austria, Sweden, Serbia, Slovenia, Bosnia Herzegovina	
Mesozoic-Cretaceous	46	5	15	104	28	22	Denmark, Portugal, Poland, France, Austria, Romania, Spain	
Mesozoic-Jurassic	40	4	15	79	30	24	France, Poland, Portugal, Spain, Sweden, Austria, Romania	
Mesozoic-Triassic	49	5	15	175	33	24	France, Sweden, Hungary, Romania	
Paleozoic	26	3	15	1000	73	25	France, Spain, Austria, Sweden, Ireland, Romania, Hungary	
Precambrian	24	2	15	77	29	21	Sweden	
Metamorphic	128	13	15	610	55	27	France, Sweden, Austria, Spain, Portugal, Poland	
Igneous	91	9	15	180	41	26	Sweden, France, Spain, Hungary, Iceland, Ireland, Portugal, Austria, Poland	
	985	100						

Country	Unit/Rock	(b)
Austria	Cenozoic, Cretaceous, Paleozoic, Metamorphic, Igneous	
Belgium	Cenozoic	
Denmark	Cenozoic, Cretaceous	
France	Cenozoic, Cretaceous, Jurassic, Triassic, Paleozoic, Metamorphic, Igneous	
Hungary	Cenozoic, Triassic, Igneous	
Iceland	Igneous	
Ireland	Paleozoic, Igneous	
Poland	Cenozoic, Cretaceous, Metamorphic, Igneous	
Portugal	Cenozoic, Cretaceous, Jurassic, Metamorphic, Igneous	
Romania	Cenozoic	
Serbia	Cenozoic	
Slovenia	Cenozoic	
Spain	Cenozoic, Cretaceous, Jurassic, Paleozoic, Metamorphic, Igneous	
Sweden	Cenozoic, Jurassic, Triassic, Paleozoic, Precambrian, Metamorphic, Igneous	

N	%	Groups	(c)
582	59	Cenozoic	
86	9	Mesozoic (Jurassic and Cretaceous)	
49	5	Mesozoic (Triassic)	
269	27	European ancient Massifs	
986	100		



Almost 60% of the highest As concentration values (the highest BCR_{As} values) are found in the areas covered by Cenozoic materials. This group is followed in order of priority by the set of samples (27%) with maximum arsenic concentration located on ancient European massifs. In third and fourth place, respectively, are the areas covered by Mesozoic materials from the Jurassic-Cretaceous and Triassic, with 9% and 5%, respectively.

From the results table it is also extracted that metamorphic and igneous rocks are the main (primary) source of arsenic, with average values of 55 $\mu\text{g/L}$ and 41 $\mu\text{g/L}$, respectively. Groundwaters associated with Cenozoic materials (secondary sources) have similar concentrations, although slightly lower. Another conclusion that is drawn is that As from groundwater is related with practically all geological materials, which confirms the ubiquitous nature of this element.

Results for 4,442 groundwaters with As concentrations $\geq 4 \mu\text{g/L}$ (NBL/BL, P_{90}), are similar. 54% of samples are sited in Cenozoic areas, while 33% corresponds to groundwaters from European Ancient Massifs, EAM (Paleozoic, Metamorphic, Precambrian, and Igneous rocks). Only 13% are associated with Mesozoic outcrops: 8% are linked to Mesozoic Cretaceous-Jurassic carbonated rocks and 5% to Triassic Mesozoic outcrops (mainly in France).

The results of these spatial analyzes on the effect of the factor 'lithology' (and water-rock interaction) in the distribution of As in Europe agree between BRC and NBL, being more discriminating when the threshold corresponding to the BRC index is applied.

For fluoride, a similar spatial analysis was developed about interrelation between BRC of F (2.3 mg/L , BRC, P_{98}). The maximum values of fluoride values in the groundwater set are found in Cenozoic sediments and igneous rocks. The relation between the highest F concentration and the litho-chronostratigraphy reveals that the highest percentage (70%) of samples are associated with igneous and metamorphic rocks, together Paleozoic and Precambrian materials, grouped as EAM. A high percentage is found also associated to the Cenozoic sediments (21%). As in the previous case of As, data from mineral and thermal waters have been included.



Table 12. (a) Summary about the intersection of F concentration >2.3 mg/L ($\geq P_{98}$) with igneous and metamorphic rocks and different chronostratigraphic units (Precambrian, Paleozoic, Mesozoic-Triassic, Mesozoic-Jurassic, Mesozoic-Cretaceous, and Cenozoic. (b) Distribution by countries. (c) Summary.

	N	% Samples	Max F mg/L	Min F mg/L	Average mg/L	F Median F mg/L	Countries
Cenozoic	294	21	326.0	2.3	7.1	3.8	Austria, Belgium, Denmark, France,
Mesozoic-Cretaceous	38	3	29.2	2.3	5.0	3.5	France, Denmark, Poland, Italy, Portugal
Mesozoic-Jurassic	73	5	13.0	2.3	4.1	3.5	France, Spain, Italy, Poland, Sweden
Mesozoic-Triassic	13	1	14.9	2.3	4.3	3.1	France, Sweden, Spain, Austria, Slovenia
Paleozoic	39	3	15.0	2.3	4.1	3.1	Sweden, France, Latvia, Spain
Precambrian	218	15	7.0	2.3	2.9	2.7	Sweden
Metamorphic	451	32	38.1	2.3	4.1	2.9	Sweden, France, Portugal, Spain, Austria, Poland, Serbia, Slovenia
Igneous	281	20	150.0	2.3	4.7	3.0	Sweden, France, Iceland, Portugal, Spain, Italy, Serbia, Hungary, Slovenia
	1407	100					

Country	Unit/Rock	(b)
Austria	Metamorphic, Triassic, Cenozoic	
Belgium	Cenozoic	
Denmark	Cenozoic, Cretaceous	
France	Cenozoic, Cretaceous, Jurassic, Triassic, Paleozoic, Metamorphic, Igneous	
Hungary	Cenozoic, Igneous	
Iceland	Cenozoic, Igneous	
Italy	Cenozoic, Cretaceous, Jurassic, Igneous	
Latvia	Cenozoic, Paleozoic	
Poland	Cenozoic, Cretaceous, Metamorphic	
Portugal	Cenozoic, Cretaceous, Metamorphic, Igneous	
Serbia	Cenozoic, Metamorphic, Igneous	
Slovenia	Cenozoic, Triassic, Metamorphic, Igneous	
Spain	Cenozoic, Jurassic, Triassic, Paleozoic, Metamorphic, Igneous	
Sweden	Cenozoic, Jurassic, Triassic, Paleozoic, Precambrian, Metamorphic, Igneous	

N	%	Groups	(c)
294	21	Cenozoic	
111	8	Mesozoic (Jurassic and Cretaceous)	
13	1	Mesozoic (Triassic)	
989	70	European ancient Massifs	
1407	100		

When the set of samples are analyzed using the NBL/BL index as threshold (4,942 samples), the results are similar to that obtained with the BRC: 76% of the samples with concentrations ≥ 1.2 mg/L (NBL/BL (P_{90}) for F) are associated with EAM, whereas that 16% to samples are located in Cenozoic basins. The remaining 8% corresponds to Mesozoic rocks, mainly carbonated (Jurassic and Cretaceous).

As a consequence of this data analysis, it can be said that the main sources of F (this is valid also for As somehow) are metamorphic, igneous rocks, and the Paleozoic and Precambrian litho-chronostratigraphic levels. Therefore, groundwater with high concentrations of F may be



associated with minerals that form different endogenous rocks, as ore deposits, hydrothermal flows, etc. In general, these rocks constitute aquifugal formations (or poor aquifers) in altered or fracture zones (where they can constitute fissured aquifers of relative importance). In fact, the fractures would have a particular importance in the distribution of groundwater flows enriched in F or other PTGTE in Fissured Hard Rocks, FHR. Cenozoic basins, covered by Tertiary and Quaternary materials, rank second in percentage. When the distribution of concentrations in the geological maps in these areas is appreciated, it is observed that they are sedimentary areas related to FHR outcrops and not so much with Mesozoic carbonate reliefs. These latter are apparently of greater importance (only 8% of the samples studied), but occasionally it can also be a source of F and other PTGTE if, for example, during lake or marine carbonate sedimentation there were significant contributions of F to the basin or from the basement through flows enriched in F.

From this analysis it is concluded that the main lithological source must be found in the FHR that outcrop in Ancient European Massifs. These areas are, at the same time, source areas of the sediments that fill the sedimentary basins and that, as a secondary source, also become a potential source of PTGTE to the groundwater. The sedimentary environment is both a source and a means of dispersal. Detrital aquifers are intensely exploited. The groundwater is extracted, used and returned, acting as a scattering vehicle for PTGTE in the environment. In this environment pollution, overexploitation, land use, etc. coexist. These factors can change the physico-chemical conditions of the environment and turn a point or concentrated focus in an area affected by high concentrations of PTGTE or cause changes that increase or decrease its concentration in the water (changes in pH and or Eh).

These considerations that are made with respect to F, are valid in general for all PTGTE and, in particular for As. In this case, the sedimentary environment takes on greater prominence and this must probably be related to its geochemical behaviour. The formation of As oxyanions in water gives rise to a high affinity for the positive charges of some minerals present in the sedimentary medium, such as iron oxy-hydroxides. Like fluorine, arsenic is related to the circulation of fluids (sometimes with hydrothermal character in nature) in the FHR, but, when these flows enter the sedimentary medium and the conditions change, new sources are generated (they would be of secondary order) and other processes related to the local physical-chemical environment intervene.

From this reflection, several possible conclusions are drawn that we will return to at the end of the report, but which are now being pointed out to introduce the second section. The primary sources of PTGTE (As and F, in this case) would be the FHR of the European Ancient Massifs (EAM) formed by rock constituent minerals and with frequent hydrothermal ore deposits. The way to distribute the trace elements inside these rock masses would be the fissures. Therefore, the structural factor, as well as the lithological one, are important in the distribution of trace elements in the groundwaters that circulate through it.

Sedimentary basins develop on basements formed by these source rocks, which continue to be fissured and which, from the fractures, provide flows rich in PTGTE. In short, it is not unreasonable to think that the structural factor is important when we try to analyze the geographical distribution of PTGTE, whether it is fissured or sedimentary aquifers; for this reason, this factor is analyzed below, with special emphasis on the FHR outcrops and the Cenozoic sedimentary basins, where fault lines are not always apparent.



5.3.4 Relationship between HGT_{As} and HGT_F , and BRC_{As} and BRC_F with fault structures at Pan-European scale

As previously mentioned, in order to take into account the influence of fractures on the distribution of As and F in groundwater, new structures have been added to those marked by the geological map of the BGR. It was done taking into account research works that included maps on a regional-European scale (Debelmas, 1974; Arthaud and Matte, 1975; Marfil and de la Pena, 1987; Martínez-Catalán, 1990; Matte et al., 1990; BRGM- SGN, 1996; Clausen and Pedersen, 1999; Pharaoh, 1999; Wéber, 2002; Marović et al., 2002; Nielsen et al., 2003; De Vicente et al., 2004; Lagerbäck, and Sundh, 2008; Nielsen et al., 2010; Juhlin et al., 2010; Bergman et al., 2012; Thorsen, 2013; Małolepszy et al., 2015; Nielsen et al., 2015; Sušić et al., 2015; Barford et al., 2016; Briais et al., 2016; Hseinat and Hübscher, 2017; Békésia et al., 2018; Kufrasa et al., 2019; Baroň et al., 2019). The areas covered by Cenozoic sediments and rocks, where there is little information on fault structures or their prolongations from the surrounding mountain systems, which would form the basement or socle, have been especially taken into account. With these new faults, a new shape file has been created with which to contrast the distribution pattern of As and F with respect to the fault structures.

Four distances between the water point and the fault line have been considered: 500 m, 1 km, 5 km and 10 km. The maximum value of 10 km is considered an acceptable distance of approach in the calculation, given the scale of the map. (1:28,000,000). It is not necessary to rule out a certain margin of error in the design of the fault line, but it should be borne in mind that faults are not net lines (not always) and that they have their areas of influence and 'ramifications' that are often more permeable than the fault itself. In the case of detrital aquifers over FHR basement, the exact coincidence between the position of the point and the 'supposed fault line' is more unlikely, especially considering the dispersal effect that the detrital aquifer undoubtedly exerts on the flow coming from the faults of the FHR basement. When the method is applied to smaller areas and there is sufficiently detailed knowledge of the fault network (even supported by geophysical studies that allow the recognition of the basement structure, in the case of detrital aquifers), smaller distances can be chosen.

The relationship between BRC_{As} and BRC_F (only for samples with As and F concentration above 15 µg/L and 2.3 mg/L, respectively) are analysed in relation their respective intersection with faults.

Table 13 shows the results between the highest As concentrations in groundwater (let's remember that also includes mineral and thermal waters) and fault structures for the different distances alluded, within each litho-chronostratigraphic group of considered in the simplified geology.



Table 13. Summary about the intersection of As concentration $>10 \mu\text{g/L}$ ($\geq P_{98}$) with faults at different distances, taking into account the main lithological groups (1) Cenozoic, (2) Cretaceous-Jurassic, (3) Triassic, and (4) European Ancient Massif with igneous and metamorphic rocks and Precambrian-Paleozoic units.

GROUPS	Number of Samples	Distance to fault	Samples	Percentage	Countries
Cenozoic	369 (53%)	$\leq 1\text{km}$	175	47%	Hungary, Spain, Denmark, Poland, Portugal, Serbia, France, Sweden
		$\leq 5\text{km}$	43	12%	Denmark
		$\leq 10\text{km}$	151	41%	Denmark, Hungary, Spain, France, Poland, Portugal, Slovenia, Serbia, Sweden, Bosnia-Herzegovina, Austria
Cretaceous and Jurassic	69 (10%)	$\leq 1\text{km}$	45	65%	Denmark, France, Poland, Spain, Sweden, Portugal
		$\leq 5\text{km}$	3	4%	Denmark
		$\leq 10\text{km}$	21	30%	Denmark, France, Portugal, Austria
Triassic	27 (4%)	$\leq 1\text{km}$	13	48%	France, Romania, Sweden
		$\leq 5\text{km}$	0	0%	-
		$\leq 10\text{km}$	14	52%	France, Hungary
European ancient Massif	233 (33%)	$\leq 1\text{km}$	159	69%	France, Sweden, Spain, Portugal, Hungary, Portugal, Iceland, Poland, Romania
		$\leq 5\text{km}$	0	0%	-
		$\leq 10\text{km}$	74	31%	France, Sweden, Austria, Spain, Hungary, Iceland, Ireland, Poland, Portugal
TOTAL	698 (100%)				

698 samples with As concentrations higher than the BRCAs value (71% of samples with $[\text{As}] \geq \text{BRCAs}$ are near a fault line) show a relationship with fracture lines at a distance of $\geq 10\text{km}$. Most of them interact with the structure within a radius of 1km. Most of them are observed, in relation to Cenozoic and FHR outcrops (86%).

From database, analysis done for set of samples with As concentration $\leq 4 \mu\text{g/L}$ (NBL/BL, P_{90}) a similar conclusion follows: 87% samples of samples with higher NBL_{As} values are sited near a fault ($\leq 10\text{km}$) and mainly for samples corresponding to Cenozoic areas (51%) and EAM (36%).

It is verified that the maximum As concentration values (BRC_{As}) are clearly associated with detrital aquifers of Cenozoic areas, where there is also an evident structural control by fault lineaments (more than 50% of the samples with the highest As concentrations in Cenozoic aquifers are within 10 km of a fault). Likewise, this structural factor is also important in the control of high concentrations of water collected in EAM (FHR aquifers).

