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## Analysis of the geological control on the spatial distribution of potentially toxic concentrations of As and F<sup>-</sup> in groundwater on a Pan-European scale

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### ABSTRACT

The distribution of the high concentrations of arsenic (As) and fluoride (F<sup>-</sup>) in groundwater on a Pan-European scale could be explained by the geological European context (lithology and structural faults). To test this

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 Spatial Analysis

hypothesis, seventeen countries and eighteen geological survey organizations (GSOs) have participated in the dataset. The methodology has used the HydroGeoToxicity (HGT) and the Baseline Concentration (BLC) index. The results prove that most of the waters considered in this study are in good conditions for drinking water consumption, in terms of As and/or F<sup>-</sup> content. A low proportion of the analysed samples present HGT ≥ 1 levels (4% and 7% for As and F<sup>-</sup>, respectively). The spatial distribution of the highest As and/or F<sup>-</sup> concentrations (via BLC values) has been analysed using GIS tools. The highest values are identified associated with fissured hard rock outcrops (crystalline rocks) or Cenozoic sedimentary zones, where basement fractures seems to have an obvious control on the distribution of maximum concentrations of these elements in groundwaters.

**1. Introduction**

Drinking water quality is an issue of concern in countries around the world because of its impact on the health of the population (WHO, 2011). It should be noted that water is the essence of life and plays a vital role in almost all body functions; it is therefore a requirement that water should be accessible and safe (WHO, 2003). Exposure to various levels of certain chemical compounds through drinking water leads to numerous non-communicable diseases. At the same time, chemical elements form the base of all life on earth, and many elements are essential for good health, as health problems related to deficiency of the elements occur if minimum requirements are not reached. However, some elements are toxic when continued exposure to moderate concentrations occur over time, and this may lead to serious health problems by chronic toxicity. Many elements can be both beneficial (in low concentrations) and toxic (in high concentrations) and many times the appropriate concentration range for certain elements is very narrow (Reimann and Banks, 2004).

People tend to assume that natural, unpolluted groundwater is always healthy, but this is, unfortunately, not necessarily the case. In the absence of contamination, the inorganic chemical quality of natural groundwater reflects to a great extent the different geological settings and physicochemical conditions in which it has been encountered along its flow path. Because of the strong solvent properties of water, the reactions of water with the aquifer matrix and mineral dissolution largely control groundwater chemistry (Lloyd and Heathcote, 1985) and the release of trace elements (some of them considered *incompatible*) to groundwater (Edmunds et al., 1992; Banning, 2021). Along the flow path, from recharge to discharge area, other natural processes as mixing of waters, precipitation of secondary minerals, evaporation, cation and anion exchange, redox reactions, microbial processes, take place (Dowling et al., 2002; Appelo and Postma, 2006; Li et al., 2018).

Low concentrations of trace elements should not be a reason to pay little attention to them, as at very low concentrations these elements can compromise the use of groundwater as drinking water in many communities around the world (Embaby and Redwan, 2019). Some Potentially Toxic Geogenic Trace Elements (PTGTEs) are sometimes the reason why some groundwater is no longer suitable for human consumption. Arsenic (As) and fluoride (F<sup>-</sup>) are two good examples, with important implications for drinking water supplies in a wide variety of aquifer formations around the world (Chandrajith et al., 2019). The World Health Organization setting its drinking water standards at 10 µg/L and 1.5 mg/L, respectively (Kim et al., 2012; WHO, 2017). Both of them are recognized as the most dangerous and frequently occurring inorganic contaminants in groundwater, and in some areas human population is co-exposed to high As and F<sup>-</sup> concentrations (Mondal et al., 2021; Kimambo et al., 2019; Ahmad et al., 2020). According to Kumar et al. (2020), epidemiology indicates that the interaction of these two elements is very complex. At present, knowledge about the effects of co-exposure to As-F<sup>-</sup> is uncertain.

The relationship between water quality and human health is most evident in developing countries, where centralized water supply systems are not available (Ijumulana et al., 2022). In contrast, developed countries have centralized water supply systems and therefore water quality could be regulated and monitored, so that adequate standards are maintained, even though there is a percentage of the population in

rural areas that are supplied with water that is not routinely monitored (Dissanayake and Chandrajith, 2017; Li and Wu, 2019).

In developed countries, regulatory authorities often have to take into account not only public health, but also economic and political factors (Reimann and Banks, 2004). Van der Wens et al. (2016) analyse the issue regarding the problem of arsenic in drinking water stating that some state policies propose lower and lower concentration thresholds, which raises the question of assessing the cost difference between providing health care and removing As from water (Ahmad et al., 2020). A few years earlier, van Halem et al. (2009) argued that it is clear that As deserved more attention in the drinking water supply sector in Europe. Arguably, this is valid even in countries that do not have to cope with severe contamination, the health risk of As in drinking water cannot be neglected. One of the goals should be to optimize drinking water treatment to remove them to minimum concentrations (<1 µg/L for As, Ahmad et al., 2020), especially in countries with low to moderate concentrations. One of the objectives should be to optimize drinking water treatment (e.g. nanomaterials, Zinatloo-Ajabshir et al., 2022) to minimum concentrations (Ahmad et al., 2020), especially in countries with low to moderate concentrations.

Another measure would be to know the areas and population potentially most exposed to these moderate-high concentrations of PTGTE according to the geochemical environment and hydrogeological conditions in general (Postma et al., 2012, Kazmierczak et al., 2022). The characterization of groundwater chemistry/quality on a regional scale ensures sustainable water resources management on a large scale, as it can serve as a basis for the establishment or optimization of groundwater quality monitoring network and sustainable groundwater management.

Arsenic is considered as a harmful element and, although dermal and inhalation exposure is possible, food and drinking water are the main routes of exposure to arsenic (WHO, 2011; IARC, 2012). Soluble arsenic compounds are rapidly absorbed from the gastrointestinal tract (Hindmarsh and McCurdy, 1986). The International Agency for Research on Cancer (IARC) has classified As and As compounds as carcinogenic to humans. It is one of the 10 chemicals that the WHO considers most dangerous to public health (WHO, 2017). The Environmental Protection Agency (EPA), the National Research Council (NRC) affirm that prolonged consumption of water with a concentration of As as low as 5 µg/L (EPA) or even 3 µg/L (NRC) may cause chronic effects on humans (Hogue, 2001a; Hogue, 2001b; Tamasi and Cini, 2004).

In groundwater, As is usually naturally present in inorganic forms. Inorganic arsenic compounds not only contaminate the hydrosphere, they also accumulate in biological organisms, and the arsenic biogeochemical cycle affects the food chain (Masuda, 2018). Francesconi (2005) establishes that As enters the food chain mainly through water and soils with high concentrations of this element. In the human body, due to its chemical similarity to phosphorus, As can alter the metabolic pathways in which P is involved (Medunić et al., 2020). It also cause harm to the human dermal, gastrointestinal, hepatic, neurological, pulmonary, renal and respiratory systems (ATSDR, 2007). Moreover, As is accumulating in distinct organs, especially in the liver and it is related to cardiovascular diseases (CVD), including stroke, ischemic heart disease and peripheral vascular disease, and specifically hypertension (Rahaman et al., 2021). On their side, Xu et al. (2021) stated that

chronic exposure to arsenic from drinking water is related to increased risk of CVD in As-contaminated areas of India, according epidemiological studies.

As is state by EFSA (2014), currently in the EU, for water intended for human consumption (Council Directive 98/83/EC) a maximum parametric value of 10 µg/L is set, the same value as set for natural mineral waters (Commission Directive 2003/40/EC) (EFSA, 2014), consistent with provisional guideline value established by WHO (2017). For Denmark, the guideline value for As in drinking water was lowered to 5 µg/L at the consumers tap in 2017 (Ministry of Environment and Food of Denmark, 2017; Ersbøll et al., 2018).

Loukola-Ruskeeniemi (2022) state that there are no globally accepted recommendations, regulations or guidelines for arsenic (As) in agricultural soil and water (for irrigation), even though dietary intake is an important source of exposure (e.g., Nachman et al., 2017; Shibata et al., 2016) and As-contaminated irrigation water leads to transfer into crops and vegetables (e.g., Bhatti et al., 2013).

In Europe, there are studies about occurrence of As-groundwaters in different countries, as Austria (e.g. Eder et al., 2018), Belgium (e.g. Coetsiers and Walraevens, 2006), Bosnia-Herzegovina (e.g. Dangić, 2007), Denmark (e.g. Jakobsen et al., 2020), France (e.g. Barats et al., 2014), Hungary (e.g. Varsanyi and Kovacs, 2006), Iceland (Weaver et al., 2019), Ireland (e.g. McGrory et al., 2017), Latvia (e.g. Gosk et al., 2007), Netherlands (e.g. Ahmad et al., 2020), Poland (e.g. Kubicz et al., 2021), Portugal (e.g. Andrade and Stigter, 2013), Romania (e.g. Senila et al., 2017), Serbia (e.g. Dangić, 2007), Spain (e.g. Ventura-Houle et al., 2018; Giménez-Forcada and Smedley, 2014), and Sweden (e.g. Svensson, 2007).

According to Rowland et al. (2011), there are few references on high As concentrations in detrital sedimentary aquifers in Europe, as Pannonian Basin, where almost one million people could be exposed to natural As in drinking water at levels higher than the WHO and EU 10 µg/L (Rowland et al., 2011) or Duero Basin (Spain), where arsenic is released to groundwater in oxidizing environment and alkaline pH (Giménez-Forcada et al., 2017a). High concentrations have been identified in reducing conditions such as in northern Greece (Katsoyiannis and Katsoyiannis, 2006), the Netherlands (Frapporti et al., 1996), Belgium (Coetsiers and Walraevens, 2006) or Denmark (Ramsay et al., 2021). In addition, significant As concentrations have been reported in groundwater from aquifers in crystalline fissured rocks in western Alps (Tisserand et al., 2014), and in fissured aquifers with mineralisation associated as the Sherwood Sandstone aquifer in the UK (Smedley and Edmunds, 2002) and in the Upper Triassic Keuper Sandstone in Germany (Heinrichs and Udluft (1999). Also in geothermal fields of the Massif Central in France and Bulgaria (Criaud and Fouillac, 1989) and Greece (Karydakis et al., 2005), Iceland (Arnórsson, 2003), NE Spain (Navarro et al., 2011; Piqué et al., 2010), Italy (Aiuppa et al., 2006), and NE Ireland (Russell et al., 2021).

Arsenic is a ubiquitous metalloid that can be found everywhere in the environment (Rahaman et al., 2021). Human activity contributes to As mobilization through different activities as mining processing or the use of As in pesticides, herbicides, etc. (Bowell et al., 2014), however As occurrence in groundwater is overall geogenic, involving interactions among the geosphere and hydrosphere, and in the last case with biosphere.

In most natural groundwaters, arsenic occurs either as the trivalent arsenite [As(III)] as oxyanions  $\text{H}_3\text{AsO}_3^0$  or  $\text{H}_2\text{AsO}_3^-$  at pH ~9–11, or pentavalent arsenate [As(V)] as oxyanions  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  at pH ~4–10 (Smedley and Kinniburgh, 2002).

Arsenopyrite (FeAsS) is the most abundant arsenic mineral; however, it is much less abundant than arsenious (As-rich) pyrite (Fe(S,As)<sub>2</sub>), which is probably the most important source of As in mineralized zones and geological materials (Nordstrom et al., 2000; Tabelin et al., 2012). Arsenic is also present in many rock-forming minerals, albeit in very low concentrations in various mineral structures. When these primary minerals are altered, the formation of secondary As minerals begins as

simple As oxides or more complex phases with As, oxygen and various metals (Bowell et al., 2014).

