French Food Safety Agency

GUIDELINES FOR THE SAFETY ASSESSMENT
OF NATURAL MINERAL WATERS

May 2008

CONTENTS

FOREWORD

As part of its scientific and technical support for the Directorate General for Health (DGS), the French Food Safety Agency (AFSSA) created, on the recommendation of the Scientific Panel on 'Water' ('Water' CES), a working group named 'Natural mineral waters' responsible for:

- *"firstly, providing the expertise needed to revise the regulations related to the safety of natural mineral waters,*

- *secondly, prior to the publication of Decree no. 2007-49 of 11 January 2007 on the safety of water intended for human consumption, conducting a technical evaluation of DGS requests concerning individual applications to exploit natural mineral waters".*

The working group's members were as follows:

- Members of the 'Water' CES:
  - Mr. Gilbert ALCAYDÉ - Chair
  - Mr. Jean-Luc BOUDENNE
  - Mr. Jean CARRÉ
  - Mr. Paul CHAMBON
  - Mr. Norbert CRAMPON
  - Mr. Jean-François DUHAMEL
  - Mrs. Sylvie DUBROU
  - Mr. Pierre LEROY
  - Mr. Antoine MONTIEL
  - Mr. Jacques-Noël MUDRY
  - Mr. Jean-François MUNOZ
  - Mrs. Marie-Pierre SAUVANT-ROCHAT

- Other expert:
  - Mrs. Aline MARCELLI

- Associate members (AFSSA Laboratory for study and research in hydrology (LERH), DGS):
  - Mr. Xavier DAUCHY
  - Mr. Romain MÉHUT
  - Mr. Georges POPOFF
  - Mr. Christophe ROSIN
  - Mrs. Roselyne TARDIVEL

- Scientific panel:
  - Ms. Audrey COMMIEN
  - Ms. Mathilde HARVEY
  - Mrs. Juliette HOSPITALIER-RIVILLON

The following were also consulted:
  - Mr. Bernard ANDRÉ (Directorate General for Competition, Consumer Affairs and Fraud Control – DGCCRF)
  - Mr. Jean DOLQUES (National Division for Mineral and Spring Water - DNEMT)
  - Mrs. Nezha LEFTAH-MARIE (DGS)
  - Mrs. Anne NOVELLI (DGS)
  - Mr. Charles SAOUT (DGS)

This report was presented and approved by the 'Water' CES in its 5 February 2008 session.

INTRODUCTION

France produces 6.6 billion litres of natural mineral water per year[1], 4.4 billion of which are intended for the French market and 2.2 billion for export. Production has increased over a 10-year period: in 1996, only 3.9 billion litres were intended for the French market and 1.3 billion for export.

Packaged natural mineral water is considered to be a food under several European regulations and may be an ingredient in foodstuffs such as beverages. Like all waters intended for human consumption, natural mineral waters are subject to specific regulatory texts due to their special characteristics.

Article R. 1322-2 of the French Public Health Code transposes the European Community definition of natural mineral water:

"Natural mineral water is microbiologically wholesome water, within the definition set down in Article R. 1322-3, originating in an underground water table or deposit and emerging from a spring tapped at one or more natural or bore exits. Within the limits of known natural fluctuation, its composition, temperature and other essential characteristics must remain stable; in particular, they must not be affected by possible variations in the rate of flow.
It can be clearly distinguished from ordinary drinking water:
1) by its nature, which is characterised by its mineral content, trace elements or other constituents;
2) by its original state, both characteristics having been preserved intact because of the underground origin of such water, which has been protected from all risk of pollution.
These characteristics must have been assessed from the following points of view: geological and hydrogeological, physical, chemical and microbiological, and, if necessary, pharmacological, physiological and clinical, in accordance with the provisions of Articles R. 1322-5 and R. 1322-6".

The packaging, distribution in public drinking fountains and use of natural mineral water for therapeutic purposes in spas are subject to regulations.

The safety of natural mineral waters used in spas has already been examined in several publications by the French High Council for Public Health and will therefore not be discussed in this report. In addition to the regulatory texts that have been published on this topic, the following documents may be consulted:
- "Recommended good health practices in spas"
- "Recommendations regarding management of microbial risk related to mineral water in spas"
- "Recommendations regarding management of microbial risk related to natural mineral water in spa swimming pools".