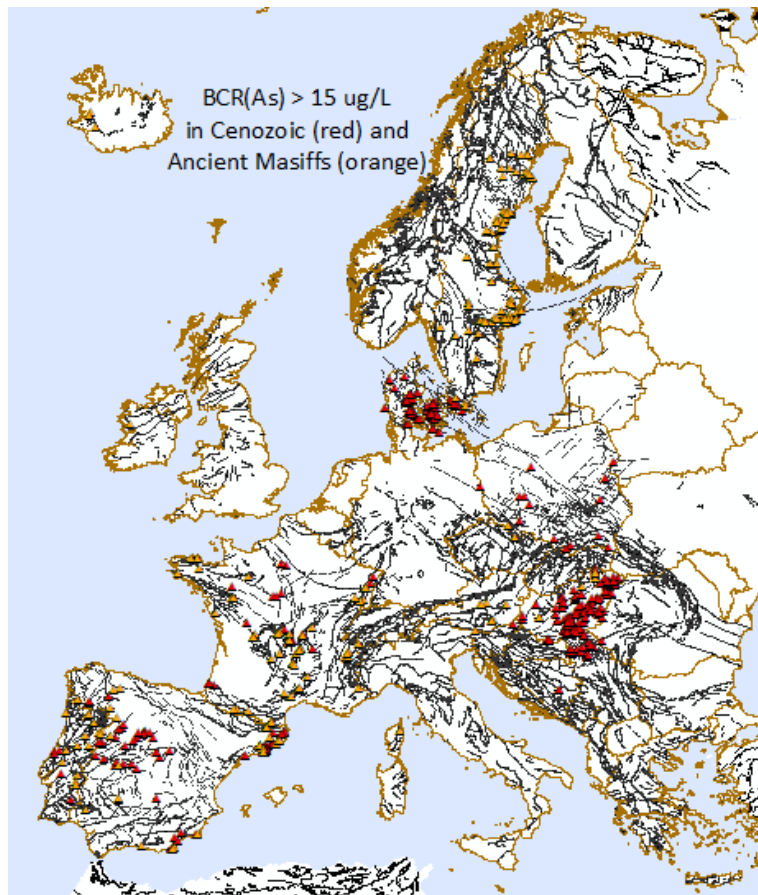


Figure 45a. Map with the distribution of As values $\geq 15 \mu g / L$ (BRC_{As}), associated with a HGT_{As} of 1.5, in Cenozoic areas (71% samples) (red) and in Ancient Massifs (33%) (orange), and their relationship with fault lines (BGR and others).

The Great European Plains covered with Cenozoic materials stand out, where it is more difficult to recognize the faults of the basement or its prolongation from the edges of the mountain systems. Hungary, Denmark, Spain, Poland or France are some of the examples of the probable influence of the structural factor on the geographic distribution of waters enriched in As in Cenozoic materials. All of them are sedimentary basins developed at the feet of EAM: Carpathian Mountains (Hungary, Serbia, Romania), Scandinavian Mountains (Denmark), Iberian Massif, Pyrenees, Betic Mountain Range (Spain), Tatras Mountains (Poland), Central Massif, Armorican Massif, French Alps (France), Austrian Alps (Austria, Slovenia) are some examples (see Figure 45a,b).

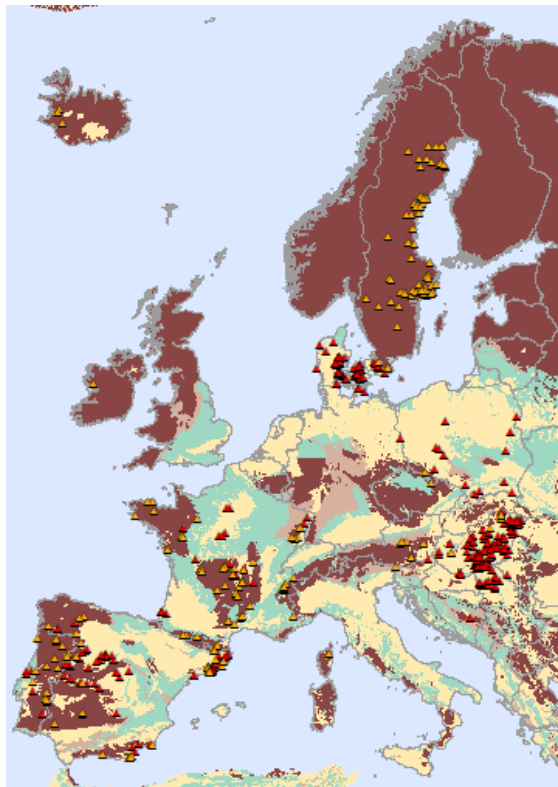


Figure 45b. Map with the distribution of As values $\geq 15 \mu\text{g/L}$ (BRC_{As}), associated faults in Cenozoic areas (red) and EAM (orange).

For fluoride, 847 monitoring points with concentrations equal or above P_{98} (2.3 mg/L) interact with some fault structure at 0.5, 1, 5 or 10 km. They represent the 60% of samples with F concentration $\geq 2.3 \text{ mg/L}$ (Table 14).

The EAM, formed by FHR (Precambrian, Paleozoic, metamorphic and igneous rocks constituting fissured aquifers), group 81% of the samples that have highest concentrations of fluoride dissolved in the water ($\geq 2.3 \text{ mg/L}$) and are located at $\leq 10 \text{ km}$ of a fault structure (Figure 46).

These percentages are again similar when analyzing the NBL index: 76% of the water samples with F concentrations equal to or greater than this index are associated with EAM and located $\leq 10 \text{ km}$ of a fault structure.

In percentage, this set is followed by waters associated with Cenozoic lands (12%, 14% for set waters analysed in relation to NBL_F/BL_F index or P_{90}). The percentages of samples related to Mesozoic rocks represent 7% (11% for NBL_F/BL_F index) of the total water sites whose fluorine concentration can be related to some fault structure.

In view of the results, it could be said that the structural factor is important in controlling the distribution pattern of high concentrations of fluoride in groundwater, but also the litho-chronostratigraphic factor. In fact, the endogenous rocks that make up the large European massifs. They are the main source of this minor element. The flow of groundwater in this environment is mainly through fractures. The structural element would also be important in controlling the distribution of F in some Cenozoic detrital aquifers, **in relation to the circulation of water through fractures of the basement.**



Table 14. Summary about the intersection of F concentration >2.3 mg/L ($\geq P_{98}$) with faults at different distances, taking into account the main lithological groups (1) Cenozoic, (2) Cretaceous-Jurassic, (3) Triassic, and (4) European Ancient Massif with igneous and metamorphic rocks and Precambrian-Paleozoic units.

GROUPS	Number of Samples	Distance to fault	Samples	Percentage	Countries
Cenozoic	102 (12%)	≤1km	12	12%	Austria, Belgium, Bosnia-Herzegovina, Denmark, France, Hungary, Italy, Poland, Serbia, Slovenia, Spain, Sweden
		≤5km	49	48%	Austria, Denmark, France, Hungary, Serbia, Slovenia, Spain
		≤10km	41	40%	Austria, Belgium, Denmark, France, Italy, Slovenia, Spain
Cretaceous and Jurassic	52 (6%)	≤1km	20	39%	France, Sweden
		≤5km	21	40%	France, Italy, Sweden
		≤10km	11	21%	Denmark, France, Poland, Portugal, Spain
Triassic	5 (1%)	≤1km	1	20%	France
		≤5km	2	40%	France, Sweden
		≤10km	2	40%	Austria
European ancient Massif	688 (81%)	≤1km	107	15%	France, Portugal, Iceland, Spain, Sweden
		≤5km	398	58%	France, Hungary, Iceland, Poland, Portugal, Serbia, Slovenia, Spain, Sweden
		≤10km	183	27%	France, Iceland, Poland, Portugal, Serbia, Spain, Sweden
TOTAL	847 (100%)				

Total samples F>2.3 mg/L
1408 samples

847 (60%) Lithology and faults (≤10 km)

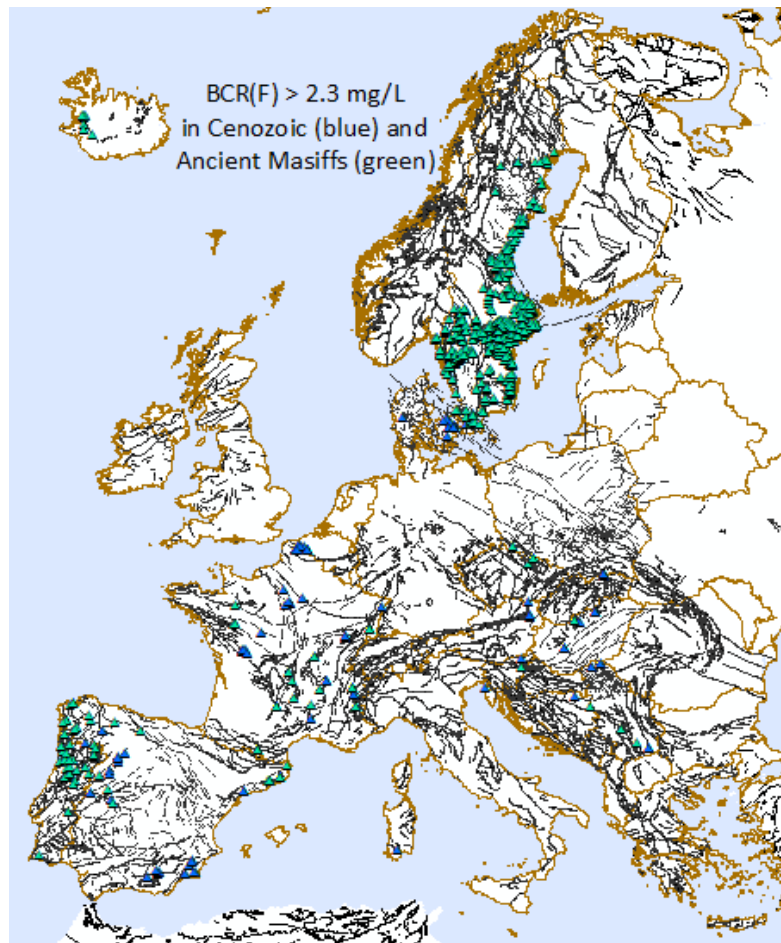


Figure 46a. Map with the distribution of F values ≥ 2.3 mg / L (BRC_F), associated with a HGT_F of 1.5, in Cenozoic areas (12%) (in blue) and in Ancient Massifs (81%) (en green), and their relationship with fault lines (BGR and others).

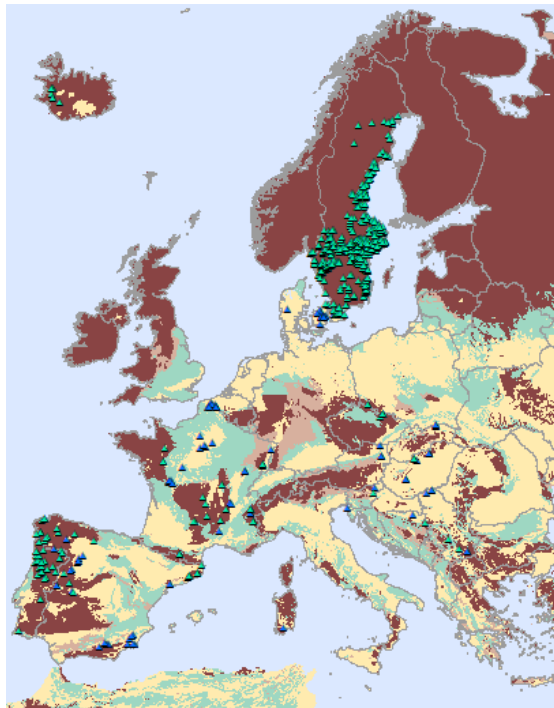


Figure 46b. Map with the distribution of F values ≥ 2.3 mg/L (BRC_{As}), associated to faults in Cenozoic areas (blue) and EAM (green).

Figure 46 shows the distribution of F concentrations equal to or greater than the BRC value, both in the areas covered by Cenozoic materials (12% of the samples considered in the analysis), and in the mountain massifs formed mainly by endogenous rocks (81% of the samples). In some areas, such as the border between Portugal and Spain, it is observed that the distribution of F in the waters in the outcrops of fractured endogenous rocks (Portugal) is repeated in the neighboring Cenozoic areas (Spain). Something similar can be observed on the border between Denmark and Sweden: the distributions in the ancient rock masses of southern Sweden coincide with the distribution pattern observed in northern Denmark (Cenozoic). In some carbonate basins (e.g. Paris Basin, in France) relevant anomalies of F associated with carbonated Mesozoic basins can be seen: they are few in percentage, but they are significant.

Lithology and basement structures are combined to give an explanation for the distribution pattern of the maximum As anomalies in groundwater on a Pan-European scale.

5.4 In summary

5.4.1 Arsenic, As

- Of the all samples considered for the spatial analysis of the distribution of As (groundwaters and mineral and thermal waters), **only 3% exceed concentrations of BRC_{As}** ($15 \mu\text{g/L}$). This value corresponds to the P_{98} of the entire set of samples at the European level, the scale chosen to carry out this analysis. As already mentioned, there are differences in BRC values between the different participants, that can be taken into account in analyzes carried out on a larger scale.
- Of the 3% that have the highest As concentrations,
 - 86% of samples corresponds to (i) Cenozoic areas developed close to FHR outcrops (igneous and metamorphic rocks, and Paleozoic and Precambrian



litho-chronostratigraphic levels) or (ii) FHR mountainous ranges, demonstrating the influence of the *Lithology* in the distribution pattern of As on at a Pan-European scale.

- The same percentage, 86% of highest concentrations of As corresponds to samples located near from a fault line (≤ 10 km), with a relevant percentage of samples sited at ≤ 5 km and ≤ 1 km. *Structural factor* is especially significant when samples are located in Cenozoic detrital aquifers.

5.4.2 Fluoride, F

- In relation to the spatial analysis of the distribution of F in groundwaters at Pan-European scale (including mineral and thermal waters), only **3% exceed concentrations of BRC_F** (1.2 mg/L). As in the case of arsenic, there are differences between the water sets provided by each participating country.
- Of the 3% that have the highest As concentrations,
 1. 91% of samples show F concentration related with lithologies associated to (i) FHR outcrops (igneous and metamorphic rocks, and Paleozoic and Precambrian litho-chronostratigraphic levels) or (ii) Cenozoic areas linked with these mountainous reliefs, confirming the influence of the *Lithology* in the distribution pattern of high concentrations of F on a Pan-European scale.
 2. 86% are positioned at ≥ 10 km from a fault lines (a significant number of samples are sited at ≥ 5 km and ≥ 1 km). *Structural factor* is essential to explain distribution of the highest values of F concentration in Cenozoic detrital aquifers.

The applied methodology in Task 3.4 has given good results. Both the hydrogeotoxicity (HGT) analysis and the BRC index have been satisfactory. The BRC index has been an appropriate threshold to indicate the maximum anomalies of high concentrations of As and F (and other PTGTEs) and to do the spatial analysis. Matching results with the NBL confirms the results.



6 AREAS OF SPECIAL INTEREST FOR HGT_{As} AND HGT_F IN EUROPE

To establish the areas of special interest, respect that they represent a potential risk for human health due to the possibility of finding waters with As and/or F concentrations greater than the limits established for drinking water, the distribution of HGT_{As} and HGT_F ($HGT \geq 1$) was represented jointly in figure 47.