Masuda (2018) stated that there are three major natural sources of arsenic contamination: *hydrothermal activity (mineralized fluids)*, *ore deposits*, and *Cenozoic sediments*. This classification can be interpreted by differentiating original endogenous primary As sources (PS) (*hydrothermal activity* and *ore deposits*, linked often to fractured crystalline rocks) from derived secondary sources (SS) (*Cenozoic sediments*).

Arsenic is recognized as a tracer in geothermal systems, for being an important trace constituent of hydrothermal fluids, varying in concentration over a wide range of concentrations up to 50 mg/L (e.g. Webster, 1999; Aiuppa et al., 2006). In this environment arsenic is one of the incompatible elements, along with F<sup>-</sup> and other trace elements, in high-temperature geothermal environments (Webster and Nordstrom, 2003). This reflects what is going on in the endogenous environment, in processes of metamorphism, metasomatism, and magmatic differentiation. When incompatible elements cannot be accommodated in the lattice structures of rock-forming minerals remain behind and are concentrated in the mobile residual fluid. The progressive enrichment of trace elements in the residual fluid makes possible the formation of minerals containing these elements as major constituents. Water is continuously enriched in the residual fluids and in incompatible trace elements. The hydrothermal vein deposits that comprise most of our base-metal sulphide deposits are generally believed to be precipitated at this stage in the primary geochemical cycle. Eventually the residual fluids reach and mix with groundwater or surface waters (Hawkes, 1957). It should be noted that hydrothermal systems are controlled by global tectonics and local structural settings, which ultimately define heat and fluid flow regimes. This association of geothermal systems with tectonic settings advocates for tectonic control on distributing and disseminating As in groundwater (Alam et al., 2021).

Therefore, endogenous environment (crystalline rocks) constitute an outstanding primary geogenic reservoir source of As (PS), even if the research about geogenic arsenic high concentrations in groundwater has focused on porous, unconsolidated, detrital aquifers, where As is mainly present in SS.

The concentration of As in sedimentary rocks is slightly higher than the average terrestrial abundance and its abundance varies according to the grain size of the sediment. Part of the materials that fill these beads are rock fragments from PS. Moreover, in detrital rocks and sediments, clay deposits have higher average As concentrations than sandstones, reflecting the higher proportion of sulphide minerals, oxides, organic matter, and clays (Smedley and Kinniburgh, 2002). Arsenic is frequently released by oxidation of sulphides, modified by various biogeochemical processes, and attenuated by adsorption and co-precipitation with Fe minerals, clays, and organic matter. Fe-(hydr)oxides have great capacity to adsorb As in their surface (Kim et al., 2012). Arsenic adsorbs strongly on the surface of these minerals making them a major source of arsenic in groundwater (Smedley and Kinniburgh, 2002; Howell et al., 2014). The adsorption/desorption of dissolved As species in groundwater onto the surface of minerals is largely regulated by physicochemical conditions, especially pH and Eh. Much of the research on arsenic in groundwater has been carried out in this environment because this is where the biggest problems of arsenic-enriched water are found (e.g. Smedley and Kinniburgh, 2002; García-Sánchez et al., 2005, Rowland et al., 2011).

Fluorine has no known essential function in human growth and development, and no signs of fluorine deficiency have been identified. In the body, it is mainly associated with calcified tissue (bone and teeth) (Whitford, 1994). In bone, the partial substitution of fluoride for hydroxyl groups of apatite alters the mineral structure of the bone and, depending on the dose, can delay mineralisation (EFSA, 2013). Fluoride ions stimulate bone formation by a direct mitogenic effect on osteoblasts altering hydroxyapatite crystals in the bone matrix. At low doses, fluorides induce lamellar bone, and at higher doses abnormal woven bone of inferior quality. The effect of fluorides on normal and abnormal (e.g.,

osteoporotic) bone is therefore dose-dependent (Dunstan et al., 2007). High fluoride and low calcium levels in drinking water is associated with low bone mass, reduced bone quality and fragility fractures in sheep (Simon et al., 2014).

Though fluorine is not essential for tooth development, exposure to fluorine leads to incorporation into the hydroxyapatite and the formation of fluorohydroxyapatite, which is more resistant to acids than hydroxyapatite. Thus, teeth which contain fluoroapatite are less likely to develop caries. Fluorine has been known to be useful in the control of caries development for more than a hundred years (Sampaio and Levy, 2011). Since 1962, the Public Health Service from U.S. Department of Health and Human Services (USA), recommends that public water supplies contain fluoride in a concentration range between 0.7 and 1.2 mg/L (ATSDR, 2003) a very narrow range of optimal dose. Water supply is sometimes fluoridated, but this apparently good measure has a risk.

Major dietary fluoride sources are water and water-based beverages or foods reconstituted with fluoridated water, tea, marine fish, and fluoridated salt. On average 80–90% of ingested fluoride is absorbed. Fluoride absorption occurs by passive diffusion in both the stomach (20–25%) and the small intestine (EFSA, 2013).

The maximum guideline value set by the WHO for fluoride in drinking water is 1.5 mg/L. Many countries use this value as a national standard for drinking water, but others require higher values, such as the USA (4 mg/L by US-EPA, 2011), 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 (2011), either due to water shortages or high regional concentrations in many areas around the world. In Europe, Council Directive 98/83/EC of 3 November (1998) (Council Directive 98/83/EC) determined a fluoride level (both naturally occurring and as a result of fluoridation) for water intended for human consumption of less than 1.5 mg/L.

An estimated 200 million people worldwide (mainly in Asia, Africa and America but also in Europe) are affected by skeletal and dental fluorosis (Ayoob and Gupta, 2006; Tian, 1989; Wang et al., 1999; Fordyce et al., 2007; Amini et al., 2008; Kimambo et al., 2019). In addition, high concentration (>10 mg/L) of F<sup>-</sup> has been associated with neurological disorders, infertility, thyroid, arthritis, cancer and hypertension, and leads to change in the DNA structure (Kimambo et al., 2019).

In aqueous solution, fluorine is usually in the form of the fluoride ion, F<sup>-</sup>, which occurs naturally in the biosphere with ubiquitous presence in the environment (Buzalaf and Whitford, 2011; Dunstan et al., 2007). Even if anthropogenic activities can exacerbate fluorine contamination in the environment, high F<sup>-</sup> concentrations in groundwater are usually related to natural sources (Ozsvath, 2009; WHO, 2011; Cinti et al., 2019).

Boyle (1976) establishes that fluorine is concentrated in a large variety of mineral deposits, although, certainly, hydrothermal mineralization is one of the primary ore-forming processes, related to extensional tectonic settings. The average F<sup>-</sup> concentrations in hot spring waters can reach until some tens of mg/L, very high values in comparison with those found in ocean water, where the range concentration is 0.03–1.35 mg/L (Allman and Koritnig, 1978).

The most abundant fluorine mineral is fluorite (CaF<sub>2</sub>), which is found in virtually all rock types (excluding ultrabasic rocks). Fluorine also occurs in significant quantities as apatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,Cl,OH)), the most common phosphate mineral. In turn, fluoride (F<sup>-</sup>) is present in silicate minerals containing OH<sup>-</sup> and/or O<sup>2-</sup> ions, where it may occur in trace amounts or as a major component. In sedimentary environment, the presence of fluorine depends essentially on the occurrence of fluorine-containing minerals. Clay minerals, active alumina and Fe(III) oxyhydroxides are common and preferential adsorbents of fluoride in this media.

In groundwater F<sup>-</sup> is an extremely mobile element over a wide range of redox and pH conditions. Its concentration is usually controlled by water temperature, pH, the presence of complex/precipitating ions and colloids, solubility of F-bearing minerals, residence time and climate

(Ozsvath, 2009). The effect of the presence of Ca<sup>2+</sup> in water is of primary importance, because Ca<sup>2+</sup> combined with fluoride forms fluorite (CaF<sub>2</sub>). As a consequence, water hardness is a factor to be taken into account since water of high hardness will have a lower fluoride content than water of lower hardness. The fluorite precipitation process is also temperature-dependent: a decrease in temperature favours the formation of this mineral phase and an increase favours its remaining in solution (Boyle, 1976).

Fluoride concentration in groundwater in the EU is generally low, but there are large regional differences due to different geological conditions. High natural fluoride concentrations in groundwater (including thermal waters) have been studied by different authors in various European countries, such as: Belgium (e.g. Carvalho et al., 1998), Bosnia-Herzegovina (e.g. Jolović 2017), France (Malcuit et al., 2014), Hungary (e.g. Fordyce et al., 2007), Iceland and Nordic Countries (e.g. Knutsson, 2008), Ireland (e.g. Tedd et al., 2007), Italy (e.g. Parrone et al., 2020), Latvia (e.g. Retike et al., 2014), Malta (e.g. Vella and Borg, 1989), Poland (e.g. Dragon and Górski, 2015), Portugal (e.g. Alfonso and Chaminé, 2019), Romania (Butaciu et al., 2017), Serbia (e.g. Mandinic et al., 2010), Slovenia (e.g. Kralj and Kralj, 2020), Spain (e.g. Mas-Pla et al., 2013), and Sweden (e.g. Berger, 2016).

Concerning the co-occurrence of As and F in groundwater in endogenous environments, the work of Morales et al. (2015) in a volcanic aquifer in Mexico identified a good correlation between As and F, relating the source of As to the occurrence of metallic sulphides (As), while primary minerals would be the source of F. The mobilisation of both elements would be favoured by the ascent of thermal water through faults and fractures.

For sedimentary media, desorption of Fe-(hydr)oxides is considered the main process for As-F groundwater co-contamination (e.g., Kim et al., 2012; Currell et al., 2011). Parrone et al. (2020) found a strong positive correlation between F<sup>-</sup> and As in groundwater from a region of China, concluding that these elements had been mobilized and enriched by common processes that included de-sorption of As and F<sup>-</sup> anions from Fe, Mn, and Al-(hydro) oxides.

A common feature of many aquifers characterized by high As concentrations, as mentioned in the work of Smedley and Kinniburgh (2002), is the pronounced spatial variability of their concentrations in groundwater, or patchy distribution, making it difficult to predict their concentration in a particular zone or well based on the results of nearby wells. Most As research on groundwater focuses on the local water-rock or water-sediment interaction processes that control As mobilisation in the area concerned. However, it is necessary to consider the ubiquitous character of this element and to assess whether its distribution in a regional geological context follows any pattern.

Alam et al. (2021) establish an interesting perspective in addressing this issue. These authors consider that the PS of As are globally associated to areas as *magmatic arcs at continental convergent margins* of some of the most prominent *orogenic systems* worldwide, and it ends up in *arc-derived sediments* in the adjacent *foreland basin*, where secondary As in the aquifer matrix would induce high concentrations of As in groundwater.

The discussion made so far on the factors that explain the occurrence and distribution of As in groundwater can be valid for other PTGTEs, always taking into account the geochemical peculiarities of each element. In our case, it would extend to fluoride and its own PS and SS distribution.

Geochemical prospecting for trace elements aims to discover a geochemical "anomaly" with a pattern, indicating the presence of a mineral in the vicinity. Anomalies caused by the movement of metals in groundwater were an effective means of locating buried mineral deposits and a good prospect for nearby deposits (Langmuir and Chatham, 1980; Wanty et al., 1987; Langmuir, 1997).

The work of Carranza (2009) analyses the spatial pattern of occurrence of some *mineral deposits*, significant source of PTGTEs. This author states that the occurrence of these deposits is not random because there

is (1) an interaction of certain geological processes or features that have genetically controlled their occurrence and (2) they show a spatial association with some (but not all) geological factors. For this author, analysis of the spatial pattern of ore deposits of a given mineral type could provide information on the geological features controlling their formation in their present locations. This conceptualisation could be extended to the distribution of PTGTEs in groundwater.