The European Court of Justice judgment of 17 July 1997 states that "*a Member State cannot require that a water have favourable health properties to enable it to be recognised as natural mineral water*". This judgment explains why the health benefits of natural mineral waters are not discussed in this report.

Moreover, in 2006, the French Academy of Medicine published a report on the role of mineral water in food.

Regulatory analyses were hitherto undertaken by the Laboratory for study and research in hydrology and AFSSA issued its Opinion on applications to exploit natural mineral waters after consultation of the Scientific Panel on 'Water', but Decree no. 2007-49 of 11 January 2007 on the safety of water intended for human consumption (Official Journal of 12 January 2007) devolved the examination of authorisation applications for natural mineral waters to the departmental level.
In light of this change in the regulations, AFSSA deemed it useful to review current knowledge in order to establish guidelines necessary for the safety assessment of natural mineral waters for the authorities that are now responsible for examining these applications.

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[1] **Source: DRIRE/DNEMT data for 2004.**

PART ONE:
BACKGROUND AND REGULATIONS

I - BACKGROUND

In ancient times, the therapeutic properties of mineral-spring waters were recognised and sought after for curative treatments. In Ancient Greece, around 500 BC, doctors recommended the consumption and therapeutic use of natural mineral waters because they associated them with numerous health benefits. This tradition could also be found in the Roman and Arab civilisations, which consumed water onsite or used it in baths.

The Romans built the earliest spas.

In France, the medical use of hot water began in the Palaeolithic period and, later, the Gauls sought out water's beneficial effects: the cult of healing water was born.

In the Middle Ages, interest in spring water increased. Hot springs were not formally recognised however until 1549 with the letters patent signed by Henri II, which made all hot springs State property.

In 1605, Henri IV introduced the first State controls of the kingdom's spring and medicinal waters by creating the Superintendence of Mineral Waters and appointing a Superintendent of the Kingdom's Mineral and Medicinal Waters.

In 1687 and 1694, Louis XIV confirmed the State's ownership of hot springs, although this measure was not respected by many landowners who exploited the spring waters on their property for private use. While confirming the State's right in 1772, Louis XV also recognised the right of citizens who owned land containing springs. This problem would not be definitively settled until the Council of State ruling of 5 May 1781 which distinguished between springs belonging to the State and those located on the property of private citizens, which the latter could exploit after obtaining authorisation from the Royal Society of Medicine and as long as they complied with the legislation in force.

In 1709, letters patent established a monopoly for the transport and sale of natural mineral waters bottled by the people authorised by the general superintendant.

With the Revolution, this system was no longer respected and new regulations were not drafted until the Orders of 23 Vendémiaire year VI and 29 Floréal year VII.

There was no French legislation on the law enforcement and surveillance of natural mineral waters until the early 19th century. The major texts were the Royal Ordinance of 20 December 1820, which created the Royal Academy of Medicine, which had authority over everything related to natural mineral waters; the Royal Ordinance of 18 June 1823; and the Decree of 28 June 1860 concerning the surveillance of springs and spas and the use and management of natural mineral water springs in France. The measures that were taken at this time aimed firstly to monitor water quality and preserve its physical and therapeutic properties and secondly to harmoniously distribute spa establishments in order to manage most efficiently a capital with high economic potential.

With the appearance and rise of boring, the need to protect natural mineral water springs from the risk of diversion and recession became evident and the Act of 14 July 1856 made it possible to create a perimeter of protection around each spring to protect its flow. At the time, it was a quantitative measure which aimed to put an end to the frequent diversion of natural mineral waters, known in Vichy as the 'war of the springs'.

Since natural mineral water was still not considered a mine resource, it was not subject to mining law. It was therefore not possible to impose large easements on third parties to benefit the owner of a natural mineral water spring. To circumvent this problem and protect a resource that benefited many people taking the waters, the aforementioned Act of 1856 added a mandatory declaration of public interest (DIP) to this perimeter of protection.

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An 1856 Decree, amended in 1930, set the terms for declaring a spring and defining its perimeter of protection, but the qualitative protection of springs was not taken into consideration until the Water Act of 3 January 1992.