Some sectors of Sweden, Belgium, France, Denmark, and Spain stand out due to a complex $HGT_{As, F}$. Also other areas characterized by high levels of HGT_{As} , as Pannonian basin (Hungary, Serbia, Romania), or NE of France (As associated to Triassic outcrops).

Figure 48 plots the distribution of BRC (P_{98}) for As and F, used as representative of the main geogenic anomalies, in a simplified geological European map.

Relevant geogenic anomalies are associated north with the Teisseyre-Tornquist Fault Zone. Its influence is evident over the hydrochemical anomalies of As and F in groundwaters at north of Denmark and south of Sweden. This relevant fault zone is extended towards Poland until the Carpatos reliefs. Associated with this mountainous structure towards west is developed the Panonian basin where important anomalies of As in groundwaters in Hungary, Serbia and Romania are identified. If we continue towards the SW of Europe, we find hydrogeochemical anomalous high concentrations in Alps and Dinarides, in Austria and Slovenia, and Cenozoic areas associated.

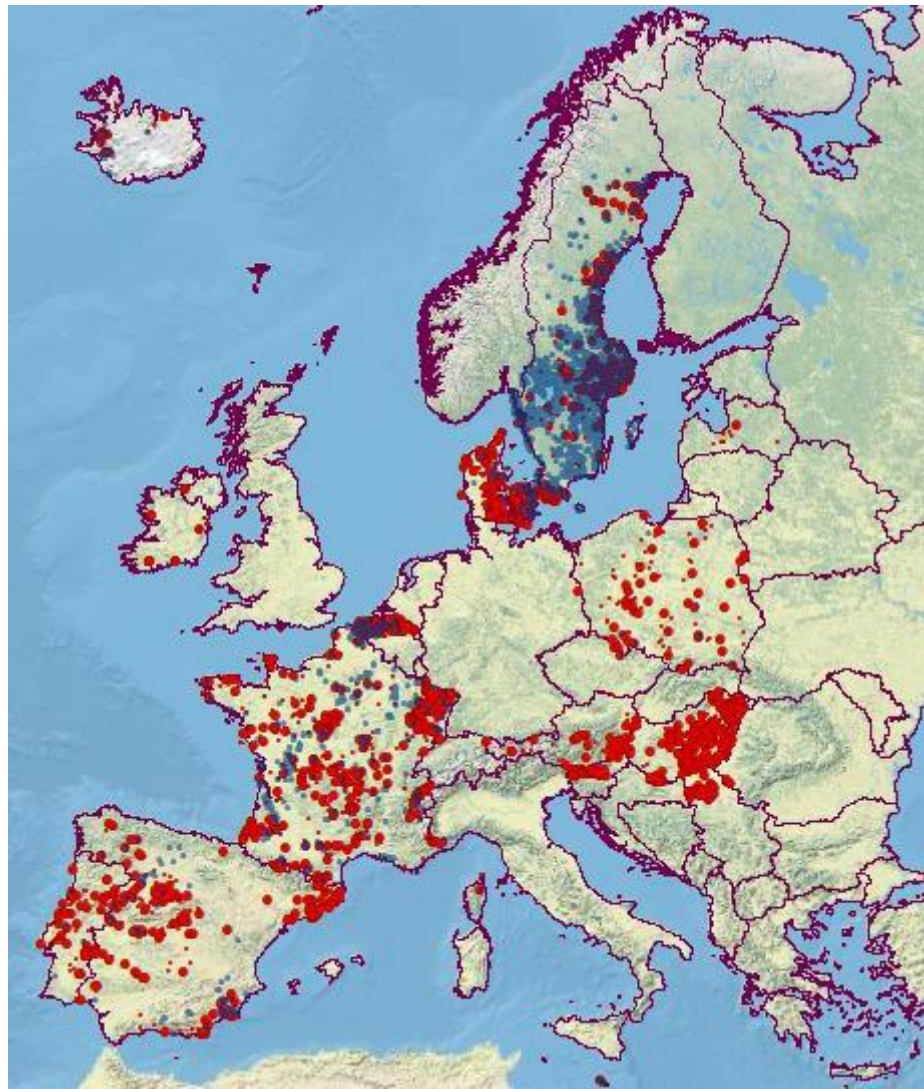


Figure 47. HGT_{A5} and HGT_F at Pan-European level. The red dots represent values of $HGT_{A5} \geq 1$ and the blue dots values of $HGT_F \geq 1$.

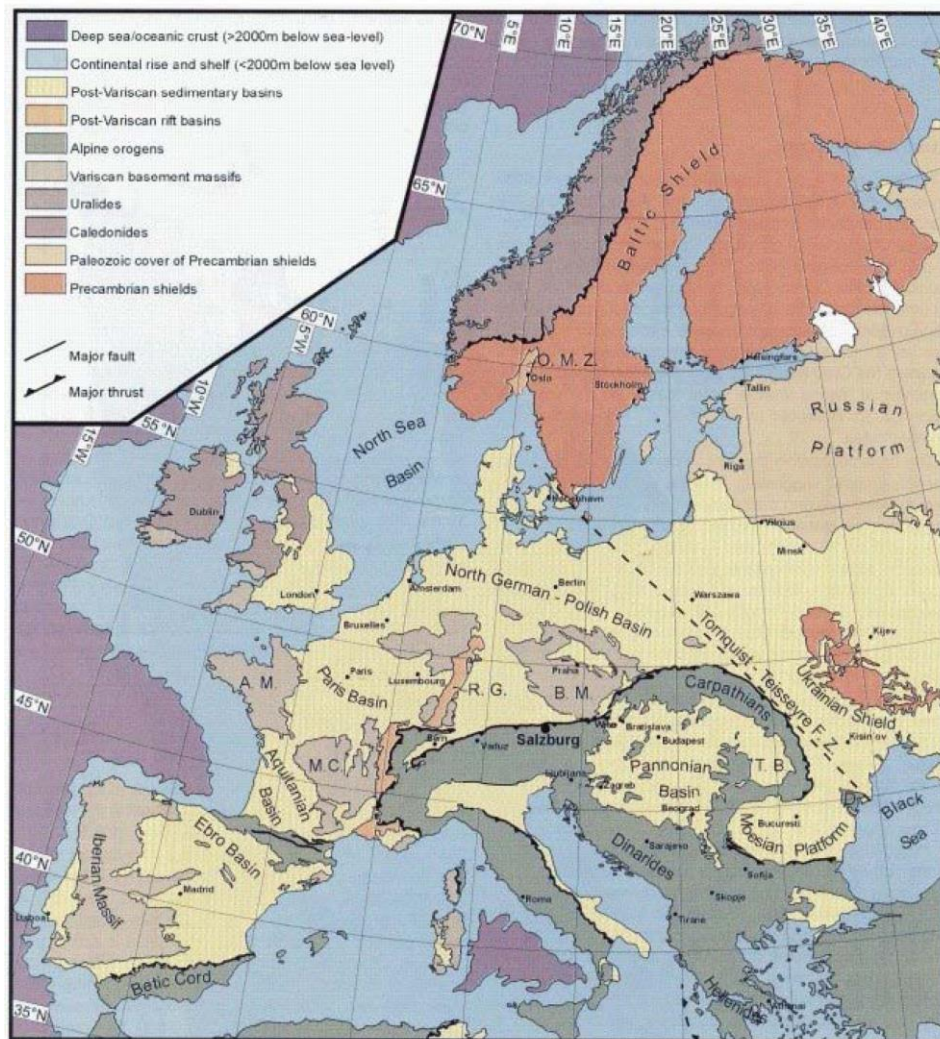


Figure 48. Simplified geological map of Europe showing the main orogenic systems (in Neubauer, 2003)

Already in the west of Europe, we found the Iberian Massif (Spain), and Armorican and the Central Massif (France) representing the main outcrops of pre-Variscan rocks in this part of Europe. Both in these ancient mountainous massifs of FHR as in the associated Cenozoic basins it is possible to find interesting geogenic anomalies of As and F. The primary sources of As and F should be understood as endogenous, linked to FHR outcrops, while secondary sources are associated to detrital deposits filling attached Cenozoic areas (and sometimes carbonate Mesozoic basins, in a lesser proportion).

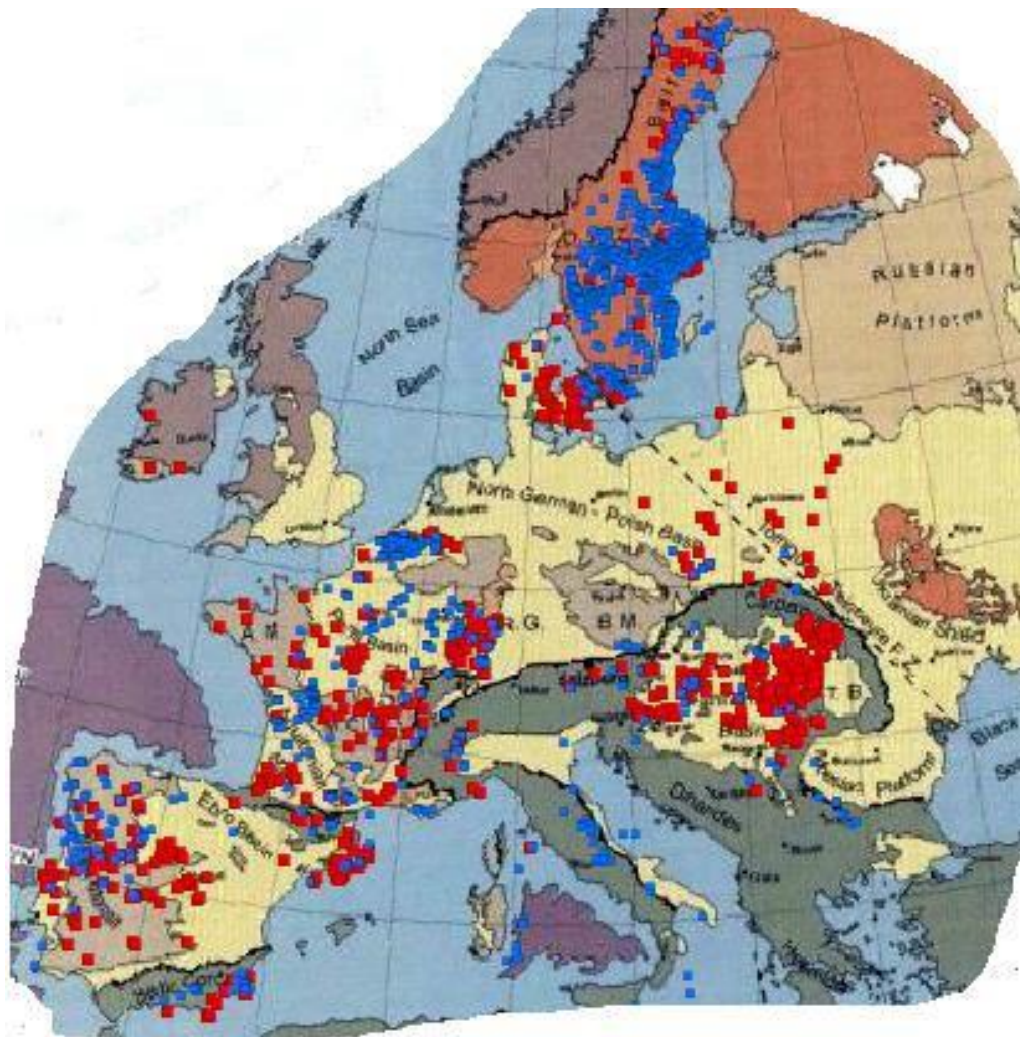


Figure 49. Representation of BRC_{As} y BRC_F at European scale using the simplified geological map of Europe from Neubauer (2003).

7 STUDY AREAS

7.1 Country study areas (Austria, Belgium (Flanders), Denmark, Serbia, Spain, Sweden)

Following a short presentation of some consideration on the general hydrochemistry related to the As and F concentration in the countries that brought data: Austria, Belgium, Denmark, Spain and Sweden.

7.1.1 Austria

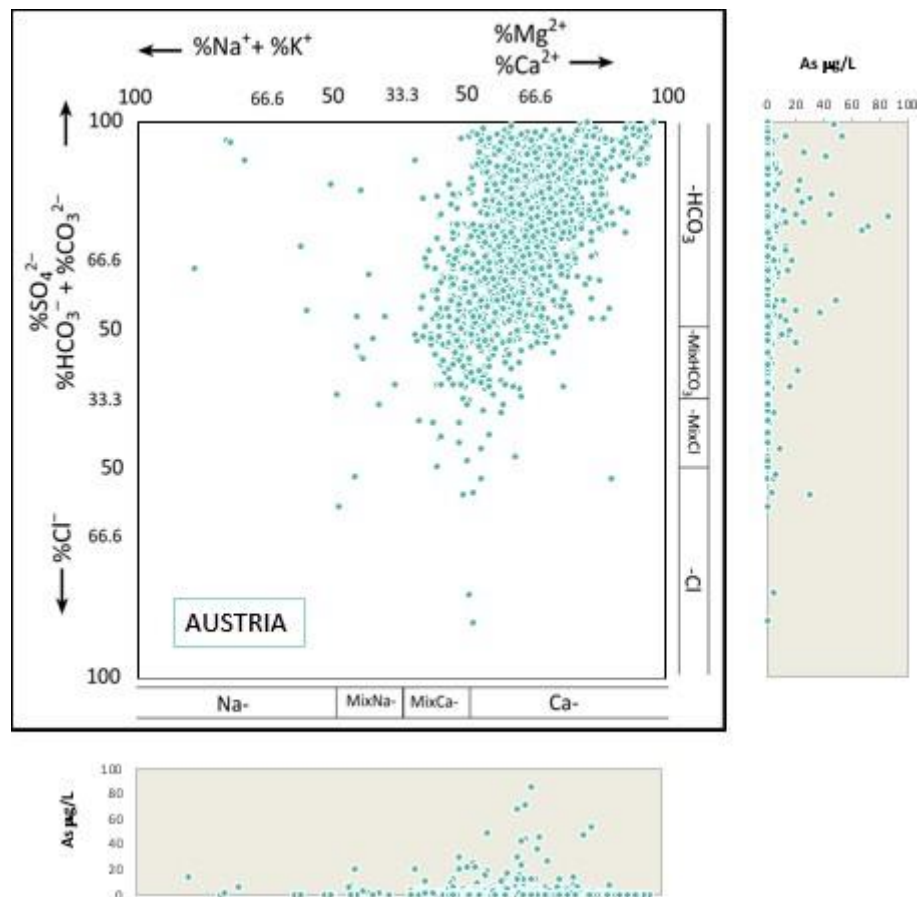


Figure 50. HFE-Diagram for groundwater from Austria study area, with As evolution in relation cation and anion percentages.