The antecedents of this approach would be several studies carried out in Spain previously (Giménez-Forcada and Smedley, 2014; Giménez-Forcada and Vega-Alegre, 2015; Giménez-Forcada et al., 2017a, 2017b), which revealed that the spatial distribution of some trace elements in groundwater can be analysed in the geological context, working on a regional scale and considering the interaction with certain geological factors (Geo-Hydrochemistry). Based on the results of these studies, the hypothesis of this work was extended to a Pan-European scope.

The main objective of this work is to test the veracity of this hypothesis by testing whether the distribution of the main As and F<sup>-</sup> anomalies in groundwater on a Pan-European scale follows a geological pattern (represented by two geological factors: *lithology* and *fault structures*). For this purpose, the Baseline Concentration index, BLC (BLC<sub>As</sub> and BLC<sub>F</sub>), will be used. Previously, the natural water quality as drinking water will be considered through the HydroGeoToxicity index: HGT<sub>As</sub> and HGT<sub>F</sub>.

## 2. Geological setting: a summary of European Geology and tectonic evolution

Geologically, most of the major mountainous lineaments of Europe are believed to be very ancient features related to the movement of crustal plates that periodically separated and reunited Europe, North America and Africa (Ager, 1975; Neubauer, 2003).

A large part of the European continent consists of ancient pre-

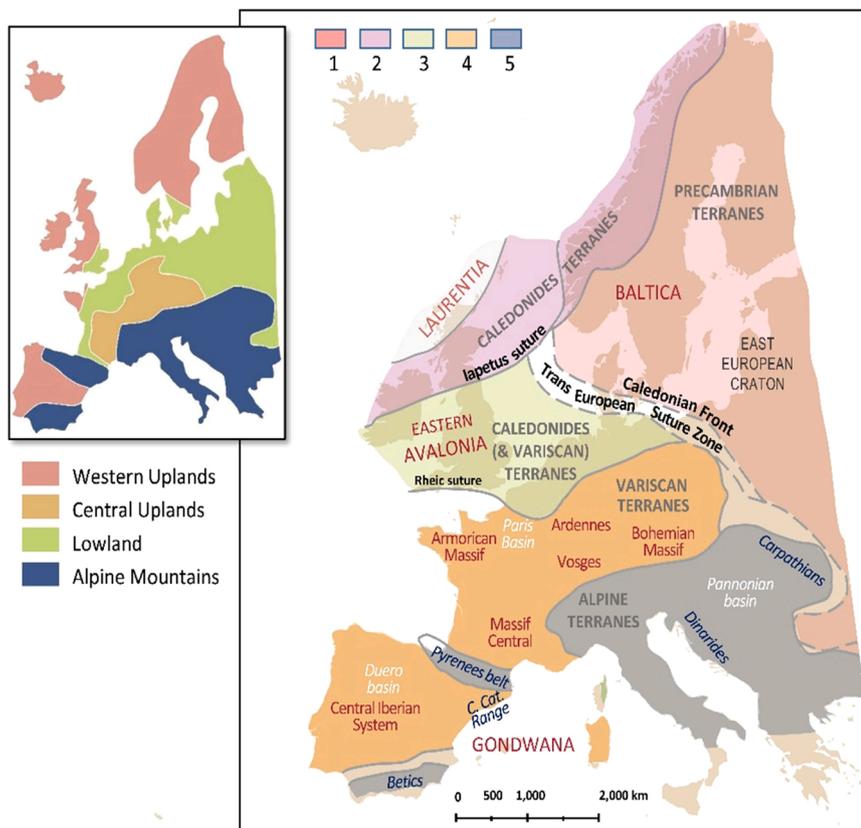
Variscan massifs as Western and Central Uplands (*Precambrian Terranes*, *Variscan Terranes*) and Alpine reliefs (*Alpine Terranes*), between which emerge depressions that are filled in during subsequent periods (Lowland) (Fig. 1). Large sedimentary assemblages of marine facies appear (e.g. the Paris Basin), along with inland areas filled with continental facies materials. Cenozoic deposits cover much of the lowlands of Europe overlaying the initial bedrock geology. The Quaternary period was clearly a time of frequent and marked climatic oscillations, with glacial periods where deposits were created.

It is possible to distinguish five different tectonostratigraphic units or terranes in the European territory (*Precambrian Terranes*, *Caledonian Terranes*, *Eastern Avalonian (Caledonian and Variscan) Terranes*, *Variscan Terranes*, and *Alpine Terranes*), which are accreted through important *suture lines*, such as the *Iapetus suture*, the *Rheic Suture*, and the *Caledonian front* and the *Trans-European Suture zone (Tornquist suture)*, who separate the East European Craton from the southern terranes (Fig. 1).

## 3. Materials and methods

The applied methodology has consisted of five stages, which are described below (see flow diagram in Graphical Abstract).

- (1) *HOVER European Geology*, setting up the European geological reference map.
- (2) *Data collection* from existing observation networks for As and F<sup>-</sup> on a Pan-European scale (study area).
- (3) Representation of groundwater chemistry in *HFE-Diagram*, relating the hydrochemical facies to the concentrations of As and F<sup>-</sup>.
- (4) Calculating the *HGT<sub>As</sub>* and *HGT<sub>F</sub>* for each sampling point and determining the threshold values corresponding to *BLC<sub>As</sub>* and *BLC<sub>F</sub>*.



**Fig. 1.** Physical landscapes in Europe (*Western Uplands*, *Central Uplands*, *Lowland* and *Alpine mountains*), together with a simplified sketch of the Precambrian and Phanerozoic "terrane collage" of Precambrian and Phanerozoic Europe. Sutures and orogenic fronts are shown as gray lines (by Plant et al., 2005, modified and simplified). Legend: 1. Precambrian Terranes; 2. Caledonide Terranes; 3. Eastern Avalonian (Caledonian and Variscan) Terranes; 4. Variscan Terranes; 5. Alpine Orogen/Terranes.

- (5) Analysis of the *spatial distribution* of HGT and the samples with [As] (As concentration)  $\geq$  BLC<sub>As</sub> and [F<sup>-</sup>] (F<sup>-</sup> concentration)  $\geq$  BLC<sub>F</sub>.

### 3.1. HOVER European geology

For the purpose of this work it was necessary to have a geological map of Europe as a strong reference. The map selected in its version for ArcGis was prepared by the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR, 2020) (Federal Institute for Geosciences and Natural Resources), whose purpose was and is to 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 a harmonized geology at the scale 1:1.000.000 (Fig. 2A). The simplified geological map of Europe (Fig. 2B) was further summarized and used for the following analysis of the distribution of F<sup>-</sup> and As.

In the original map, igneous and metamorphic rocks were considered independent of the stratigraphic column and this differentiation has been respected because it was understood that these rocks were significant as PS of As and F<sup>-</sup>.

In order to carry out the spatial analysis of highest [As] and [F<sup>-</sup>] in groundwater against European geology, *lithology* was summarised and simplified considering only 4 units, even more to deliver more easily visible results: (1) European Crystalline Massifs, ECM (Western and Central Uplands (*Variscan Terranes*), East European Craton (*Precambrian Terranes*), and *Alpine Terranes*, Fig. 1), which include Precambrian, Paleozoic, Igneous and Metamorphic rocks), (2) Mesozoic-Triassic (sometimes forming fissured hard rock (FHR) aquifers); (3) Mesozoic-Carbonated rocks (belonging to Jurassic and Cretaceous and forming karstic/fissured carbonated aquifers); and (4) Cenozoic (sedimentary areas forming relevant porous detrital aquifers) (Fig. 2B).

Interpreting the influence of fault structures on the distribution of As and F<sup>-</sup> required a higher network density than the initial map provided. With the aim of expanding this density respect the initial geological BGR map, different technical and research works were considered. The Figs of these works were 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 Fig.

Fig. 3 shows fault traces according to BGR (2020) and 'other faults'.

### 3.2. Data collection

The second step was to set up an observation network of all participating members, creating a single network with Pan-European entity. For participating countries, it was required to contribute [As] and [F<sup>-</sup>] in groundwater. If possible, further information was required (physicochemical parameters and major chemistry).

The collection of information followed the following criteria.

- The selected time period for data was in the range 2010–2016. For data belonging to only one year, 2016 was selected as representative (as the date closest to the date of the data request, which was made in 2018). If this is not possible, in any case include data from a representative year or range within the last 20 years. Different possibilities were proposed in order to make it easier for participants to take part. For the study carried out, small fluctuations in the concentration values due to the time factor do not influence the results for the research objectives.
- The coordinates system offered in two ways: geographic/UTM coordinates or EEA1km grid (according the EEA reference grid, <https://www.eea.europa.eu/data-and-maps/data/eea-reference-grids>). At

the end, all samples were referenced with geographic coordinates creating a single table.

- The average choice is based on the fact that it provides higher values than the median values. Average values are influenced by positive outliers and, therefore, they are better help to recognize hydrochemical anomalies by As and F<sup>-</sup>. This choice is consistent with the methodology devised and the objectives set. For average calculation, the values of the detection limits provided in the different data bases were substituted with half of this value according the methodology usually applied (e.g. Asante-Duah, 2021).

A total of 17 countries (Austria, Belgium (Flanders), Bosnia-Herzegovina, Denmark, France, Iceland, Ireland, Hungary, Latvia, Malta, Poland, Portugal, Romania, Serbia, Slovenia, Spain, Sweden) and 18 geological survey organizations (GSOs) (including GSO from Catalonia, Spain) have participated providing their databases on [As] and/or [F<sup>-</sup>] in groundwaters. Several European island areas (e.g. Canary Islands, Balearic Islands, Corsica, etc.) are not included in this study.

Arsenic concentration data were provided by 17 countries (Austria, Belgium (Flanders), Bosnia-Herzegovina, Denmark, France, Hungary, Iceland, Ireland, Latvia, Malta, Poland, Portugal, Romania, Serbia, Slovenia, Spain, Sweden), while the F<sup>-</sup> data network was set up with data supplied by 14 countries (Belgium (Flanders), Bosnia-Herzegovina, Denmark, France, Iceland, Latvia, Malta, Poland, Portugal, Romania, Serbia, Slovenia, Spain, and Sweden).

Austria, Belgium (Flanders), Denmark, Serbia, Spain, Sweden, provided in addition information on major chemistry.

At the Pan-European scale, 39,002 monitoring sites (ms) with As concentration (database for As) in groundwater have been provided from seventeen participating countries. In relation to dissolved fluoride in groundwater, the network consists in 50,531 ms, corresponding to the database for F<sup>-</sup>, and provided by twelve countries.

The construction of the As and F<sup>-</sup> databases has been done by extracting data from regional or national databases, followed by the use of a set of checks and corrections to detect systemic errors that can be observed (duplicate values, different units, error in point coordinates, anomalous data etc.). The errors detected have been attempted to be corrected; where this has not been possible, the sample has been eliminated.