For the surveillance of springs, the Decree of 28 January 1860 divided up power between the Mining Authority and the Departmental Health Inspector.

As for spa activity, it did not start to truly develop until the Second Empire and then escalated in the second half of the 20th century, when it was no longer a privilege for the rich but became accessible to the masses.

The use of natural mineral water for purposes other than spa treatment appeared in France in the 16th century with the practice of bottling, but the water was reserved for the Dukes of Lorraine. In 1632, Louis XIII issued an edict authorising the transport of mineral water in bottles sealed with wax and in 1709, letters patent established a monopoly for the transport and sale of natural mineral waters bottled by people authorised by the general superintendant.

After several other amendments, the Decree of 28 March 1957 subjected the transport, treatment, mixing and bottling of natural mineral waters to ministerial authorisation.

In the 19th century and early 20th century, the bottled water market expanded with people 'taking the waters', who got into the habit, at the end of their cure, of bringing home some of the mineral water used for their therapy.

In France, the first major bottling companies were founded shortly before World War II, but the market did not truly expand until later, reaching 11 billion litres in 2004 including 4.4 for export[2].

Sixty-seven natural mineral waters (representing 48 operating sites) recognised as such appear on the official list[3]. At the present time (August 2007), only 58 natural mineral waters are actually bottled at 44 production sites.

It was not until Act no. 2004-806 of 9 August 2004 on public health policy, classified under Articles L. 1322-1 to 13 of the Public Health Code, that statutory bases applicable to natural mineral waters were laid down. The Act introduced new provisions concerning recognition and authorisation procedures to be followed by the relevant administrative authority. Any significant modification to a natural mineral water's characteristics and any significant change to a spring's operating conditions had to be the subject of a request to revise the recognition or authorisation to exploit. The implementation terms, defined in Articles R. 1322-1 to 1322-44 of the Public Health Code and in the ensuing implementation Orders, are described in the following section.

II - RECOGNITION OF NATURAL MINERAL WATERS IN THE PUBLIC HEALTH CODE

The Chapter devoted to natural mineral waters is included in Book III of the Code entitled 'Protection of health and the environment' and more specifically in its Title II on 'Water and food safety'.

Chapter 1 is devoted to drinking water and Chapter 2, on natural mineral waters, aims exclusively to guarantee their safe exploitation and provides a definition related to their three regulated uses: packaging, use for therapeutic purposes in spas, and distribution in public drinking fountains. The following Articles pertain to natural mineral waters: L. 1322-1 to L. 1322-13 and R. 1322-1 to R. 1322-44-23.

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[2] **Source: DRIRE/DNEMT data.**
[3] **Source: European list of natural mineral waters recognised by the European Union's Member States published in 2007.**

Furthermore,
- the Environmental Code aims to guarantee the protection of groundwater before it may be defined as a natural mineral water,
- the Consumer Code constitutes the legal basis of provisions related to the labelling of packaged waters and the general obligation of product compliance,
- the Social Security Code addresses contractual relations between spas and health insurance organisations.

The legal basis for the safety of natural mineral waters in the Public Health Code was partially amended in 2003 and the regulations were completely revised in 2007. They now define operators' obligations and set forth administrative and criminal sanctions if operators fail to comply with legal or regulatory obligations or individual orders.

The goals of these new regulations are to:
1. simplify procedures,
2. bring procedures into line with those governing water intended for human consumption,
3. implement European Community packaging regulations, through the following provisions:
   - devolution of administrative decisions to grant individual authorisations to exploit;
   - global request to exploit water for human consumption (Article R. 1322-7 of the Public Health Code) for which the project must be presented in its entirety according to the anticipated use. Proof that the water has the properties of natural mineral water shall be provided by the operator;
   - global authorisation to exploit issued for a project that covers all operating stages (source, treatment, transport, mixing, distribution) for each use (exploitation of the spring, packaging, spa use, distribution in public drinking fountains) valid automatically after a compliance inspection;
   - hygiene of packaging plants and spa facilities with implementation of quality assurance processes and good trade practices. The regulations set performance objectives rather than means objectives;
   - use of disinfection products and processes and of permanent equipment with health compliance certification (harmonisation of procedures with those governing water intended for human consumption);
   - packaging materials for which the compliance obligation and controls undertaken by the Directorate General for Competition, Consumer Affairs and Fraud Control (DGCCRF) have replaced the Minister of Health's prior administrative authorisation;
   - monitoring by operators including ongoing monitoring on their initiative and monitoring at frequencies and according to the content stipulated by the regulations;
   - health controls and management of non-compliances harmonised with the procedures applicable to water intended for human consumption, and operator accountability.