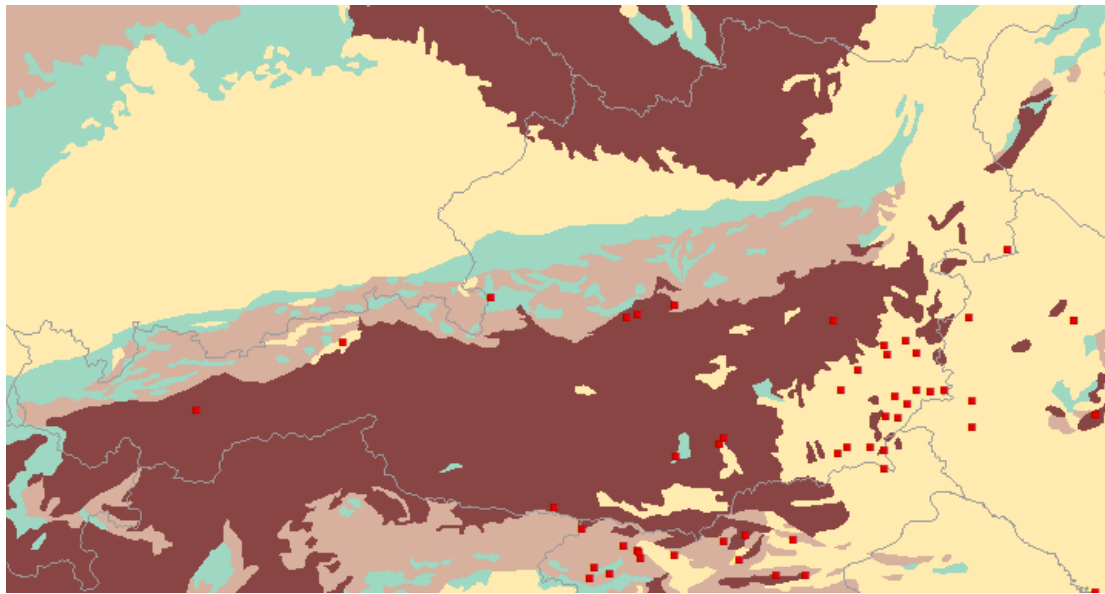


Figure 51. Distribution of BRC_{As} in Austria study area. In red, samples with As concentration above BRC_{As} (15 µg/L).

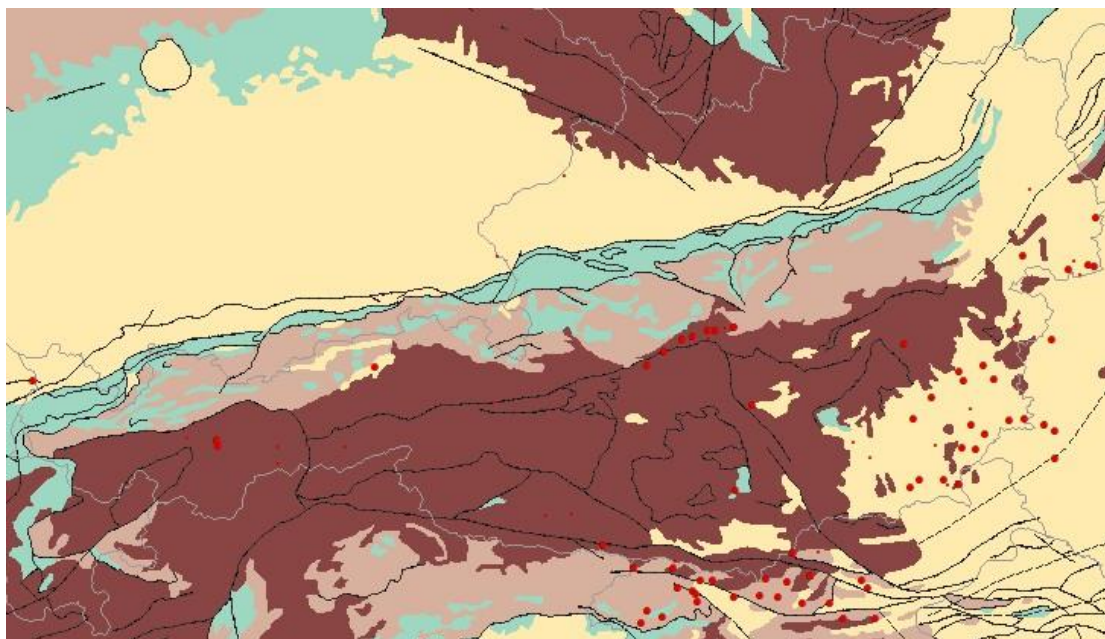


Figure 52. Distribution of HGT_{As} in Austria study area. Symbols: small red points HGT_{As} ≥ 0.5; big red points HGT_{As} ≥ 1.

The main hydrochemical facies of groundwater in Austria is Ca HCO₃ and the highest As concentrations are associated with this type of facies.

The general conclusions (see last epigraph) are applicable to the case of Austria. The largest anomalies are associated with FHR aquifer outcrops and associated sedimentary areas. Perhaps a more detailed tectonic structure mapping would be interesting.

7.1.2 Belgium

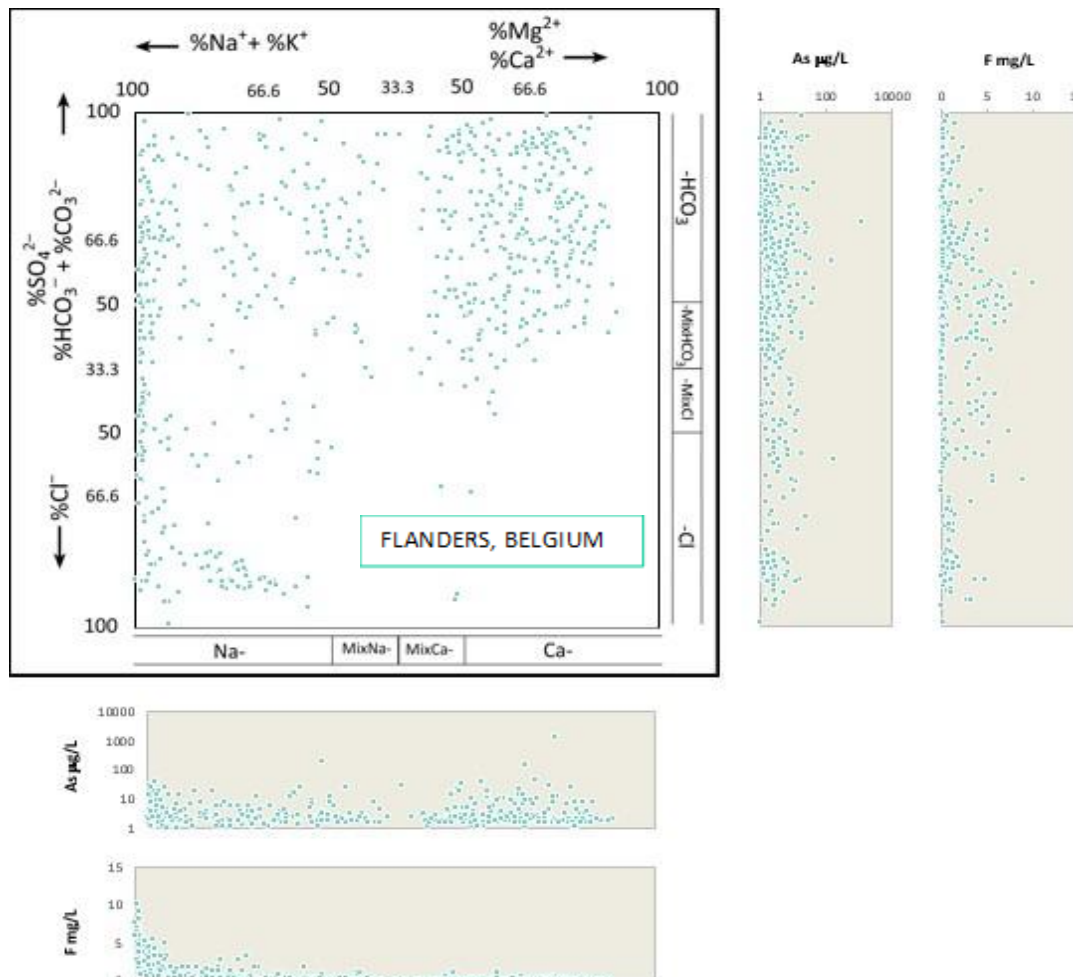


Figure 53. HFE-Diagram for groundwater from Belgium study area, with As and F evolution in relation cation and anion percentages.

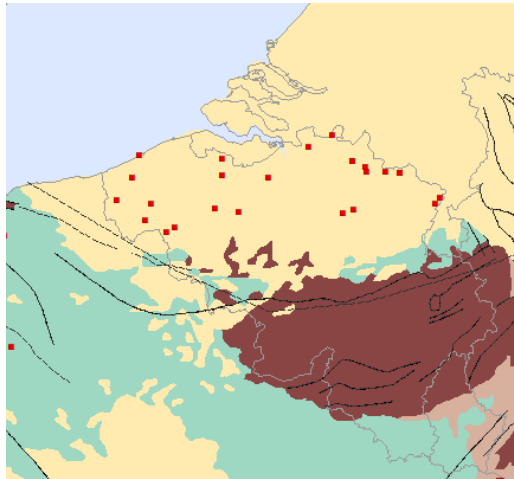


Figure 54. Distribution of BRC_{As} in Belgium (Flanders) study area. In red, samples with As concentration above BRC_{As} ($15 \mu\text{g/L}$).

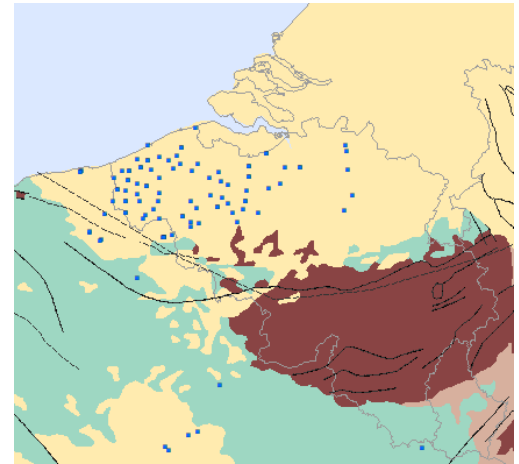


Figure 55. Distribution of BRC_F in Belgium (Flanders) study area. In blue, samples with F concentration above BRC_F (2.3 mg/L).

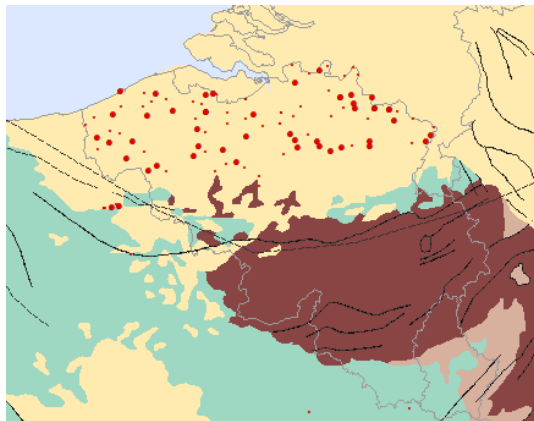


Figure 56. Distribution of HGT_{As} in Belgium (Flanders) study area. Symbols: small red points $HGT_{As} \geq 0.5$; big red points $HGT_{As} \geq 1$.

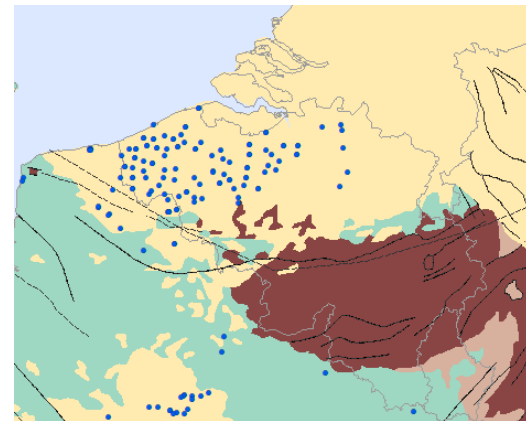


Figure 57. Distribution of HGT_F in Belgium (Flanders) study area. Symbols: blue points $HGT_F \geq 1$.

1.

The analysis of the Belgium (Flanders) database deserves a more in-depth and detailed analysis. As commented before, the measurement values for Belgium (Flanders) have all been assigned to the Cenozoic because these materials are the outcrop where geographically are located the sampling points. However, only the shallow measurement points are indeed Cenozoic; the deeper ones belong mostly to the Cenozoic but sometimes to the Mesozoic or Paleozoic. For arsenic, the higher values are measured in the Cenozoic, but for fluoride, the higher values are measured in the Paleozoic and Mesozoic.

The spatial distribution of average values for As and F concentration does not appear to offer results that can be interpreted with the available lithological and tectonic features. In this case, the hydrochemical analysis should take into account the depth of the borehole and the materials associated with each depth. Studying the individual values, taking into account the depth, is a pending task because it could reveal the influence of the basement on the concentrations of As and F in groundwater. Including the elevation of the terrain, salinity by seawater intrusion and physico chemical conditions (Eh, pH), is also a pending issue that deserves more attention.

7.1.1. Denmark

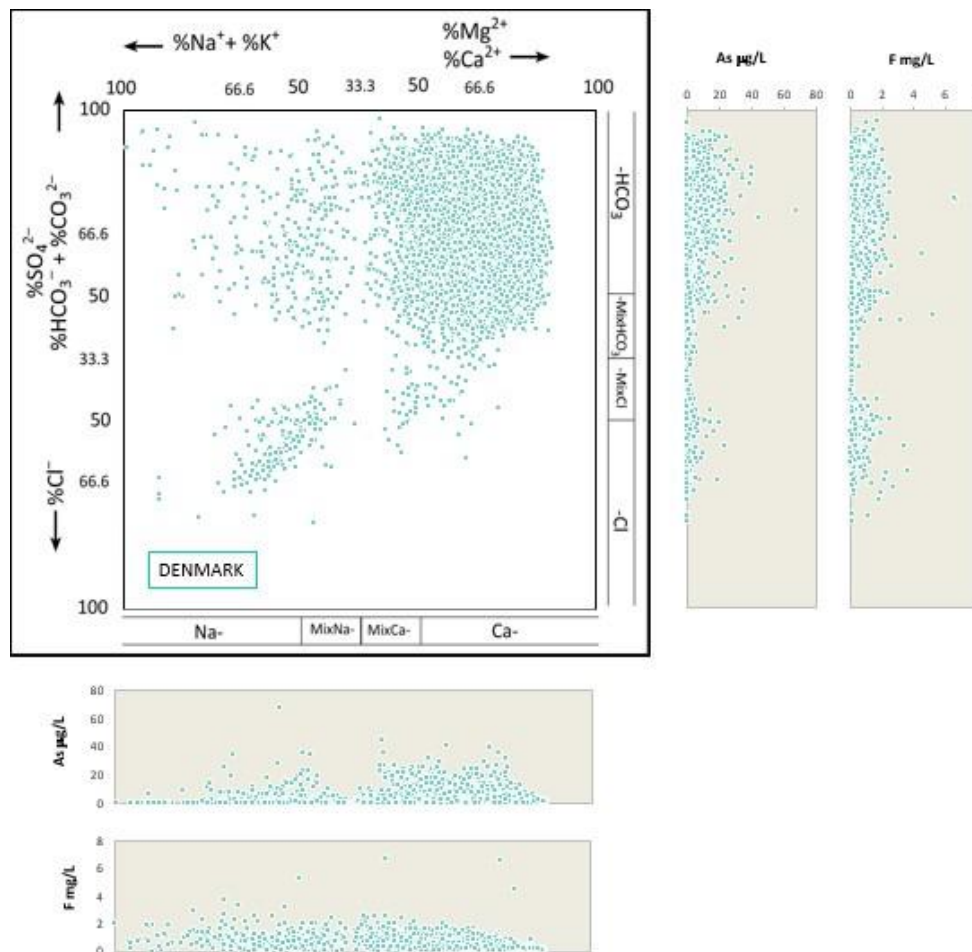


Figure 58. HFE-Diagram for groundwater from Denmark study area, with As and F evolution in relation cation and anion percentages.