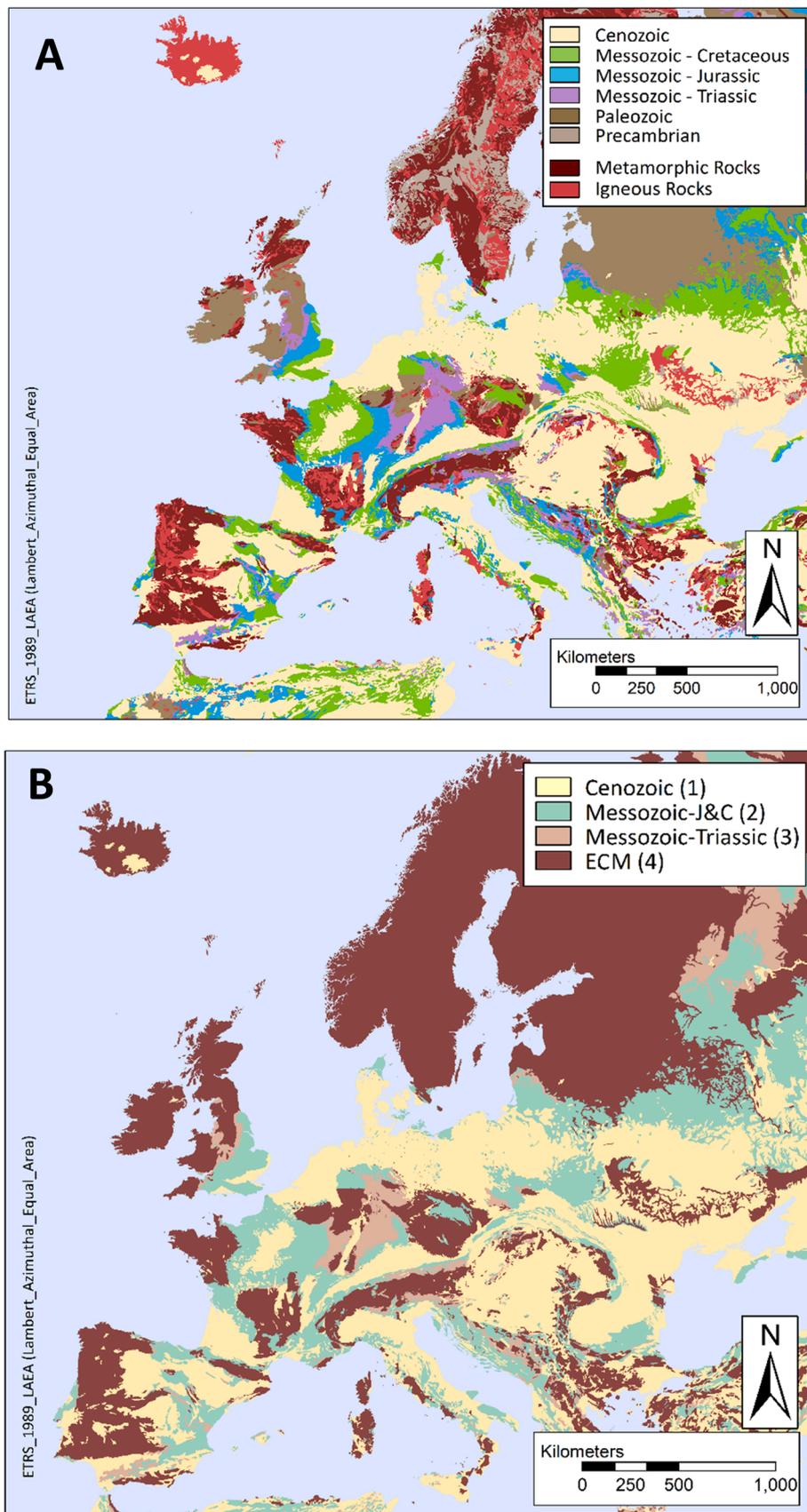
For spatial analysis about the relationship of maximum As and F<sup>-</sup> concentrations ([As]  $\geq$  BLC<sub>As</sub> and/or [F<sup>-</sup>]  $\geq$  BLC<sub>F</sub>) with European geology, the process has taken into account mineral and thermal water database for each element. For this purpose, the arsenic database (DB<sub>As</sub>) was constituted by 39,293 monitoring points and 50,339 were the monitoring sites collected in DB<sub>F</sub>. DB<sub>As</sub> and DB<sub>F</sub> are shown in Fig. 4 (A and B).

In the case where coordinates were provided using the EEA grid\_1 km (Poland and Sweden) or EEA grid\_10 km (Romania), and there were two or more points in the same cell, the mean values were selected as representative for each cell.

Each point represents a value: one per cell (in the case of data with EEA coordinates) and one per well or borehole with samples collected at different depth. If there were hydrochemical changes due to lithological differences in the borehole column, these could not be considered in this analysis. The mean value of [As] or [F<sup>-</sup>] (and major chemistry) were calculated as representative of every single point.

### 3.3. HFE diagram

Among the hydrochemical diagrams representing the chemistry of groundwater, was chosen the Hydrochemical Facies Evolution Diagram (HFE Diagram) to represent major chemistry of the samples (when available) and the relation between major cations/anions percentage, and [As] and [F<sup>-</sup>] concentration values. Although this diagram was introduced as a diagnostic element in marine intrusion studies (Giménez-Forcada, 2010, 2014; Giménez-Forcada and Sánchez, 2015), it can be applied to general cases such as other hydrochemical diagrams



**Fig. 2.** (A) Simplified Geological map of Europe (according BGR, 2020). (B) Summary of lithology in Geological map of Europe (according BGR, 2020). (1) Cenozoic; (2) Mesozoic-Carbonated rocks (Mesozoic-Jurassic and Mesozoic-Cretaceous); (3) Mesozoic-Triassic; (4) European Crystalline Massifs, ECM (Precambrian, Paleozoic, Igneous and Metamorphic rocks).

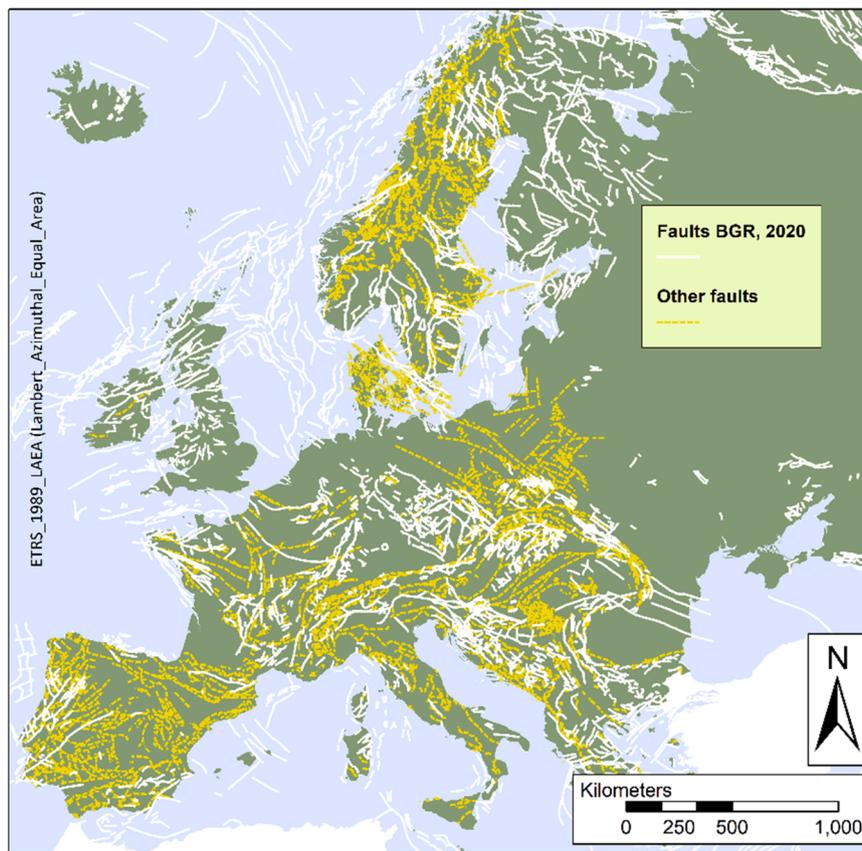


Fig. 3. Faults traces (BGR, 2020, modified) (white) and other faults according different authors (yellow).

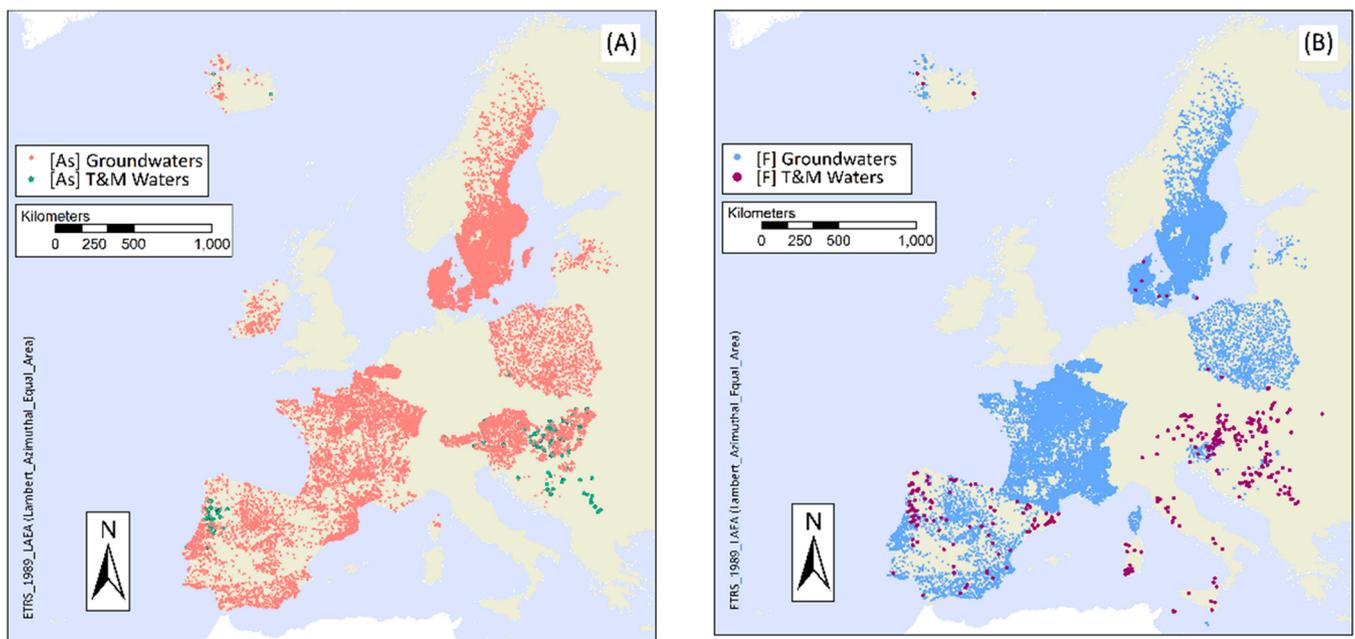


Fig. 4. (A) Distribution of points in the network of [As] in groundwater on a Pan-European scale, with the participation of 17 countries (Austria, Belgium (Flanders), Bosnia- Herzegovina, Denmark, France, Iceland, Ireland, Hungary, Latvia, Malta, Poland, Portugal, Romania, Serbia, Slovenia, Spain, Sweden). In red, data points with [As] in groundwaters; in green, mineral and thermal waters. (B) Distribution of points in the network of [F] in groundwaters on a Pan-European scale, with the participation of 14 countries (Belgium (Flanders), Bosnia-Herzegovina, Denmark, France, Iceland, Latvia, Malta, Poland, Portugal, Romania, Serbia, Slovenia, Spain, and Sweden). In blue, data points with [F] in groundwaters; in violet, mineral and thermal waters.

(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 (HF), not amalgamated (i.e. except for  $\text{Na}^+ + \text{K}^+$  (being  $\text{K}^+$  much lower than  $\text{Na}^+$ ), there is no addition of percentages), and that their representation marks evolutionary lines associated with different 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).

### 3.4. HGT and BLC index

Hydrogeotoxicity (HGT) and the Base Concentration Index (BLC) provide a study methodology that highlights the importance of studying groundwater quality in terms of the presence of potentially toxic trace elements (PTGTEs) (which compromise its use as drinking water), evaluating the spatial distribution of these elements within the natural geological environment.

The term Hydrogeotoxicity (HGT) applied in previous works (e.g. Giménez-Forcada et al., 2017b) refers to concentration values weighted with respect to the guideline or threshold values according to the national or international regulations (usually the limits set established by WHO, 2011, 2017) for water for human consumption with respect to geogenic trace elements:

$$\text{HGT}_{\text{PTGTE}} = [\text{PTGTE}_{\text{water}}] / [\text{PTGTE}_{\text{WHO}}]$$

$\text{HGT}_{\text{PTGTE}}$ : Hydrogeotoxicity for a Potentially Toxic Geogenic Trace Element, PTGTE).  $[\text{PTGTE}_{\text{water}}]$ : concentration of PTGTE in groundwater sample.  $[\text{PTGTE}_{\text{WHO}}]$ : concentration limit of PTGTE for drinking water, according WHO.