The HFE-Diagram reveals three types of hydrochemical facies, an aspect to take into account when analyzing the distribution of As and F in groundwater. Although the hydrochemical CaHCO_3 facies prevails, the NaHCO_3 and NaCl group of waters is important. All of them seem to create independent groups and the evolutionary lines between them are not evident. The highest concentrations of As are associated to Na and HCO_3 waters. For fluoride is most difficult to assign a prevalent hydrochemical facies.

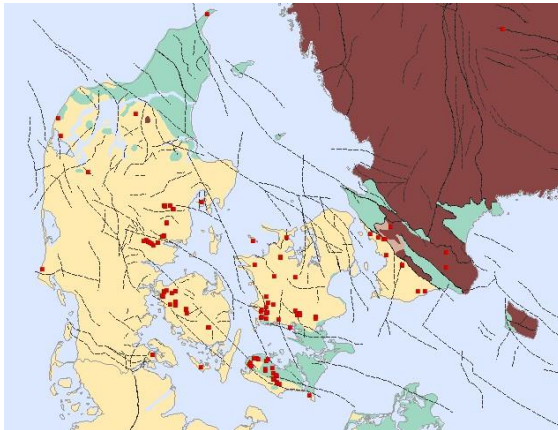


Figure 59. Distribution of BRC_{As} in Denmark study area. In red, samples with As concentration above BRC_{As} (15 $\mu\text{g/L}$).

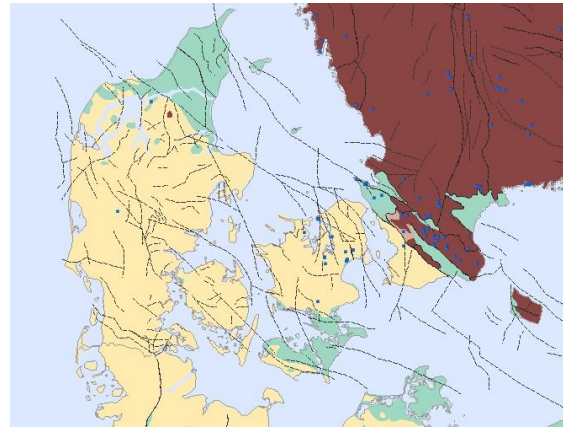


Figure 60. Distribution of BRC_F in Denmark study area. In blue, samples with F concentration above BRC_F (2.3 mg/L).

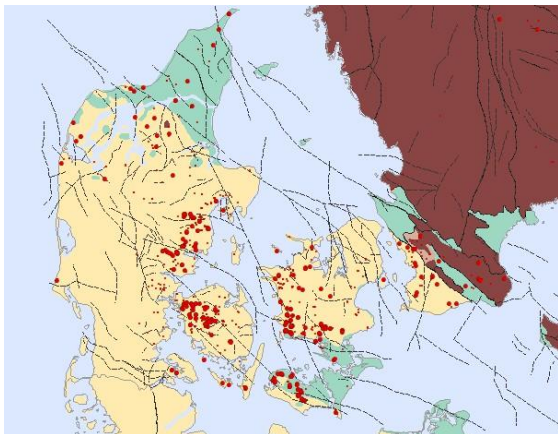


Figure 61. Distribution of HGT_{As} in Denmark study area. Symbols: small red points $HGT_{As} \geq 0.5$; big red points $HGT_{As} \geq 1$.

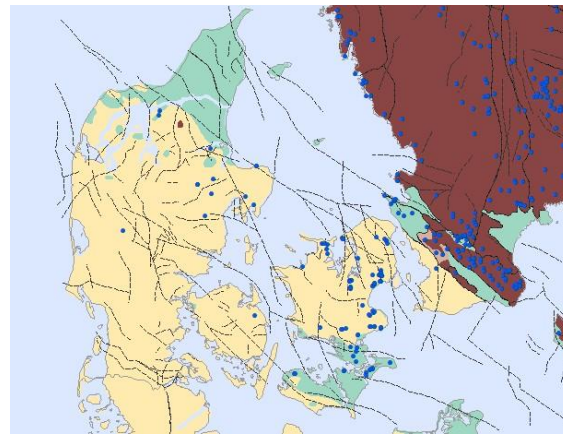


Figure 62. Distribution of HGT_F in Denmark study area. Symbols: blue points $HGT_F \geq 1$.

The maximum values of As in Denmark might be associated with fracture lines or structural forms that are interpreted under Cenozoic sediments. Most of the Danish territory lies on the great Teisseyre-Tornquist Fault Zone or Trans-European Suture Zone (TESZ), which is obscured and hidden everywhere under the Mesozoic and Cenozoic sediments.

A relative good agreement between the F anomalies in northern Denmark and southern Sweden is observed.

7.1.3 Spain

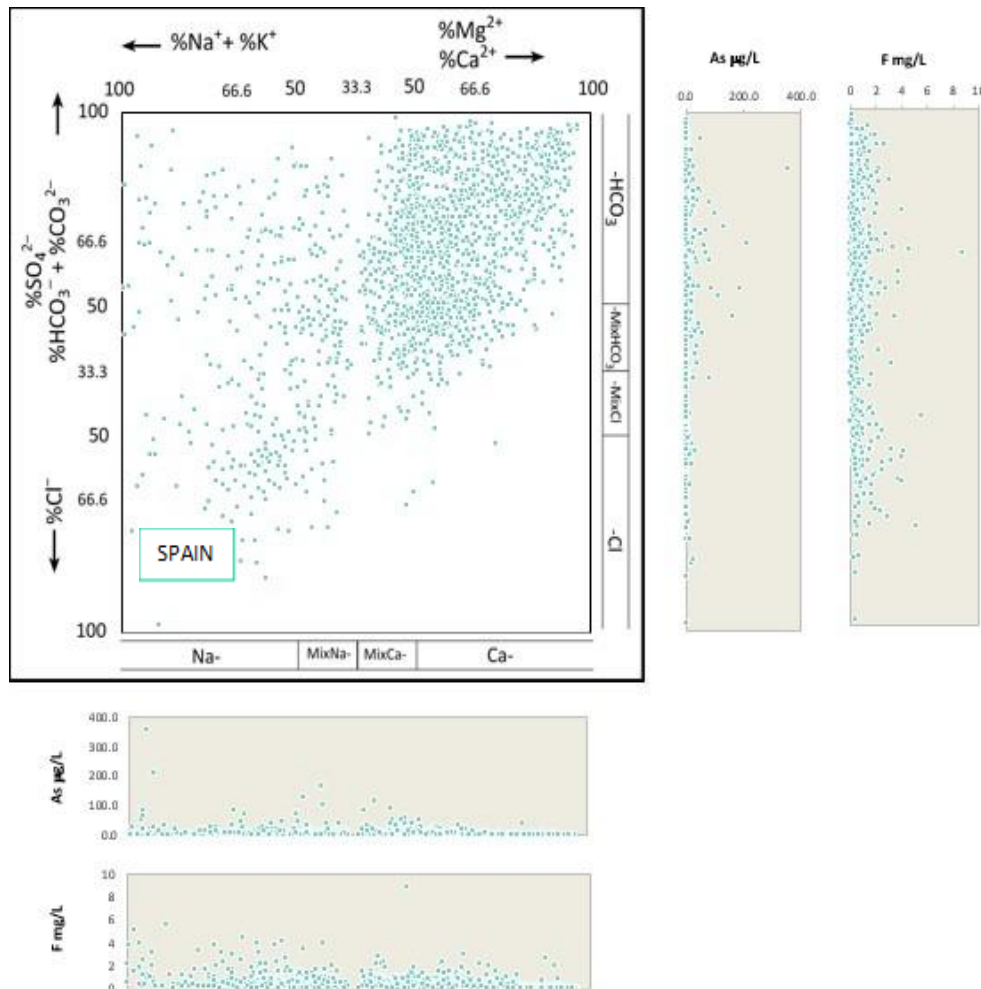


Figure 63. HFE-Diagram for groundwater from Spain study area, with As and F evolution in relation cation and anion percentages.

The NaHCO₃ waters present the most significant concentrations of As and F.

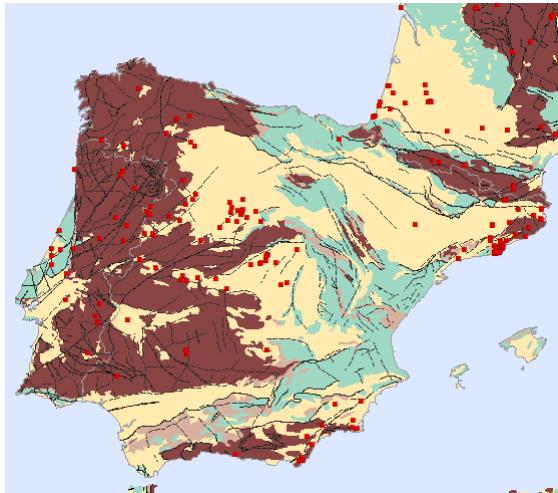


Figure 64. Distribution of BRC_{As} in Spain study area. In red, samples with concentration of As above BRC_{As} (15 $\mu\text{g/L}$).

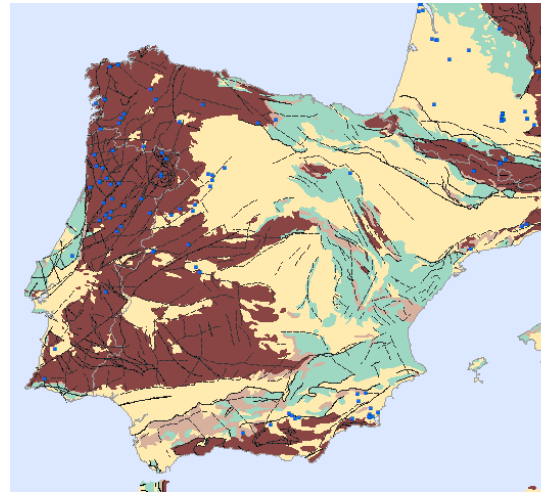


Figure 65. Distribution of BRC_F in Spain study area. In blue, samples with F concentration above BRC_F (2.3 mg/L).

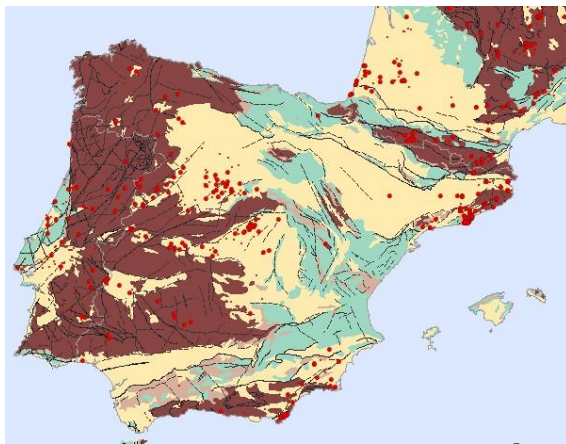


Figure 66. Distribution of HGT_{As} in Spain study area. In red, samples with $HGT_{As} > 1$. Symbols: small red points $HGT_{As} \geq 0.5$; big red points $HGT_{As} \geq 1$.

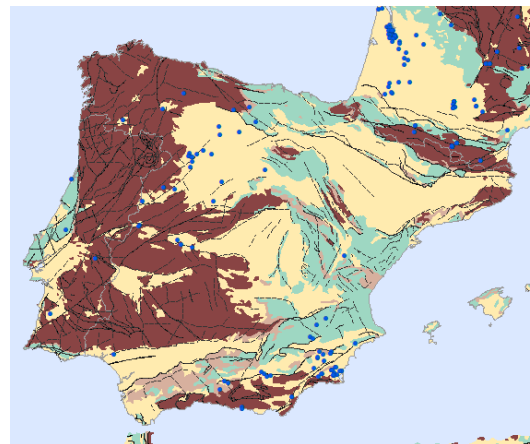


Figure 67. Distribution of HGT_F in Spain study area. In blue, samples with $HGT_F > 1$. Symbols: blue points $HGT_F \geq 1$.

In Spain, the distribution of anomalies of As and F follows the general line of argument of the report that is set out in the conclusions. The concordance between the distribution of As and F concentration anomalies in the Portuguese Iberian massif and in the Duero Basin, in Spain, is remarkable.

According to the data provided by the ICGC of Catalonia about arsenic concentration, the As spatial distribution seems to be associated with the EAM outcrops of FHR from the Coastal-Catalan Mountain Range, but also in the associated Mesozoic and Cenozoic basins developed towards south. The structural factor could play an important role in this distribution.

7.1.4 Sweden

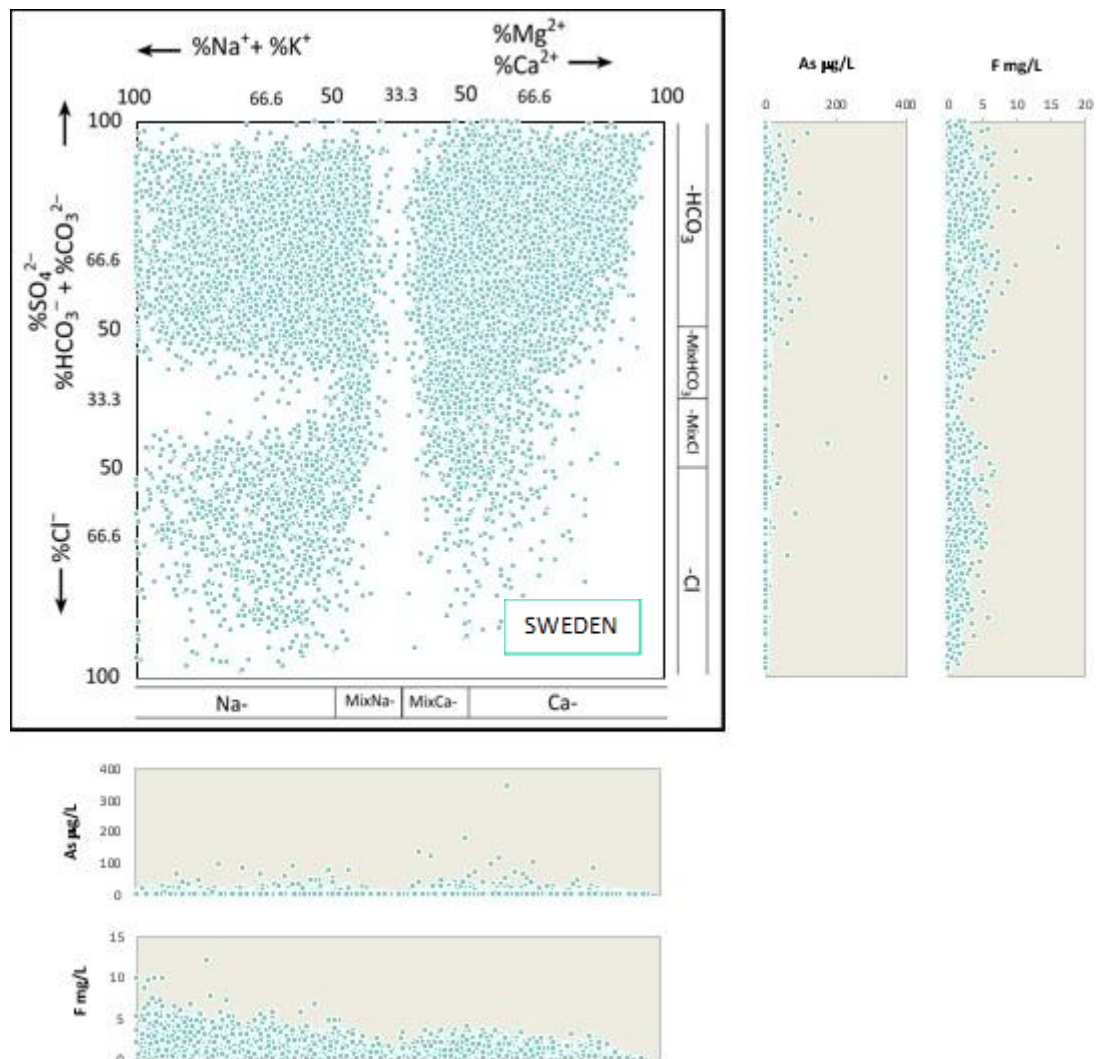


Figure 68. HFE-Diagram for groundwater from Sweden study area, with As and F evolution in relation cation and anion percentages.