This index analyses groundwater quality with regard to the potential health risk due to the occurrence and concentration of one or more PTGTE. Hence, HGT index has also been used as a guide to establish a relationship between the natural chemical composition of groundwater and the regional geology of the study area (Giménez-Forcada et al., 2017a, 2017b), with the intention of establishing links between the natural environment and health concerns.

A HGT value equal to or greater than one ( $\text{HGT}_{\text{PTGTE}} \geq 1$ ) signifies a potential health risk that must be considered. The combined HGT due to concentrations above the limit value for various elements indicates a potential natural hazard that requires further attention.

To offer the distribution scenario of As and F<sup>-</sup> in groundwater at the European level, the distribution of  $\text{HGT}_{\text{As}}$  and  $\text{HGT}_{\text{F}}$  is given, using the reference guide levels for drinking water of the European legislation (Drinking Water Directive 98/83/EC) and the WHO (2011). For As, the guideline value is established in 10 µg/L ( $\text{HGT}_{\text{As}}=1$ ), although the Danish laws have a higher level of requirement and set a lower limit of 5 µg/L. For dissolved F<sup>-</sup> in groundwater, the threshold established by WHO for drinking water is 1.5 mg/L ( $\text{HGT}_{\text{F}}=1$ ) (WHO, 2011).

HGT is an individual index calculated for each water sample on respect to a fixed concentration (limits for drinking water), independently of the set of samples considered in a study area. In contrast, the BLC is an index (or threshold) extracted from a set of samples, derived from the application of statistical data analysis.

Actually, the method for calculating the BLC index has been applied from decades ago in geochemical prospecting to recognise geochemical anomalies (e.g. Langmuir, 1997), but it has also has been used to establish threshold values and standards used to assess groundwater chemical status under the European Union Water Framework and Groundwater Directives (WFD and GWD) (Hinsby et al., 2008; European Commission, 2009). The identification of *background* concentrations in groundwater was raised as an analysis of great interest for exploration geochemistry (Langmuir and Chatham, 1980; Wanty et al., 1987) and groundwater quality status. In the work carried out by Barnes and Langmuir (1978) the authors established that for a lognormal

distribution, the value of the mean plus two standard deviations equals the 97.7th percentile, which meant that the 2.3% of the samples represented the most significant anomalies. Similar methodology was subsequently used to define *baseline* or range of concentrations of an element derived entirely from natural sources, under conditions undisturbed by anthropogenic activity (Edmunds et al., 2003; Edmunds and Shand, 2008). According this method, positive outliers were assigned to both human activity and natural geochemical anomalies (Runnells, 1992; Edmunds et al., 2003). The method was later applied to groundwater quality for human consumption when *natural background level* (NBL) was defined. The NBL is a concentration value coincident with the maximum percentile of the *baseline* range, and marks the limit beyond which outliers are associated with human impact (Lions et al., 2021; Voutchkova et al., 2021). For defining the NBL value, Guidance Document No. 18 (European Commission, 2009) mentions the 90th percentile as a practical criterion to discriminate the largest anomalies. However, for large data sets, the 97.7th percentile would define the upper limit of the range (Hinsby et al., 2008).

From these considerations it can be seen that, while geochemists have been interested in *outliers* as indicators of significant geochemical anomalies, environmental geochemistry has been concerned with the recognition of contamination (Reimann et al., 2005).

In this research work, and according methodology proposed by Guidance Document No. 18 (European Commission, 2009) and Hinsby et al. (2008), for the calculation of  $\text{BLC}_{\text{As}}$  and  $\text{BLC}_{\text{F}}$  data set, 98th ( $\cong$  97.7th) percentile has been chosen, which involves a selection of a small subset of groundwater samples (2%), representing the highest As and F<sup>-</sup> anomalies. This outliers are considered natural anomalies given the geogenic character of the two elements analysed (As and F<sup>-</sup>). "R" software for statistical computing and graphics was used for the  $\text{BLC}_{\text{As}}$  and  $\text{BLC}_{\text{F}}$  calculations.

Although it has not been possible to apply pre-selection criteria due to lack of sufficient information, it is unlikely that there are significant differences between the results obtained with this methodology and those calculated by other methods that exclude contaminated samples using indicators of contamination (e.g. nitrate in agricultural areas: Voutchkova et al., 2021).

For determining BLC index, data from mineral and thermal waters are considered. Natural waters, whether they are called groundwater or thermal waters, are one and the same entity when we are interpreting the natural chemical quality of the water. Geo-thermalism exacerbates water-rock reactions and tends to give higher values of As and F<sup>-</sup>, but since the purpose is to interpret the spatial distribution of these anomalies, they become a very useful tool for the purposes of this work.

The distribution of the highest As and F<sup>-</sup> concentration values (samples with  $[\text{As}] > \text{BLC}_{\text{As}}$  and waters with  $[\text{F}^-] > \text{BLC}_{\text{F}}$ ) will be interpreted in the light of Pan-European interregional geology, trying to find a link between these hydrochemical anomalies and regional geology.

The HGT index weights the concentration of a sample in relation to a threshold value that is established with health criteria. When the BLC value becomes HGT, the geo-hydrochemical interpretation of the As and F<sup>-</sup> distribution implies the relationship between geology, groundwater quality and health, thus a way forward for groundwater resources management and public health protection.

### 3.5. Spatial analysis

Geographical information systems (GIS) is an essential tool in many research fields such as environment, earth sciences, socioeconomics, agriculture and health, and provides a powerful and wide range of tools for analysing experimental data. Both basic and advanced procedures are available, allowing different levels of analysis of experimental information.

For the purpose of this paper, the study of the information through GIS tools is essential, allowing to set up the relationships between the hydrochemical data spatial distribution and the geological

characteristics of the study area represented in the geological map. The analysis has been carried out using ESRI ArcGIS© version 10.5.

The geographic distribution of the values of  $HGT_{As} \geq 1$  and  $HGT_F \geq 1$  have been represented, identifying the geographical and geological environments with the greatest quality problems in relation to  $HGT_{As}$  and  $HGT_F$  at Pan-European scale.

In addition, *lithology* and *fault structures* have been related to the distribution of samples with  $[As] \geq BLC_{As}$  and  $[F] \geq BLC_F$ , using geoprocessing tools such as buffer, clip or intersect.

To perform the spatial analysis, each point has been geographically related to the geological material (*lithology*) in which it is located, using the intersect tool of ArcMap. Every lithological item has been selected, and its boundaries are used by the clip tool to select the points included in each item.

When applying the intersect tool to find out the relationship between the highest concentration of As and F and mapping faults, a buffer of three distances between the water point and the fault trace have been considered: 1 km, 5 km and 10 km. The maximum buffer distance (10 km) was chosen for different reasons: (1) some points have been

geographically located using a 10 km grid; (2) some fault structures, especially the most relevant at European scale, are actually fault systems associated to a main direction and, within the chosen working scale, 10 km is an acceptable distance; (3) in sedimentary areas, porous aquifers are exploited generating a dispersion should be taken into account; it is in these areas where less map information on fault structures is available. However, in cases where there is a dense and regular observation network (as is the case in Sweden) the maximum buffer distance could be reconsidered.

#### 4. Results and discussion

A Pan-European area of 3,351,145 km<sup>2</sup> has been studied in relation to the distribution of [As] and [F]. The density of the sampling network with respect to this area is 0.012 ms/km<sup>2</sup> and 0.015 ms/km<sup>2</sup> for As and F, respectively. However, it should be noted that there are marked differences between the densities of the different participating countries. The heterogeneity of the network density is more marked in the F observation network (as mentioned above, maximum in Sweden and

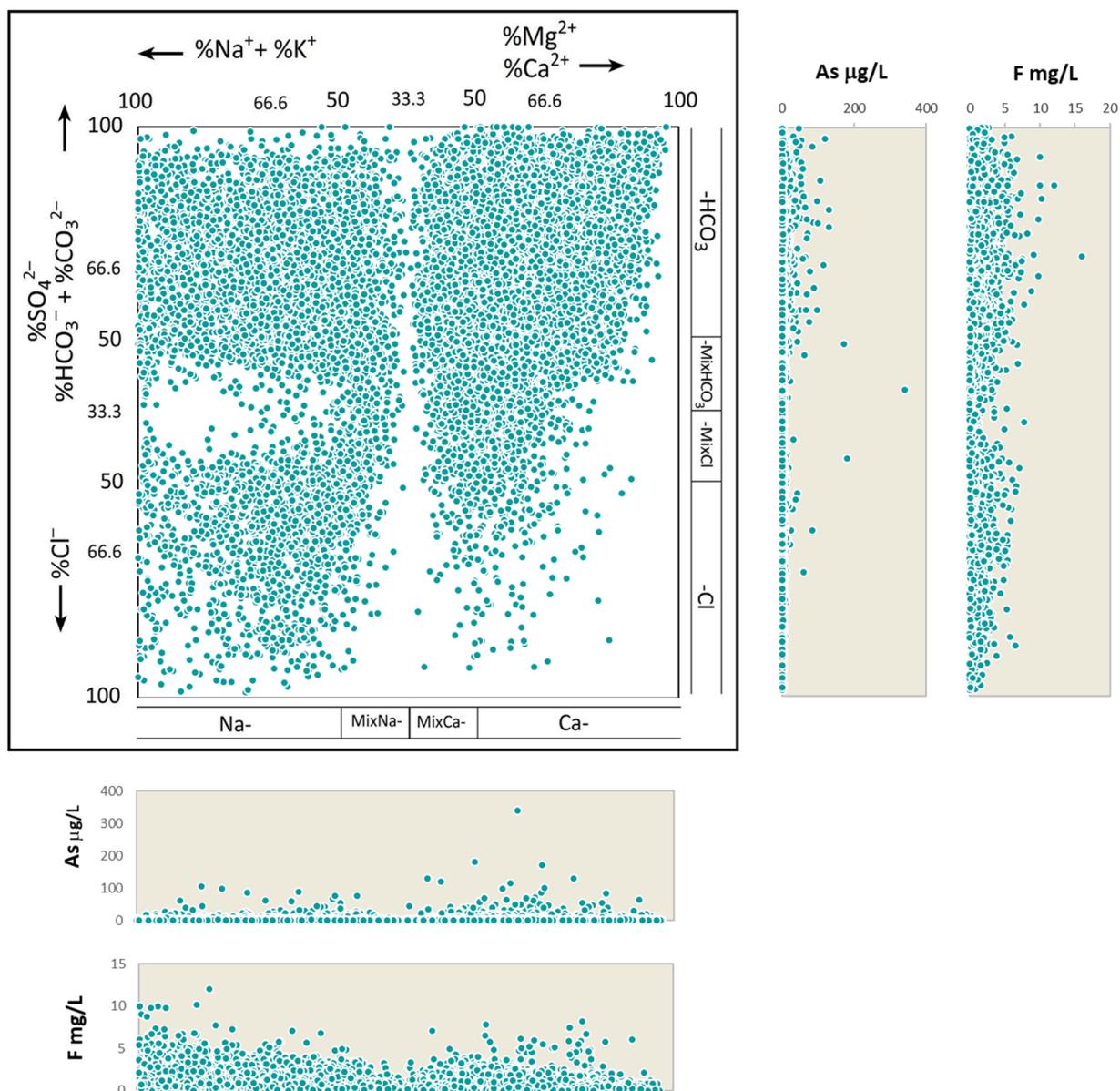


Fig. 5. HFE Diagram illustrating the evolution of [As] and [F] in relation to the general hydrochemistry at Pan-European scale (water samples from Austria, Belgium (Flanders), Denmark, Serbia, Spain, Sweden).

France).

For the groundwater set, As concentrations vary over the range <DL–1295 µg/L, with average value of 2.2 µg/L, median 0.5 µg/L and standard deviation 12.2 µg/L. Fluoride concentration values are in the range <DL–29 mg/L (average 0.4 mg/L; median 0.2 mg/L; standard deviation 0.8 mg/L).

Only 4% (n = 1356) of the samples from the observation network offer  $HGT_{As} \geq 1$ , and the 7% (n = 3500) of database samples exceed the 1.5 mg/L [F] in groundwater ( $HGT_F \geq 1$ ).

Fig. S1 shows the concentration value associated to 98th percentile (P98) for the respective Cumulative Frequency Curve (CFC):  $BLC_{As}$  (15 µg/L) (a), and  $BLC_F$  (2.3 mg/L) (b). Considering thermal and

mineral waters database (which includes dataset from other countries, as Italy), the number of samples with  $[As] \geq BLC_{As}$  and  $[F] \geq BLC_F$  are, respectively, 985 and 1409.

#### 4.1. As and F evolution vs. European hydrochemistry (HFE-diagram)

In Fig. 5, the HFE Diagram illustrates the general hydrochemistry on a Pan-European scale using major chemistry provided by Austria, Belgium (Flanders), Denmark, Serbia, Spain, and Sweden, together the evolution of [As] and [F] with respect to the percentage of cations (right) and anions (below).

With regard to samples with  $[As] \geq 10 \mu\text{g/L}$  (n = 1356), 52% belong

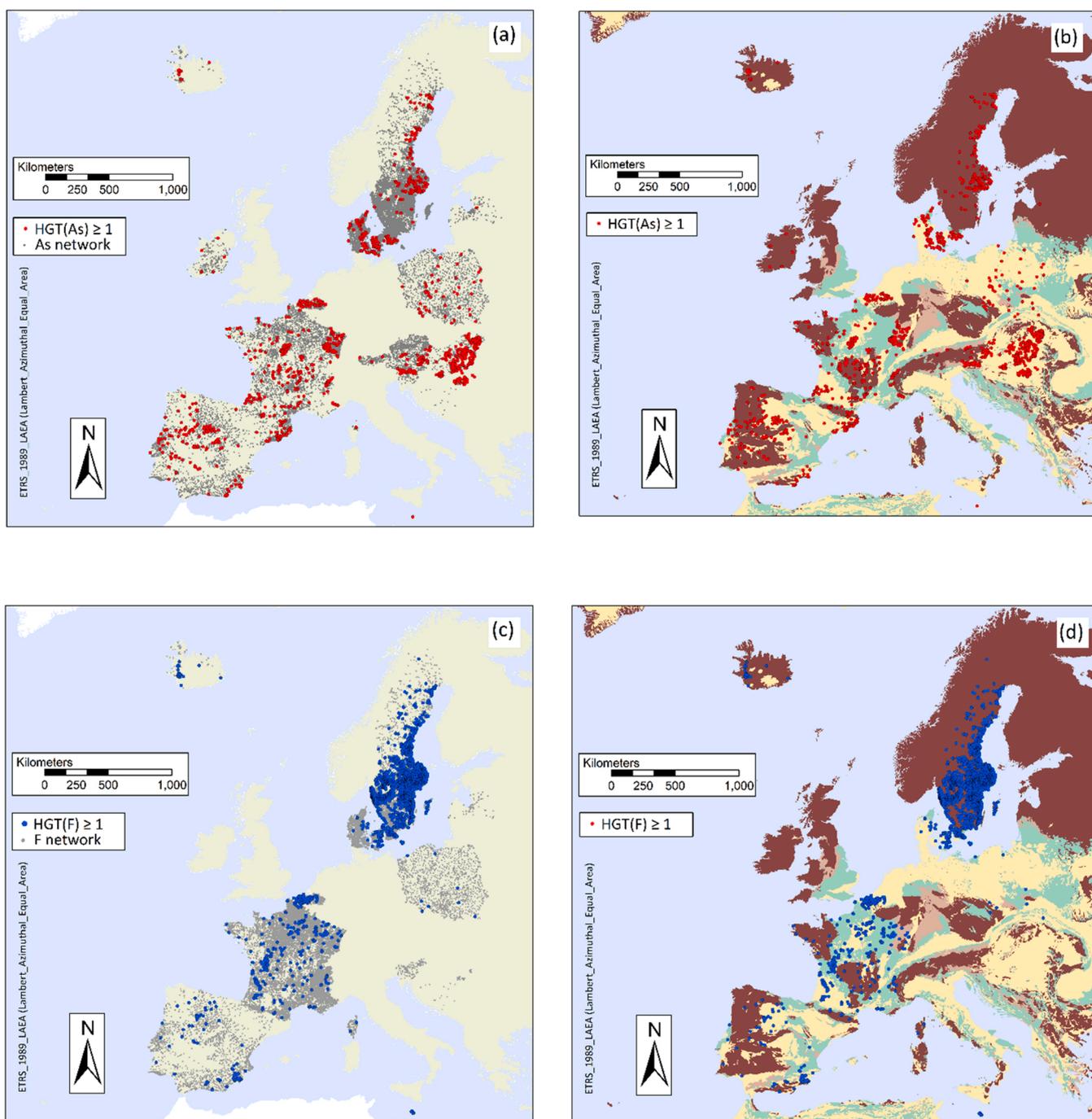


Fig. 6. Distribution  $HGT_{As}$  on general As network (a) and in summarized geological map (b); distribution  $HGT_F$  on general F network (c) and in summarized geological map (d); distribution of samples with  $[As] \geq BLC_{As}$  on general As network (e) and in summarized geological map (f); distribution of samples with  $[F] \geq BLC_F$  on general F network (g) and in summarized geological map (h).

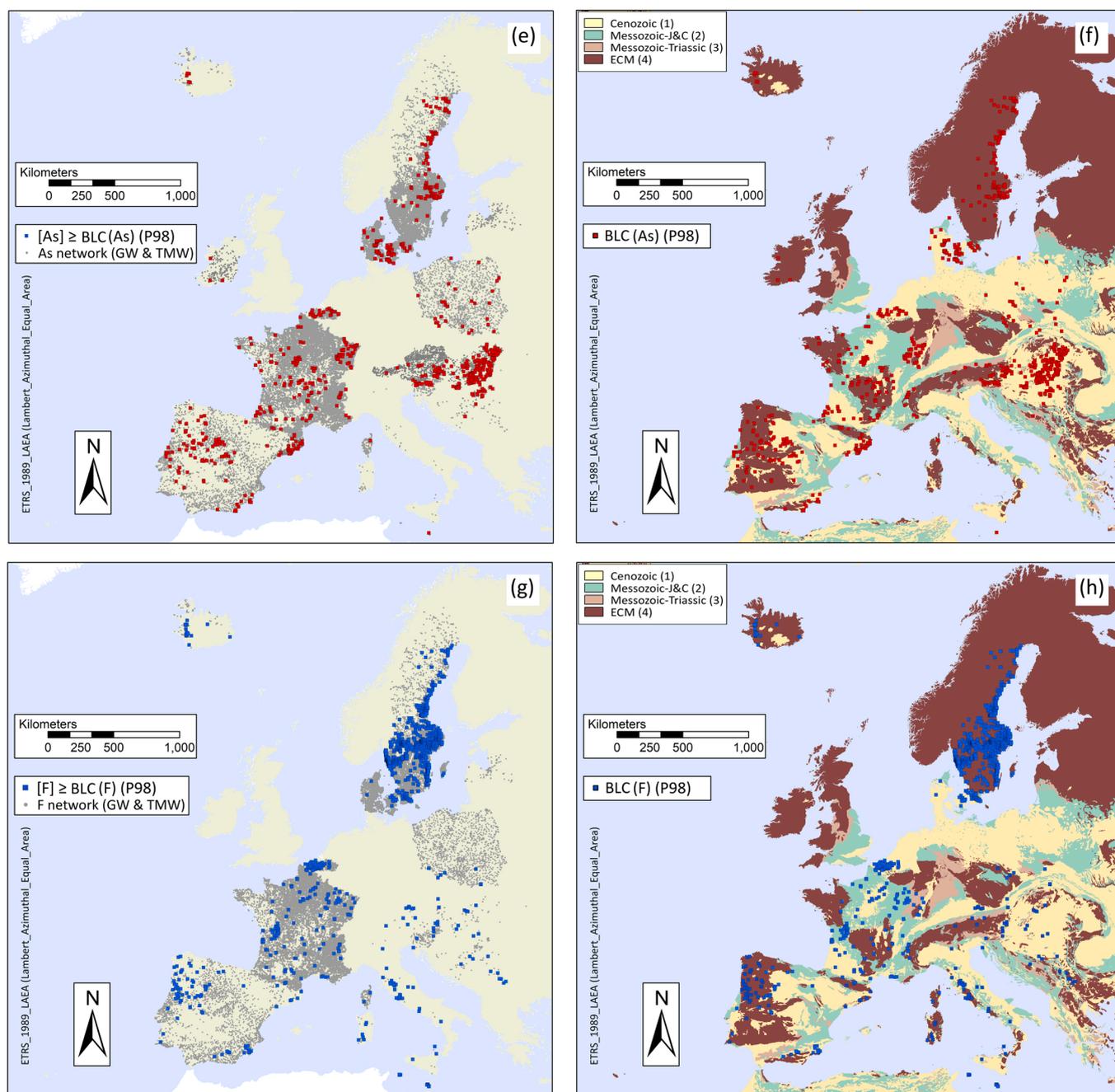


Fig. 6. (continued).

to  $\text{CaHCO}_3$  hydrochemical facies (HF) and 36% to  $\text{NaHCO}_3$  HF. Only 9% are chloride facies ( $\text{NaCl}$  (7%) or  $\text{CaCl}$  (2%)). For water samples with  $[\text{F}] \geq 1.5$  mg/L ( $n = 3500$ ), the predominant HFs are  $\text{NaHCO}_3$  (51%) and  $\text{CaHCO}_3$  (37%), followed by  $\text{NaCl}$  and  $\text{CaCl}$  (with 7% and 1%, respectively). The good relationship of F with sodium waters is justified, as stated in the introduction epigraph.

The highest  $[\text{As}]$  ( $\geq 50$   $\mu\text{g/L}$ ) are found in the main HF  $\text{CaHCO}_3$  and  $\text{NaHCO}_3$ , predominantly. The  $\text{CaCl}$  and  $\text{NaCl}$  HF have a very low representation.

For highest  $[\text{F}]$  ( $\geq 5$  mg/L) is similar, except that the main HF are at reversed order, and the most representative is  $\text{NaHCO}_3$ . Several authors have found a good correlation between  $\text{Na}^+$  (and probably also  $\text{K}^+$ ) and F content, so that, in summary, while calcium suppresses F concentration,  $\text{Na}^+$  and  $\text{K}^+$  increase both the concentration and mobility of fluoride in groundwater systems. Indeed, generally groundwaters of  $\text{NaHCO}_3$  facies, with low levels of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  have higher

concentrations of F.

#### 4.2. Distribution $\text{HGT}_{\text{As}} \geq 1$ and $\text{HGT}_{\text{F}} \geq 1$ , and samples with $[\text{As}] \geq \text{BLC}_{\text{As}}$ and $[\text{F}] \geq \text{BLC}_{\text{F}}$

Fig. 6 shows the distribution of  $\text{HGT}_{\text{As}} \geq 1$  and  $\text{HGT}_{\text{F}} \geq 1$  (a-d), as well as samples with  $[\text{As}] \geq \text{BLC}_{\text{As}}$  and  $[\text{F}] \geq \text{BLC}_{\text{F}}$  (e-h) on the respective observation networks and on the simplified geological map.