The NaHCO_3 waters present the most significant concentrations of F. For arsenic seems that the more representative hydrochemical facies for highest concentrations is CaHCO_3 .

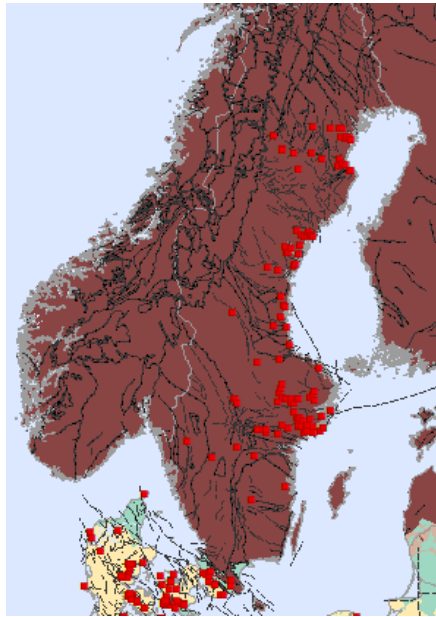


Figure 69. Distribution of BRC_{As} in Sweden study area. In red, samples with As concentration above BRC_{As} ($15\text{ }\mu\text{g/L}$).

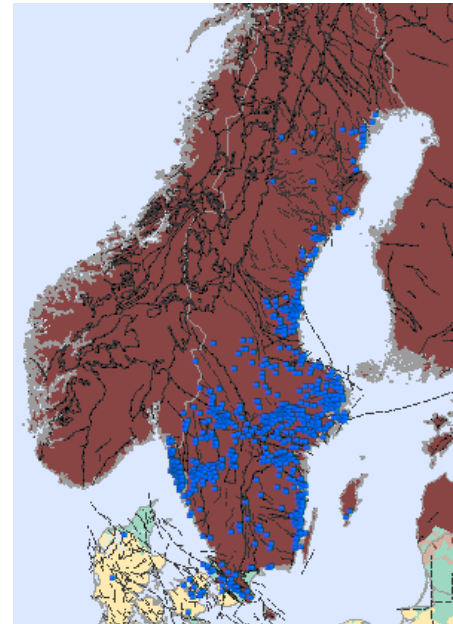


Figure 70. Distribution of BRC_F in Sweden study area. In blue, samples with F concentration above BRC_F (2.3 mg/L).

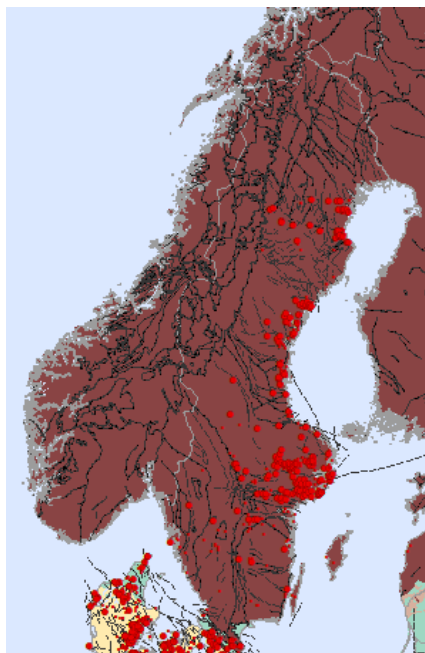


Figure 71. Distribution of HGT_{As} in Sweden study area. In red, samples with $HGT_{As} > 1$. Symbols: small red points $HGT_{As} \geq 0.5$; big red points $HGT_{As} \geq 1$.

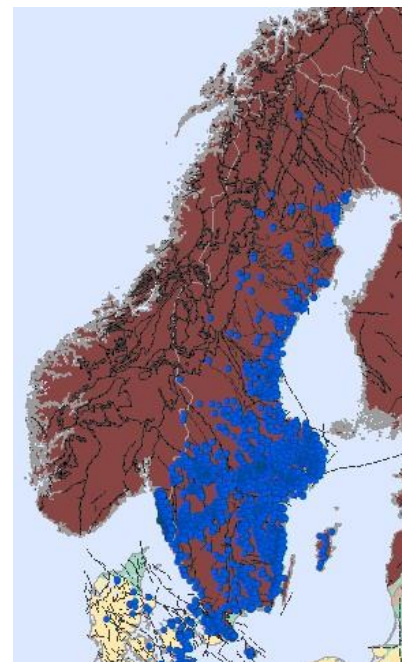


Figure 72. Distribution of HGT_F in Sweden study area. In blue, samples with $HGT_F > 1$. Symbols: bluepoints $HGT_F \geq 1$.

The distribution of F in Sweden demonstrates the importance of the mother area in controlling the concentration of this element.

The largest As concentration anomalies are located in the coastal strip, especially in the surroundings of important fault structures.

7.2 Specific study areas

7.2.1 Austria (Carinthia)

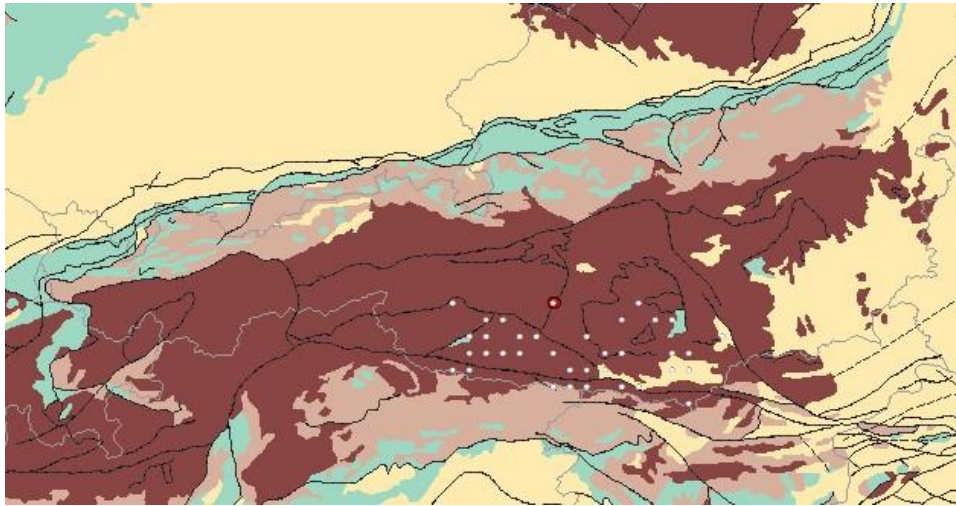


Figure 73. Distribution of groundwater samples located in Carinthia study area (Austria)

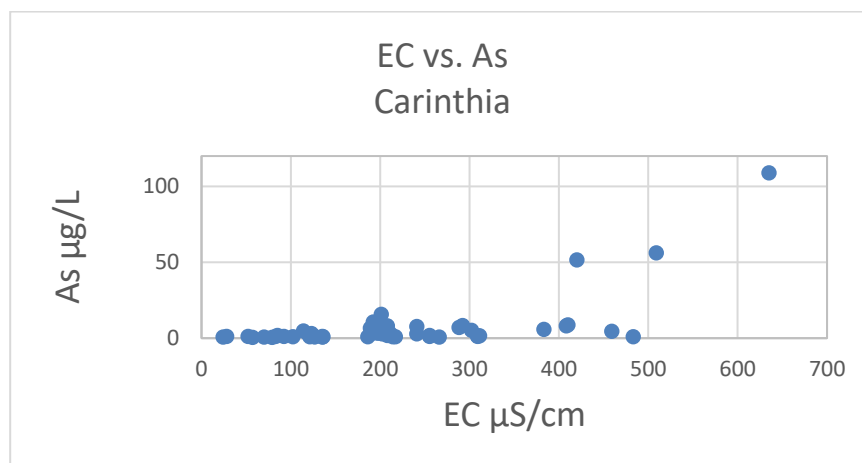


Figure 74. Relationship between As µg/L and Electrical Conductivity (EC) µS/cm for Carinthia groundwaters.

7.2.2. France (Morvan Regional Natural Park) - Morvan granitoides area

The Morvan granitoides area is located in the Central Massif in the middle of France on Loire and Seine Basins.

The Morvan is a granitic massive in the Bourgogne region with the highest altitude of 901m (Haut-Folin). The altered granite has created a cover of granitic sand. The Morvan basement is the oldest rocks of the Bourgogne region. They are composed of crystalline and metamorphic rocks (granites, gneiss, schist) from Paleozoic era or older. The massive is the remaining part of a Hercynian chain. The last phase was at the permo-carbonifere (300-250 millions years).

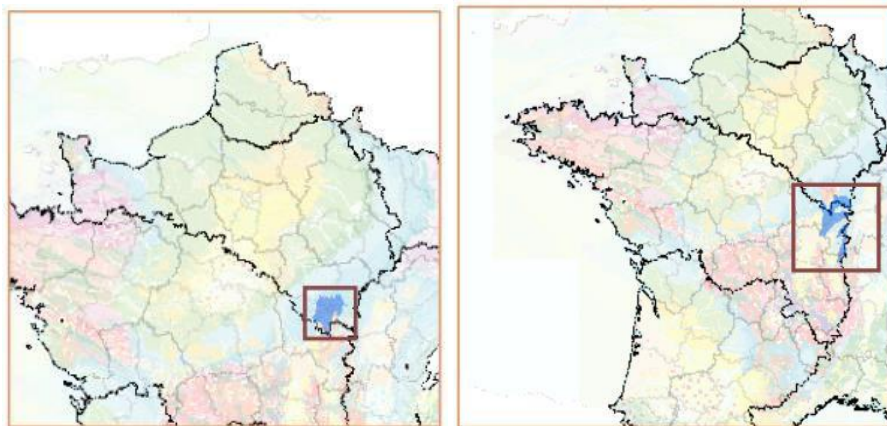
The Morvan basement is partly composed of granite and some schists, sandstones, conglomerate and volcano-sedimentary formations of Dinetian ages.

Many trace elements are in high concentration in the crystalline formation due to numerous vein with fluorite, barite, blende, pyrite, galena and chalcopryrite. Some silicified strata enriched in some elements can be found also along the faults.

In this area, arsenic is of natural origin, mainly in relation to sulfate metal mineralization (galena, blende, chalcopryrite, pyrite, arsenopyrite). The mineralization are encountered in form of veins associated to cristallines formations and heap within silicified level in the western part of the Morvan (Chitry-les-Mines). The highest concentration are ususally found in confined aquifer (low Eh) and associated with high iron concentrations.

In some areas (closed to Avallon) the groundwater may also have high concentration in fluoride. Acid water (pH 5,3-6,7) allows dissolution of trace elements (Al, As, Ag, Ti, Co, Pb, V, Ni, Cd). The hot spot are also associated to mine indicators. Some high concentrations were also encountered in basement formation (granite) and volcanic (rhyolite) formation closed to faults.

Two groundwater bodies were considered for the study, FRGG043 (Morvan, Loire Basin) and FRHG501 (Morvan basement) see below figure.



The limits of the groundwater bodies are closed to the limit of the river basins. The hydrographic network is quite dense as the soil is mainly impermeable. Two aquifers types can be found in such geological context, in the altered upper part of the rocks and in the fissures and fractures in the deepest hard-rocks. The monitoring points are mainly springs.

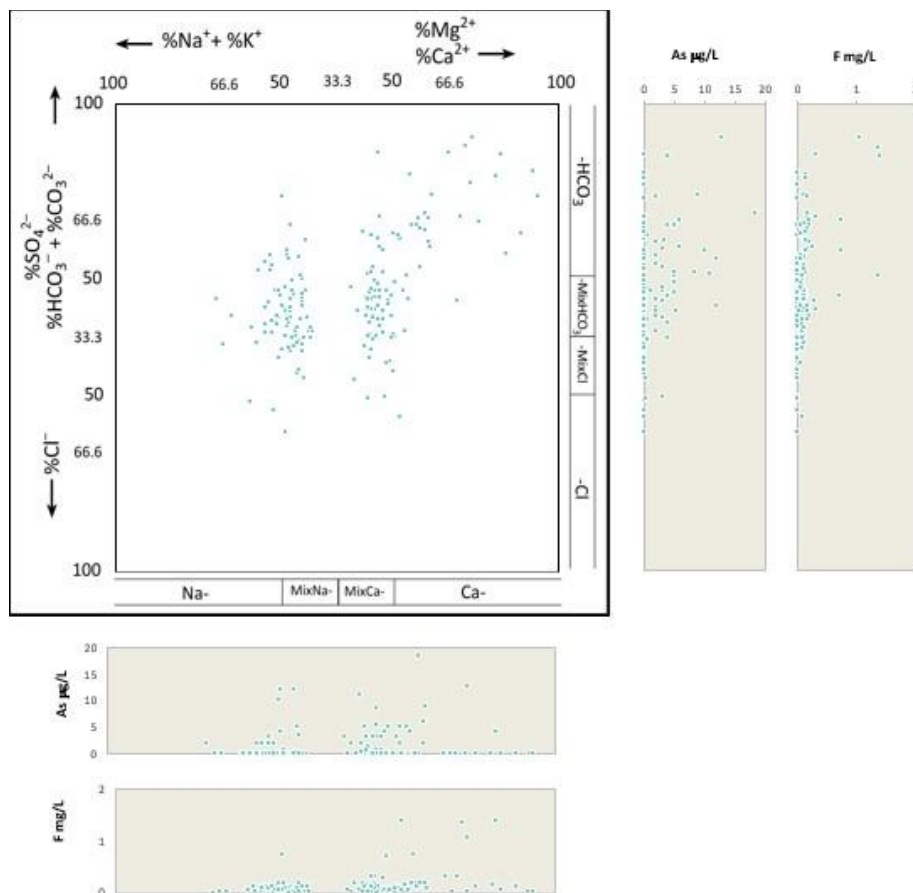


Figure 75. HFE-Diagram for groundwater from Morvan study area (France), with As and F evolution in relation cation and anion percentages.

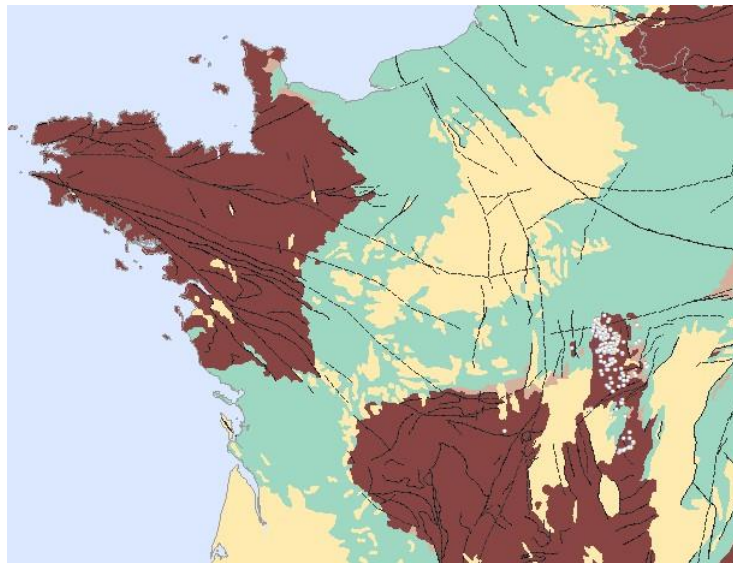


Figure 76. Distribution of groundwater samples located in Morvan study area (France).

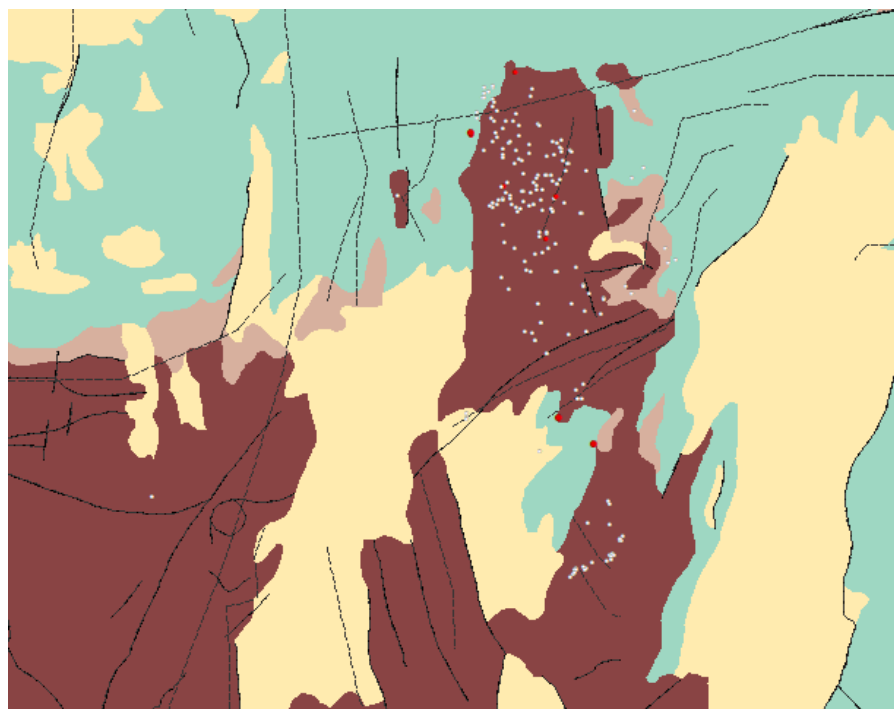


Figure 77. Distribution of HGT_{As} in groundwaters of Morvan study area (France).
In red, samples with $HGT_{As} > 1$.

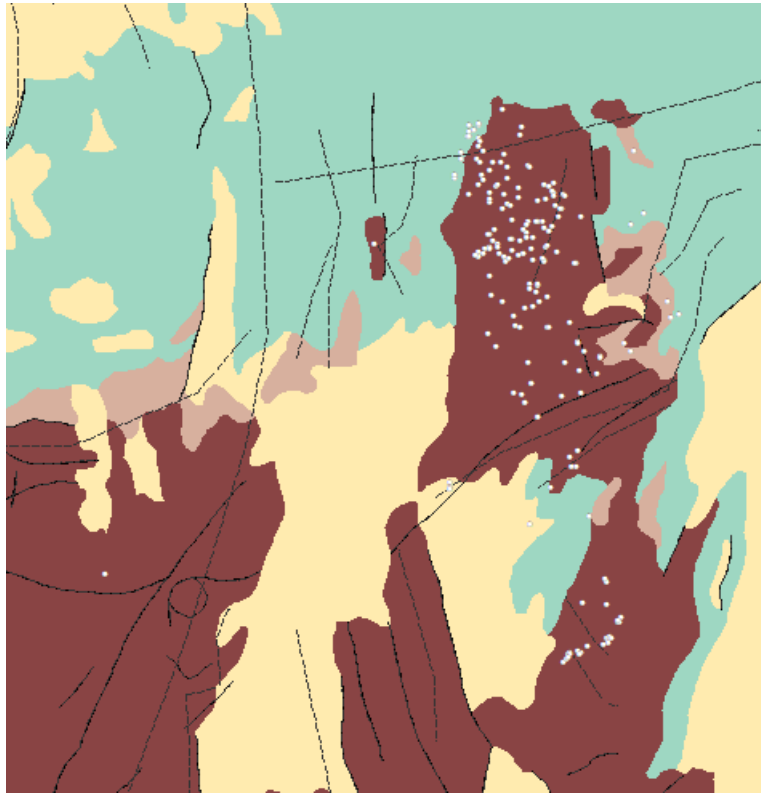


Figure 78. Distribution of F mg/L in groundwaters of Morvan study area (France). All samples have concentrations below the reference limit value, $HGT_F < 1$.



7.2.2 Serbia (*Fruška Gora*)

The geological structure of the territory of Serbia is defined based on geotectonic units(1, 2). It is divided into the following units: Pannonian Basin, Carpatho-Balkanides, Serbian Macedonian Massif, Vardar Zone, and Interior Dinarides.

The Pannonian Basin extends in the northern part of Serbia. On the surface, it is filled with lacustrine and marine deposits of Tertiary and Quaternary. Depth of Quaternary formations is in the range of a few meters to more than one thousand meters. The total maximum thickness of Paleogene, Neogene, and Quaternary sediments is about 4000 m. The base of this formation is made of older sediments, clastic and carbonate rocks (limestone, dolomite, sandstone, marls, breccia) of Mesozoic and crystalline schists (gneiss, mica schist, amphibolite, etc.) and granitoids of Paleozoic and Proterozoic.

The Carpatho-Balkanides extend in the eastern part of Serbia. This unit is characterized by very complex geological properties, composed of Triassic, Jurassic, and Cretaceous limestones, and numerous structures: syncline, anticline, nappe. This unit is divided into four geotectonic units (2, 3).

The Serbian Macedonian Massif is a crystalline core located between the Vardar Zone in the west, and the Carpatho-Balkanides in the east (4). It consists of two complexes of crystalline rocks: the lower, highly metamorphosed crystalline schists of Precambrian, and the upper complex of greenschist Proterozoic to Lower Paleozoic with granitoids and volcanic rocks of Paleozoic to Tertiary.

The Vardar Zone is composed of several blocks of diverse composition, geological history, and origin. It is divided into three subzones: external, central, and internal (Dimitrijević, 1997). The Vardar Zone includes characteristic oceanic elements, and it is composed of small blocks of crystalline schists, Carboniferous Veles Beds, Jurassic ultramafics, Triassic sediments, diabase-chert formations, Jurassic granitoids, Lower and Upper Cretaceous sedimentary rocks and Tertiary volcano-intrusive complexes.

The Interior Dinarides expands to the western part of Serbia and continues to the west. Geologically, the area is very heterogeneous both in lithological composition and in the age of the rocks. The most common are sediment rocks from Paleozoic and Mesozoic ages: Triassic limestones, dolomites, sandstones, Jurassic-Triassic Ophiolitic mélange (chaotic deposit of tectonic origin, breccia) and Cretaceous sedimentary rocks, while Tertiary deposits occur sporadically. Volcanic and igneous rocks occur only occasionally, as well as a metamorphic rock. The southwestern part of Interior Dinarides is characterized by a complex nappe structure.

Fruška Gora is a low (539 m), isolated, island-mountain rising above the Vojvodina plains in northern Serbia. The mountain spreads along 80 km, while the width is just 15 km. It is a horst, forming from late Tertiary to the end of Quaternary, as a consequence of Neotectonic uplift of the Pannonian Basin (5). The main feature of its geological structure are blocks of different composition, origin, and development. Deep dislocation on the north and south side of the mountain and erosion process created horst surrounded by Quaternary sediments.

Serpentine and highly metamorphosed Paleozoic rocks, green schists, and phyllite, which reach the surface along the ridge of the mountain, represent the base of the mountain. Triassic is presented by sandstone, clay, limestone and dolomites, conglomerates and breccia. Upper Cretaceous are presented as basal conglomerates, breccia, sandstones, mudstones, marl limestone, marl, and clay.

Magmatic rocks are found around the faults, as gabbros, diabase, trachytes, latites, dacite-andesites of Paleozoic, Triassic, Cretaceous, and Tertiary period. Hydrothermal alteration rocks are consequences of subvolcanic activity during Neogene [6]. The big spread of Tertiary sediments is in connection with lacustrine development. Tertiary sediments are represented with marls, sandstones, and conglomerates. Quaternary sediments are represented with thick loess cover, alluvial sediments and river terrace of Danube.

Loess has significant spread in the lower parts of the mountain, on the slopes of Fruška gora, and it covers the surface of the terrain. Loess represents the products of Eolian accumulation of fine dust and sand brought by the winds during the cold and dry climate. Alluvial sediments (gravel and sand) are the main source of water supply, especially for the city of Novi Sad. River terrace (Pleistocene) are present on the northern part of Fruška gora, along the coast of Danube. Three river terraces are developed: first 10-15 m, second (loess) terrace 25-35 m and third river terrace 50-60 m.

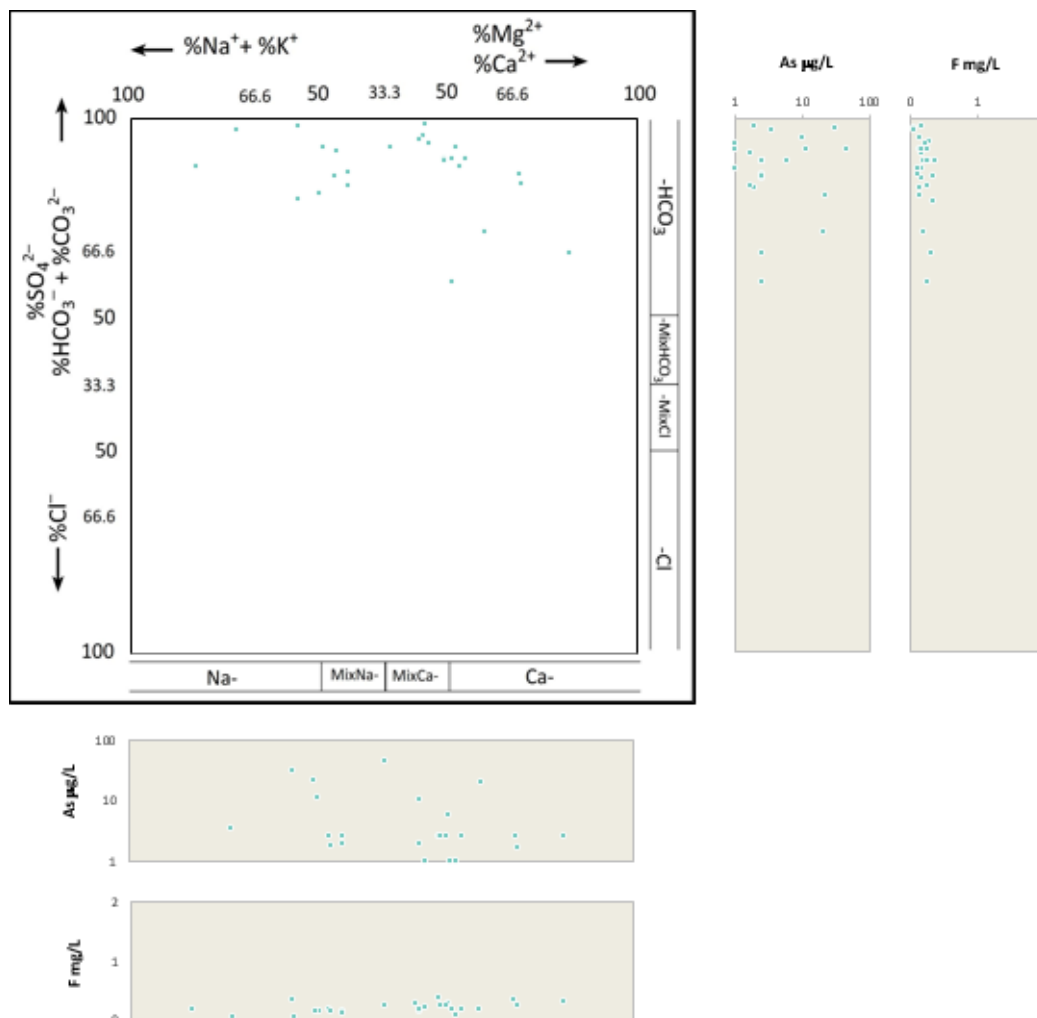


Figure 79. HFE-Diagram for groundwater from Fruška gora with As and F evolution in relation cation and anion percentages.



Figure 80. Distribution of HGT_{As} in Fruška gora study area (Serbia). In red, samples with $HGT_{As} > 1$.

As is generally the case in the Pannonian plain, the As anomalies coincide with fault lines. The model conforms to the conclusions set out at the end of the report, in the conclusions. The maximum concentrations of As are related with Ca,NaHCO₃ hydrochemical facies.

The concentrations of F are very low and do not give significant values.

7.2.3 Spain (SE Duero Basin)

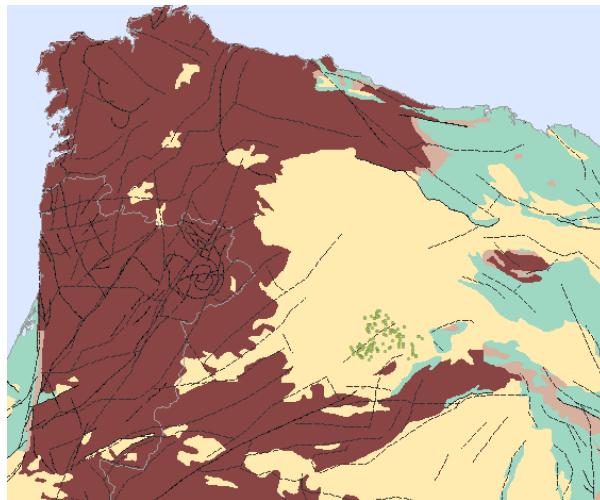


Figure 82. Distribution of groundwater samples collected in 2020 survey in Duero Basin (Spain).