The  $[\text{As}]$  network is made up of fewer points but with a more homogeneous distribution; whereas the dissolved  $[\text{F}]$  in water observation network is larger, but with fewer countries and a very uneven distribution among them.

Groundwaters with  $\text{HGT}_{\text{As}} \geq 1$  (and  $\text{HGT}_{\text{As}} \geq 0.5$  for Denmark) are identified in European lowlands (sedimentary areas), from Belgium (Flanders), Denmark, Hungary, Poland, Serbia, Spain and France, and also in uplands (fissured hard rocks reliefs) from Austria, Portugal,

Sweden, Spain, Ireland, and Iceland. Values of  $HGT_F \geq 1$  occur in hard rocks of Swedish, and France, Iceland; also in flatlands from Belgium, Denmark, and Spain.

From the north towards south, Sweden, Denmark, Hungary, France and Spain, show the most significant values of samples with  $[As] \geq BLC_{As}$ . The highest anomalies of F<sup>-</sup>,  $[F^-] \geq BLC_F$  ( $F^- \geq 2.3$  mg/L), appear to be in Sweden, France, Hungary, Portugal and Spain.

#### 4.3. Spatial analysis of samples with $[As] \geq BLC_{As}$ and samples $[F^-] \geq BLC_F$ in relation to European lithology

In the set of images comprising Fig. 6, the spatial distribution of  $HGT_{As}$ ,  $HGT_F$ , as well as the layout of samples with concentrations of As or F<sup>-</sup> above the  $BLC_{As}$  and  $BLC_F$  values, respectively, are shown.

The results are shown in the table SM1 (A and B) which collect the analysis about the interactions between the four lithological groups (in summarized geological map) and the highest outliers for As and F<sup>-</sup> (selected by  $BLC_{As}$  and  $BLC_F$  index).

985 samples have been considered to relate the maximum [As] in groundwater and to study their relationship with lithology. The limits of each lithology have been considered, using the clipping tool to select the points included in each polygon. Almost 60% of the highest values are found in areas covered by Cenozoic materials; this group is followed in order of priority by the set of samples (27%) located on the European Crystalline Massifs (ECM). In third and fourth place, respectively, are the areas covered by Mesozoic materials from the Jurassic-Cretaceous and Triassic, with 9% and 5%, respectively.

The results obtained for sedimentary detrital areas, coincide with the evidences found in detrital sedimentary aquifers as the Duero Basin (Spain) (García-Sánchez et al., 2005, 2014, Giménez-Forcada et al., 2017a,b), and Pannonian Basin (Hungary, Romania, Serbia), in Eastern Europe (Csalagovitis, 1999; Gurzau and Gurzau, 2001; Čavar et al., 2005; Varsanyi and Kovacs, 2006; Vidovic et al., 2006; Lindberg et al., 2006; Habuda-Stanić et al., 2007; Stauder, 2007; Djuric and Jevtic, 2008; Jimenez et al., 2009; Rowland et al., 2009; Ujević et al., 2010; Rowland et al., 2011). Both areas are known because numerous studies have been carried out on the presence of As-enriched groundwater. Also noteworthy are the As anomalies in Denmark, where geogenic sources of As are released through dissolution of iron oxides in sediments under reducing conditions (Ramsay et al., 2021).

In the Cenozoic sedimentary environment, sediment particles may be small portions of rock or unaltered minerals (e.g. Bundschuh et al., 2004), which would constitute small original PS of arsenic, but new mineral species would be also as a product of weathering, constituting secondary mineral phases (SS) (e.g. Smedley and Kinniburgh, 2002). In addition, the sedimentary environment offers the highest specific As-mineral surface area and, through multi-source water-rock interaction reactions, which will multiply the release and dispersion of As in groundwater with great efficiency (as opposed to more punctual/local character of PS). This could be one of the reasons why As contamination is mainly identified in porous detrital aquifers of sedimentary basins, with a wide range of significant concentrations.

In this regard, Mukherjee et al., (2007, 2008, 2009a); b (2011, 2012, 2014, 2019) and Alam et al. (2021) propose a universal mechanism(s) of As PS for aquifers worldwide, stating that PS of As in groundwater are *ex situ*, and that As in aquifers in affected foreland basins is derived through a series of geodynamic processes. These authors, along with others such as Barringer and Reilly (2013), Morales-Simfors et al. (2020), Bundschuh et al. (2020), suggest a global view of the distribution of arsenic in groundwater, putting forward geological reasons to explain this pattern. They also establish the spatial relationship between PS (in recharge areas) and SS (in discharge zones), highlighting the difficulties that sometimes exist in relating PS and SS, because the PS are usually distal to the secondary ones. Is interesting to note the conclusion that he comes to Banning (2021) when analyse distribution of As and U in Germany. This author concludes that ultimate control of the incompatible trace

elements is magmatic, even in old sedimentary systems, ending that trace element abundance directly reflects supraregional and intra-basinal geological evolution and that the distribution of areas with elevated As and U in Germany is large-scale widely determined by Variscan and Quaternary geology.

As mentioned above, the 27% of samples with related  $[As] > BLC_{As}$  located in ECM outcrops (Fig. 2) or fissured hard rock aquifers, which have historically received less attention as areas affected by high concentrations of As, because they are less exploited formations for groundwater resources; however, from the point of view of this work, are relevant in that they represent the main PS of this metalloid (Smedley and Kinniburgh, 2002; Bhattacharya et al., 2004; Mukherjee et al., 2009; Bondu et al., 2016) and in many occasions they constitute the fractured basement of sedimentary areas. Arsenic bearing minerals are an important factor controlling the occurrence and mobilization of As into groundwater but also mineral deposits associated to fractures (e.g. hydrothermal veins). There is an interesting scientific literature on As in crystalline rocks, relating the presence of arsenic to rock mineralogy or associated hydrothermal ore deposits (e.g., Meranger et al., 1984; Peters and Blum, 2003; Robinson and Ayotte, 2006; Smedley et al., 2007; Lipfert et al., 2006; Peters and Burkert, 2008; Ryan et al., 2011; Breuer and Pichler, 2013; O'Shea et al., 2015; Maity et al., 2017; McGrory et al., 2017; Pedretti et al., 2019; Lone et al., 2020, 2021).

Arsenic anomalies in groundwater are also linked to geothermal systems, when geothermal fluids flow along fracture/fault systems interact with mineral deposits especially enriched in trace elements or when hydrothermal processes are active (Ellis, 1977; D'Alessandro, 2006; Sawyer and Oppenheimer, 2006; Ozsvath, 2009; De Rita et al., 2011; Edmunds and Smedley, 2013; Wen et al., 2013; Cinti et al., 2019; Kumar et al., 2020; Parrone et al., 2020).

Tectonics seems to play an important role and imply a tectonic control over the processes responsible for the geologic distribution and diffusion of As (Hecht and Oguchi, 2017; Masuda, 2018), as will be discussed below.

The network of groundwater samples with the highest dissolved F<sup>-</sup> outliers consists of 1409 sampling points. Although there is also a relatively significant percentage of groundwater with high F<sup>-</sup> concentrations associated with Cenozoic sedimentary zones (21%), 70% of the samples with the highest [F<sup>-</sup>] are located in ECM (Fig. 2). It has been found that there are high concentrations of F<sup>-</sup> in groundwater associated with crystalline rocks (particularly igneous rocks) (e.g. Wen et al., 2013), active volcanic areas of increased heat flow or located near important structural lineaments (Edmunds and Smedley, 2005; Berger, 2016).

As state Berger (2016) in Europe, elevated F<sup>-</sup> concentrations in groundwater are frequently found in regions dominated by igneous rocks (granites) in the northern Europe, as Sweden (Berger, 2016) or North Portugal (Eggenkamp and Marques, 2013). In addition, they are a source of sediments that fill associated sedimentary basins where, also become potential secondary sources of F<sup>-</sup> to groundwater. However there are no studies that explain the geographical distribution of F<sup>-</sup> in sedimentary areas.

In the Paris basin, fluorite mineralisation at the base of the Mesozoic sedimentary series have been analysed by Gigoux (2015). This work proposes that, around the crystalline Le Morvan (Massif Central (France) in Variscan Terranes, Central Uplands), the percolation of meteoric fluids into the crystalline massifs may have occurred through the basement to a depth (2–5 km). Dissolution of carbonates by rising fluorine-bearing hydrothermal fluids would allow fluorite formation as the fluid enriches in calcium in the basin. According that, a new source of fluoride is created inside the basin. This is an interesting contribution on the relationship between PS and SS in sedimentary areas close to crystalline relieves.

As a conclusion to this section, it can be highlighted that the highest concentrations of As are found in sedimentary basins, followed by outcrops of crystalline rocks; while these outcroppings would account for

the highest concentrations of F<sup>-</sup> in groundwater, being in second place sedimentary areas.

#### 4.4. Spatial analysis of [As] $\geq$ BLC<sub>As</sub> and [F] $\geq$ BLC<sub>F</sub> in relation to fault structures at Pan-European scale

The intersection tool has been used to cross [As] $\geq$ BLC<sub>As</sub> and [F] $\geq$ BLC<sub>F</sub> with the mapped faults, applying a buffer of three distances (1 km, 5 km and 10 km). Table S2 summarizes the results of this analysis for the different buffer distance. The study reveals that 671 samples (68%), and 830 samples (59%) intersect at different distances with the mapped fault traces (Table S2A).

Most of the coincidence between maximum As anomalies in groundwater and faults are identified in Cenozoic areas (42% (1 km); 51% (5 km); 54% (10 km). In the case of fault structures related to ECM outcrops, the percentages are similar although slightly lower (41% (1 km); 35% (5 km); 32% (10 km).

The importance of crystalline rocks and their associated mineralisation in the occurrence of As in groundwater has already been discussed in the previous section. Although it is easier to find the relationship between high As concentrations and fracture structures in fissured hard rocks, the results point to the importance of sedimentary zones. Specifically, to the propagation of faults into the basins from the surrounding hard rock massifs, which would represent the sedimentary basin fractured basement.

Giménez-Forcada et al. (2017a) stated for dissolved As distribution in groundwaters from Duero Basin that, although the thickness of the sedimentary fill is relevant, the influence of basement fault structures on the distribution of As in the groundwater of the detrital aquifer is notable. This could be similar in other sedimentary areas, such as the Pannonian basin.

The Pannonian basin is an integral part of the *Alpine Terranes*, ringed by the Carpathian Mountains and resulting from convergence and collision between several different fragments of continental crust (Burchfiel, 1980). Lenkey et al. (2002) state that the occurrence of hot springs is tectonically useful because most hot springs occur along faults. Almost half of the thermal springs in Hungary are located along faults, which have been active from the late Pliocene to the Quaternary. There are faulted areas, such as the tectonic domain of the Pannonian basin, characterised by significant geothermalism and hot spring.

Another interesting area to consider is the Trans-European Suture Zone (TESZ) is the longest European tectonic and geophysical lineament extending from the Baltic Sea in the NW to the Black Sea in the SE, and represents an important crustal-scale feature with a deep boundary (Ziegler, 1982; Petersen et al., 2003; Graversen, 2004; Mazur et al., 2018; Grad, 2019; Janik, 2022). This is not a linear structure, but a terrane accretion zone 100–200 km wide. For the purpose of this paper, the areas associated with these structural features would be mainly the sedimentary lowlands of Denmark and Poland, together with the Swedish highlands of the eastern half of the Scandinavian Peninsula, located north of the TESZ and belonging to the Baltic plate of the East European craton. The Teisseyre-Tornquist Zone could be also significance in the geographic distribution of As anomalies in groundwaters in Denmark and Poland.

It is important to note that As PS could be related to faults and fissures associated with fluids or mineral deposits and this could explain, together with the effect of SS, the distribution pattern of As in sedimentary aquifers. It cannot rule out completely that there may be some human activities locally that exacerbate geogenic concentrations (e.g. exploitation of mineral resources or groundwater over pumping), but this does not alter the location of the major anomalies in the spatial analysis.