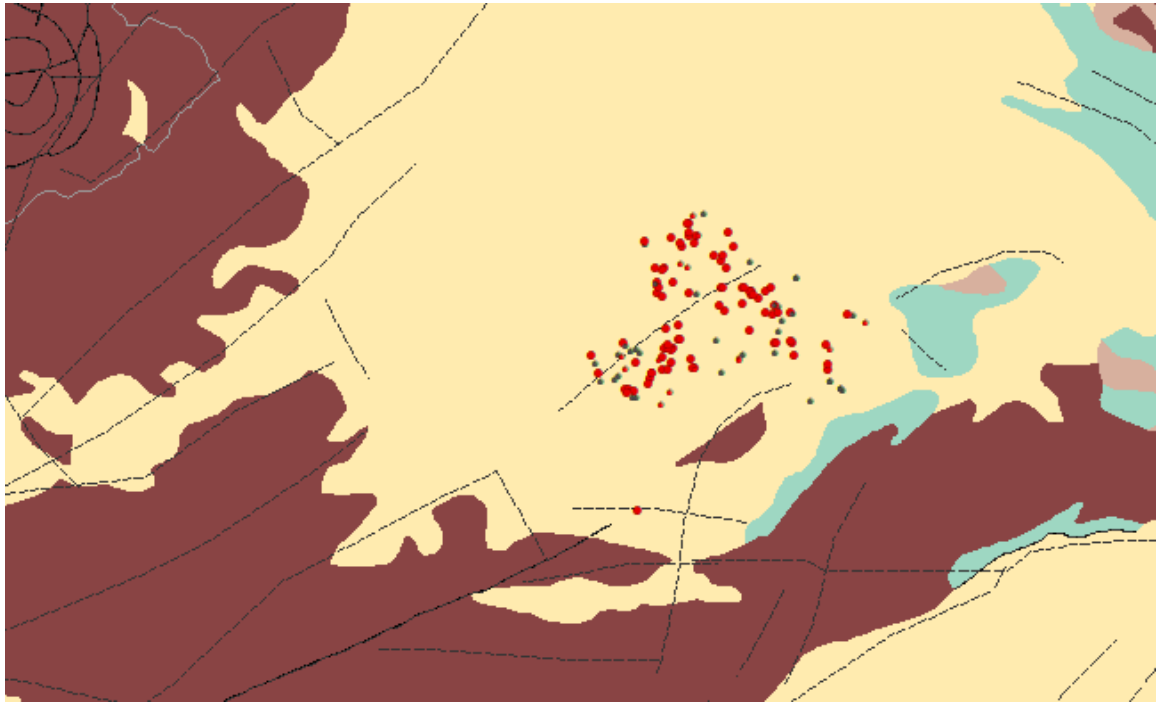


Figure 83. Distribution of HGT_{As} in Duero Basin study area (Spain). Samples collected in survey in 2020 in Duero Basin. In red: $HGT_{As} > 1$.

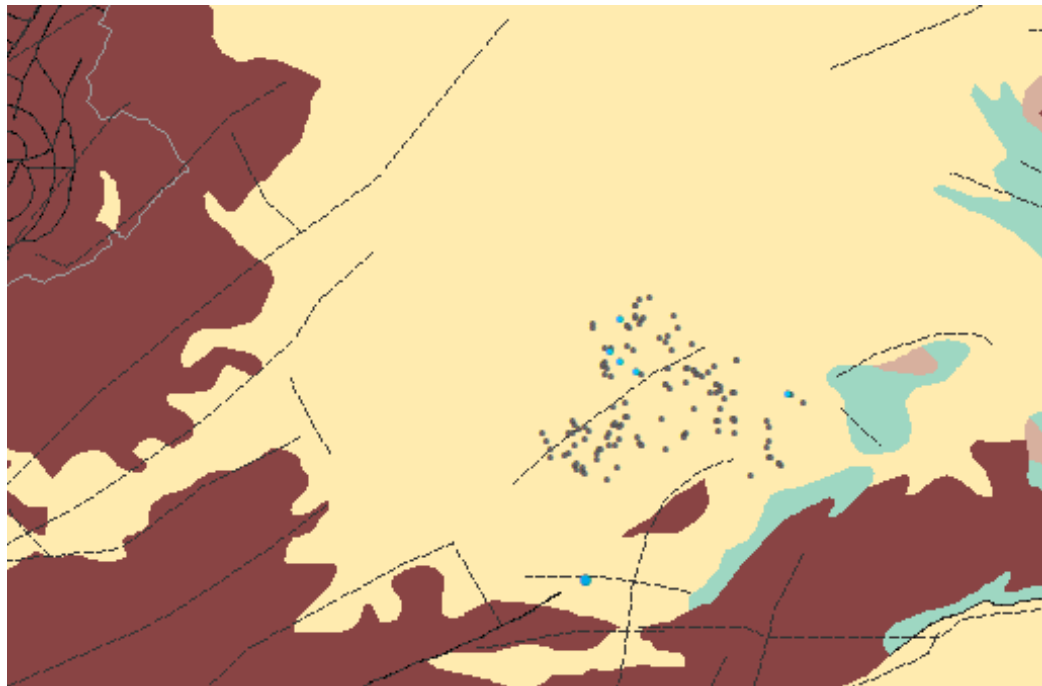


Figure 84. Distribution of HGT_F in Duero Basin study area (Spain). Samples collected in survey in 2020 in Duero Basin. In blue: $HGT_F > 1$.

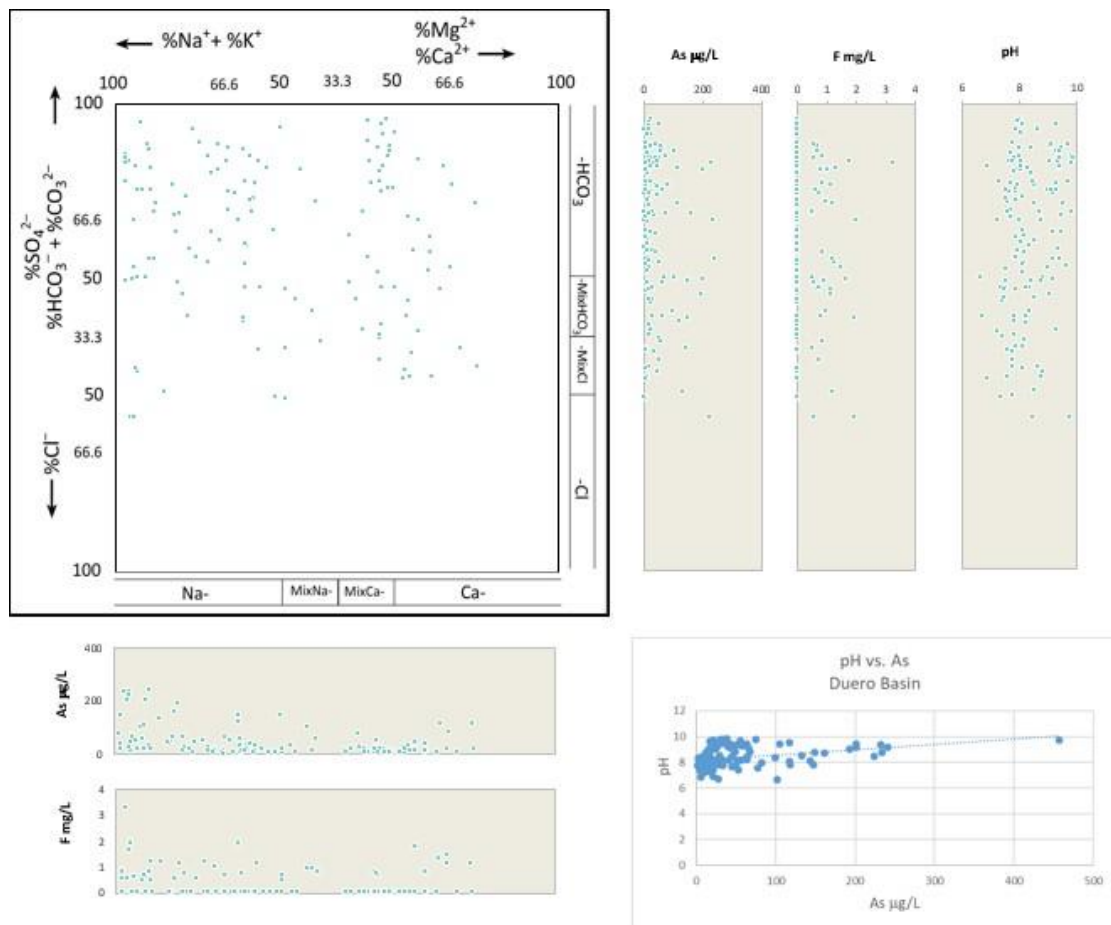


Figure 86. HFE-Diagram for groundwaters sampled in 2020 from Duero Basin, with As and F evolution in relation cation and anion percentages. Moreover relationship between As concentration and pH is shown.

In order to better understand the distribution traits of As and F in the Duero Basin, in the summer of 2020 a groundwater sampling campaign was carried out in a sector of the Duero Basin where the existence of groundwater with high concentrations of As and sometimes also of F. The anomalies of As are evident and linked to NaHCO_3 hydrochemical facies, corroborating previous studies in close areas. The As vs. pH graphic reveals the well-known control that this parameter exerts on As concentrations in groundwater. Significant F values are more local and related also with NaHCO_3 hydrochemical facies.



8 CONCLUSIONS: IMPROVING GROUNDWATER MANAGEMENT

The arguments that support the hypothesis based on the finding of this study are the following:

- The geographical distribution of concentration values of PTGTE, As and F, has been analyzed and the results indicate that there is a geological control over the distribution of these trace elements in groundwater at the European level.
- The samples with the highest concentrations of As and F (values above the respective BRC or P_{98} for Europe), reveal a pattern that can be interpreted in relation to lithological and structural factors.
- The 86% of water samples with the maximum values of As and the 91% of water samples with highest concentration in F show that these highest values are related with two main lithological environment: endogenous rocks (or FHR aquifers) and Cenozoic sediments.
- The structural control for faults and associated structures (e.g. horst and grabens) could regulate the pattern of the highest concentrations of these two trace elements: 71% of the samples of the highest content As network and 68% of the of the F highest concentration network are near fault lines. This is especially remarkable in samples located in Cenozoic outcrops, where some faults could be deducted as prolongation of significant faults in the close FHR outcrops (near the edge). It is not necessary for the water point with high concentration in As and/or F matches exactly with the fault line drawn to justify the structural control. They often point to structurally significant areas, such as the existence of *horsts*, where a thin covering of sediments allows the influence of the basement to be shown.
- The combination of lithology and structural factor is evident: 81% of the samples with high concentrations of F justified by structural control are associated with the endogenous rocks of the FHR outcrops. For arsenic, 53% of the maximum As concentrations justified by the structural factor are located on Cenozoic sediment outcrops.
- Samples with As concentrations above 10 $\mu\text{g/L}$, belong to CaHCO_3 (52%) or NaHCO_3 facies (36%). The most representative hydrochemical facies for groundwaters with the highest F concentrations is NaHCO_3 (51%) and, in second order, CaHCO_3 waters (37%).
- The 4% of water samples considered from As network show $\text{HGT}_{\text{As}} \geq 1$. For fluoride, the 7% of samples has $\text{HGT}_{\text{F}} \geq 1$. Most of these sampling points are identified in the FHR outcrops in the EAMs or in the associated Cenozoic (sometimes Mesozoic) basins. With these results, areas with special vulnerability have been mapped to high concentrations of As and/or F in groundwaters.

We consider that the methodology and the work carried out in task 3.4 has reached the following achievements:

1. **The results are a first and a novelty.** It is the first time that a spatial analysis of the distribution of two trace elements (As and F) in groundwaters has been offered at Pan European level. It is a first in the studies carried out to date about natural quality of groundwater.
2. It has been possible to do a **hydrochemical work with health prospect on a European scale.**



3. **The study area has been Europe, therefore a unit.** This has been absolutely challenging. Merge geological features into a common one and merge data from 17 countries (and more than 18 surveys and agencies) into a single database.
4. Lithology and, consequently, water-rock reactions are an indisputable controlling factor. FHR aquifers are presented as a primary source of great relevance.
5. A working method is offered based on the observation of spatial distribution and the use of indices, whose distribution pattern is contrasted with geological features on a Pan-European scale.
6. A high percentage of samples with high concentrations of As and F are related to fracturing and structural forms associated.
7. The first maps on a Pan-European scale with the distribution of As and F in groundwater are presented with a health perspective, using HGT index.
8. A first interpretation of the distribution of these two Potentially Toxic Geogenic Trace Elements (PTGTE) in groundwater considering the European geological context and BCR index.
9. This is a compatible method that allows to face with a better perspective larger-scale studies in more specific study areas with greater guarantees of success.

But some uncertainties remain. We refer to the complexity of the analysis and the simplification to which we have had to surrender. Only in this way have it been possible to give sufficiently satisfactory general results to revalidate the method. Many factors remain behind: aspects such as the characteristics of the catchments, local hydrogeological conditions, influence of land uses or exploitation of groundwater, etc. We hope to be able to include in the future these other questions, and that the methodology can be applied and contrasted in different areas of study, with more concrete analyzes.

In short, the results of this task allow us to propose to enrich the local perspective to integrate it in a whole: Europe, which is made up of countries with different surfaces, different observation networks, different densities, different geological features approached from different perspectives...

To strengthen our hypothesis, it would be desirable to continue trying to unify the observation networks and better understand the geology of Europe, its lithological and structural features, uniting under the same criteria but in detail the European geology and hydrogeology. We would need the participation of all the countries that make up Europe, that the hydrochemical data be homogeneous (e.g. with the same detection limits or similar sampling data), searching a common and homogenous hydrochemical European network, propose collaboration networks and common projects that allow to improve and enrich this analysis and other more detailed ones that may be developed.

Finally, we offer a reflection as a way to conclude this work.

Associating the high anomalies (the largest) of As and F to endogenous fissured rocks is not a mistake, anyone who has looked at the map of Europe, its geology, its geotectonic evolution with perspective, realizes that there is a geological pattern marked by the important pre-Variscan mountainous reliefs where Precambrian and Paleozoic rocks emerge, and where important metamorphic and igneous rock masses are found. We cannot doubt that they are the



origin of many metallic and metalloid trace elements, because it is known that there are important ore deposits in all these massifs. Seen now, it is not surprising. Perhaps the most surprising thing is that the geology of Europe has not been observed before with this perspective: as the natural environment from which many of the trace elements that we find in groundwater come from and which come to limit its use as drinking water.

If we continue with the reasoning, it is also logical to think that just as the PTGTE pass into the groundwater that circulates through these fissured endogenous rocks, these elements become part of the sediments that fill the plains associated with the old mountainous reliefs, but also that the circulation of groundwater through fractures continues over time, regardless of whether the area is exposed (outcrop) or forms part of the basement of the basins.

Thinking that these fluids carry with them significant amounts of trace elements and that, as in the past, they continue to circulate through fractures, generating metallic ore deposits today and before is also logical. They are, therefore, together with endogenous rocks, the origin and primary source of many PTGTE in groundwater.

The sedimentary environment, whatever it may be, is nourished by the contributions and dynamics of the sedimentation basin. New sources of PTGTE (secondary) are generated in it, so that when the water interacts with the sedimentary rocks or sediments it adds these other portions of trace elements.

The sedimentary environment also has great potential as a means of dispersal, generally linked to anthropic activity and the exploitation of groundwater, since they are important detrital aquifers that supply the population and satisfy a large part of the demand for different uses. All this anthropic activity multiplies the dispersal capacity of the sedimentary environment and converts a point or localized source of any PTGTE into multiple new foci. The interaction with the atmosphere, the evaporation, the recycling of the irrigation water, disperses the initial, concentrated foci into many more. Soil uses intervene, pH and Eh conditions change, the mobilization of some trace elements is reactivated. We change the scene and come to believe that this reality that we see so closely is very far from the original sources.

But it's not like that. It is very important to know the primary concentrated foci, the further back we can go, the better we can diagnose the origin and distribution of PTGTE in groundwater and understand the distribution pattern (remember that knowing the pattern and the laws that regulate it means better management of the groundwater and improving public health).

The processes that take place at the end of this cycle, in our argument, manage to mask the main process, but that should not hide the original geogenic sources that are behind. Let's take an example: a major fault that allows the flow of water with high concentrations of some PTGTE (for example, As) and that this water is captured by a deep borehole. All the frenetic activity that occurs on the surface when we use this groundwater manages to disperse and multiply the initial focus. On the surface, it appears that this is an area where As concentrations are regulated by low redox potential values, or by high pH values and, in part, this is the case; in fact, they are secondary factors that must be taken into account. But we must not forget that there has been a starting point. In this example, a fault with flows of water enriched in As and a borehole that has captured this groundwater and with which we have started to irrigate a cultivation area. The rest will come later.

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