The analysis performed for fluoride reveals that 59% of the samples with [F] $\geq$ BLC<sub>F</sub> (2.3 mg/L), corresponds to 830 monitoring points interacting with the fault structure at 1, 5 or 10 km buffer distance (Table S2B). The ECMs cluster 82% of the samples that have the highest

concentrations of dissolved F<sup>-</sup> in groundwater. As discussed above, the F<sup>-</sup> anomalies in the Portuguese and Swedish crystalline massifs stand out, highlighting the importance of lithology in the distribution of F<sup>-</sup> in waters on a Pan-European scale. It should be noted that fluoride is part of the minerals that form crystalline rocks, fissured environments in which rock-water interactions are capable of releasing F<sup>-</sup> into groundwater.

In order to help in the interpretation of the spatial control of F<sup>-</sup> dissolved, particularly in areas covered by sediments, an extra effort was made. Since 57% of the samples selected by P98 and located within 10 km of a fault belong to the Swedish network (where the control of lithological factor is evident), the number of network sampling has been extended by considering lower percentiles for calculating BLC<sub>F</sub>. Fig. 7B shows the distribution of values of [F] $\geq$ P98 (2.3 mg/L), [F] $\geq$ P97 (2.1 mg/L), and [F] $\geq$ P95 (1.7 mg/L). Their representation on the map shows that the BLC<sub>F</sub> (P97) and BLC<sub>F</sub> (P95) complete the pattern outlined by P98 corroborating the influence of faults on the distribution of F<sup>-</sup> in sedimentary basin areas. In reality, the percentile selected as the BLC index is a compromise between the highest concentrations and the number of samples capable of generating a pattern. For this study, and in the case of F<sup>-</sup> in relation to the influence of the structural factor, it seems that P97 and P95 could better represent the BLC<sub>F</sub> index for detrital aquifers because they have expanded the number of samples that can be associated with a structural pattern, corroborating that outlined by the initial BLC<sub>F</sub> (P98) index.

These news values and their results can be better visualised in some areas, such as the border between Portugal and Spain, where it is observed that the distribution of [F<sup>-</sup>] in groundwaters in the outcrops of fissured endogenous rocks (Portugal) is repeated in the neighbouring Cenozoic areas (Duero Basin, Spain). There is also a concordant arrangement with the fault directions in the Coastal Catalan Range and in the Betics Chains, in 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 and Mesozoic), in relation to the influence of *Trans-European Suture Zone*, TESZ. In the *Alpine Terranes*, there are faulted areas, such as the Pannonian basin, characterised by significant geothermalism and hot spring (Lenkey et al. 2002).

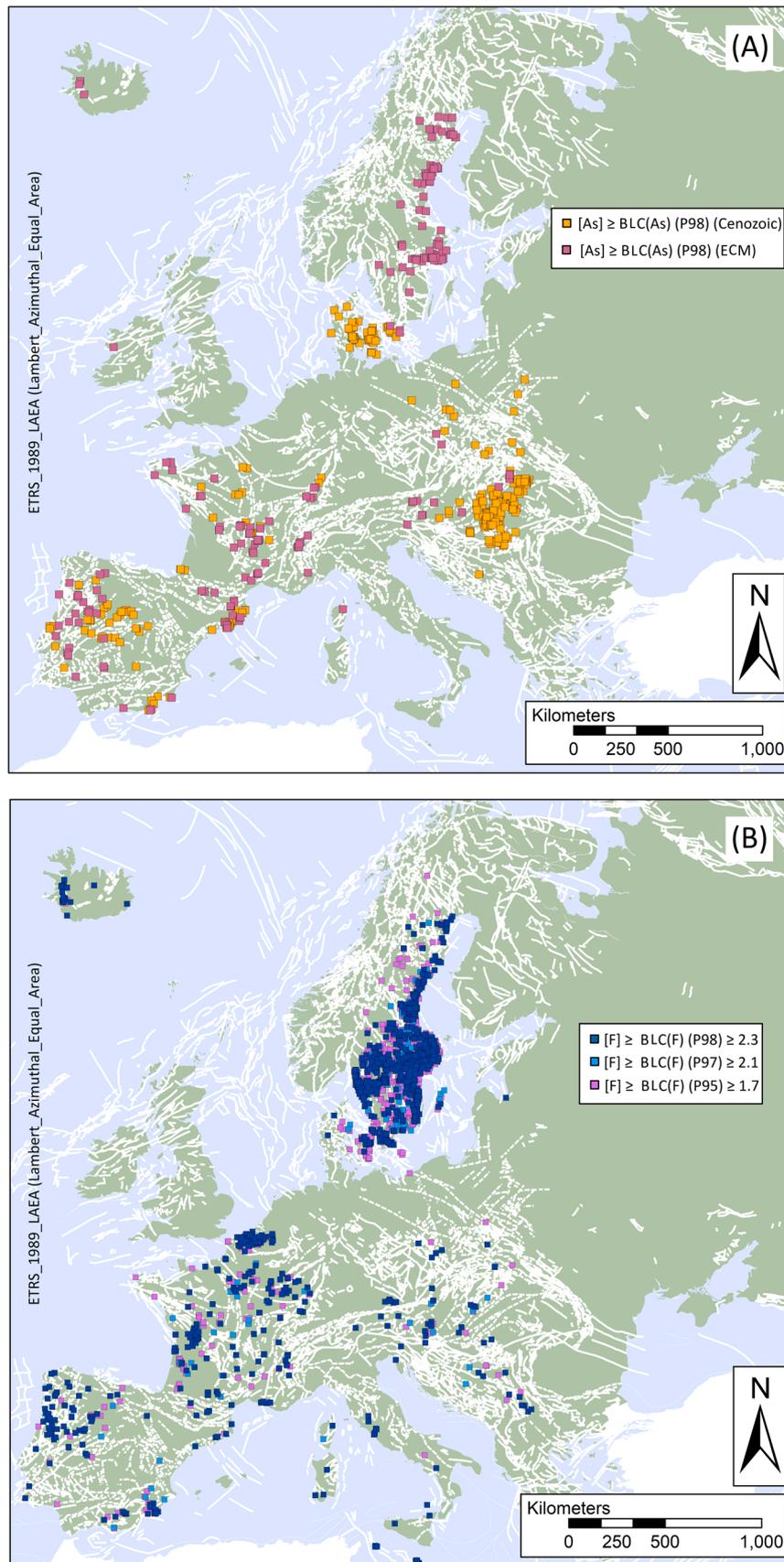
The results can be weighted in terms of health when the correspondence between BLC and HGT indices is applied. From this reading, the analysis can help to identify areas with groundwater naturally enriched in As and F<sup>-</sup>, depending on the geological setting. It would also mean that this knowledge can be applied in public health policies and, of course, in improving groundwater management. The BLC<sub>As</sub> (15 µg/L) and BLC<sub>F</sub> (P98) (2.3 mg/L) correspond to a HGT<sub>As</sub> and HGT<sub>F</sub> of 1.5, i.e. these values suggest significant health issues for longer term exposure to drinking water with these concentration levels.

## 5. Conclusions

High concentrations of As and F<sup>-</sup> in groundwater highlight a geosphere-hydrosphere-biosphere relationship and suggest an interesting etiological analysis. Perhaps the reason for such a complex and globally significant public health problem could be found in the recognition of geogenic sources of PTGTEs in an immediate or regional geological setting.

The importance of relating hydrochemical analyses to a regional geological context (Geo-Hydrochemistry) should be emphasized. The maximum anomalies of As and F<sup>-</sup> have been interpreted looking for a geological pattern. The results show that it is possible to relate natural groundwater quality to at least two geological factors. Lithology and fault structures combine to provide an explanation for the geographical distribution of the maximum anomalies of two geogenic trace elements, As and F<sup>-</sup>, in groundwater on a Pan-European interregional scale.

The most appropriate framework for a geo-hydrochemical analysis is the regional scale, which consists of analyzing with a geological



**Fig. 7.** (A) Map with the distribution of  $[As] \geq 15 \mu\text{g/L}$  (BLC<sub>As</sub>) associated to faults (buffer 10 km) in Cenozoic areas and ECM. (B) Map with the distribution of  $[F] \geq 2.3 \mu\text{g/L}$  (BLC<sub>F</sub>, (P98)),  $[F] = 2.1\text{--}2.3 \text{ mg/L}$  (BLC<sub>F</sub> (P97)), and  $[F] = 1.7\text{--}2.1 \text{ mg/L}$  (BLC<sub>F</sub> (P95)) associated to faults (buffer 10 km) in Cenozoic areas and ECM.

perspective the distribution of abnormally high concentrations of PTGTE (As and F<sup>-</sup>), identifying the primary and secondary sources of these elements. This often involves transcending non-natural geographical boundaries such as borders between countries, regions or provinces. This regional spatial analysis is compatible with more detailed local studies focused on water-rock interaction processes. The methodology applied in this research can be particularly useful in detrital aquifers of sedimentary areas over fractured crystalline basement and particularly concerns the deeper aquifer levels.

The application of prevention measures based on the identification of PS and SS would minimize the dispersion effect of the exploitation of these aquifers, as well as the increase of As and F<sup>-</sup> concentrations due to groundwater recycling. This is especially important when groundwater is intended for drinking water. Knowing the natural quality of groundwater is a prior step to consider any type of anthropic contamination. Knowing the natural quality of groundwater is a previous step to consider some type of anthropic contamination that justifies high concentrations of some chemical elements. This is especially important in the study of the distribution of PTGTEs (such as As and F<sup>-</sup>).

The methodology presented in this text can be applied in its conceptualization in other areas of the world.

#### CRediT authorship contribution statement

**Elena Giménez-Forcada:** Methodology, Investigation, Conceptualization, Supervision, Writing – original draft, Writing – review & editing. **J. A. Luque:** Methodology, Formal analysis. **M.T. López:** Data curation, Formal analysis. **J. Grima:** Formal analysis; **D. Elster:** Resources, Provision of database, Writing – review & editing. **D. Voutchkova:** Resources, Provision of database, Writing – review & editing. **B. Hansen:** Resources, Provision of database, Writing – review & editing. **K. Hinsby:** Resources, Provision of database, Writing – review & editing. **T. Szocs:** Resources, Provision of database, Writing – review & editing. **A. Felter:** Resources, Provision of database, Writing – review & editing. **A. Pereira:** Resources, Provision of database, Writing – review & editing. **G. Arnó:** Resources, Provision of database, Writing – review & editing. **I. Herms:** Resources, Provision of database, Writing – review & editing. **L. Rosenqvist:** Resources, Provision of database, Writing – review & editing. **J.A. Díaz:** Resources: Provision of database. **J. Jiménez:** Resources: Provision of database. **C. Ontiveros:** Resources: Provision of database. **F. Skopljak:** Resources: Provision of database. **J. Schullehner:** Resources: Provision of database. **E. Malcuit:** Resources: Provision of database. **L. Gourcy:** Resources: Provision of database. **D. Porbjörnsson:** Resources: Provision of database. **K. Tedd:** Resources: Provision of database. **D. Borzdins:** Resources: Provision of database. **H. Debattista:** Resources: Provision of database. **J. Cabalska:** Resources: Provision of database. **A. Mikołajczyk:** Resources: Provision of database. **J. Sampaio:** Resources: Provision of database. **D. Perša:** Resources: Provision of database. **T. Petrović:** Resources: Provision of database. **N. Rman:** Resources: Provision of database.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Final Report for HOVER WP3.4 is available here: <https://repository.europe-geology.eu/egdidocs/hover/hover+34+indicators+v2.pdf>

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#### Author Contributions

All authors have read and agreed to the published version of the manuscript.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ecoenv.2022.114161](https://doi.org/10.1016/j.ecoenv.2022.114161).

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