PART TWO:
HYDROGEOLOGICAL CONTEXT,
VULNERABILITY OF THE AQUIFER SYSTEM AND
CATCHMENT

REFERENCE TEXTS
- European Council Directive 80/777/EEC of 15 July 1980 on the approximation of the laws of the Member States relating to the exploitation and marketing of natural mineral waters, amended version. Annex I. - Articles L. 1322-3 to L. 1322-12, R. 1322-2, R. 1322-5-2, R. 1322-16 to R. 1322-27 of the Public Health Code - Order of 5 March 2007 on the preparation of applications to exploit a natural mineral water spring for packaging, use for therapeutic purposes in a spa or distribution in a public drinking fountain.

I - ORIGIN

It is widely known today that all natural mineral waters come from the infiltration of meteoric water that resurfaces after a long and slow underground traverse (Blavoux, 1995). Inflows of juvenile water[4] released via magmatic or metamorphic processes can contribute to the intake of these resources at least in some geological contexts. Elements of deep origin such as boron, lithium or natural radio-elements indicate these inflows. The endogenous origin of carbon dioxide has thereby been demonstrated in numerous cases (Risler, 1999).

Only a fraction of the precipitation that reaches the soil in the form of rain, snow or hail can become groundwater. Plants block and retain a large percentage of precipitation and send it back into the atmosphere through evapotranspiration while another highly variable percentage contributes to runoff. The latter depends not only on the terrain's permeability, slope and humidity when the precipitation falls, but also on the nature of the vegetation cover.

Meteoric water is able to infiltrate below the surface thanks to the micro-permeability of some porous rocks (sand, sandstone, etc.) and the macro-porosity of hard rocks that are usually not permeable but are themselves cracked or fractured. In limestone terrains, dissolution phenomena (karstification) can create channels favourable to infiltration.

The infiltrated water, now underground, gravitates downward until it encounters an obstacle to its vertical penetration (impermeable layer, closing of cracks or fractures) and is then able to accumulate in the terrain's pores and discontinuities (the aquifer) and flow out laterally. When the hydraulic head in the saturated part of the aquifer becomes higher than that found at possible points of emergence, the groundwater will tend to flow out through natural outlets[5], i.e. springs.

The essentially static concept of 'deposit'[6] should therefore be replaced by that of 'aquifer system'[7] (term also used in the Standard NF X 50-911 on spas and the responsible use of natural mineral water), which implies a geological structure crossed by a flow of water that generally becomes mineralised over time (Blavoux, 1998). It is therefore not unusual for water's mineralisation to vary in space (particularly according to the locations of outlets) and time (by season).

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[4] **"Juvenile water": "groundwater of deep (magmatic, volcanic) and non-meteoric internal origin" (Castany G.,Margat J., 1977) or, alternatively: "water that has not been part of the hydrosphere before, derived from the interior of the Earth" (Pfannkuch H.O, 1969).**

[5] **In the hydrogeological sense: see precise meaning in Annex 1, § 1.6.2.**

[6] **see precise meaning in Annex 1, § 1.5.4.**

[7] **see precise meaning in Annex 1, § 1.5.3.**

An aquifer system is part of a regional geological framework on which it depends heavily and, to accurately understand how it works, it is essential to have a detailed, accurate and updated description of the region's geological structure (organisation of layers, folding, fracturing) and the aquifer system's geological and hydrogeological characteristics: lithostratigraphy (nature, thickness and succession of terrains), folds and faults, gouge zones, fracture system or karstic systems, aquifer properties, surface and underground hydrology (Ministry for the Economy, Finance and Industry (MINEFI) - National division of mineral and spring waters (DNEMT), 1995 [a]).

The hydrogeological situations at the origin of natural mineral water emergence are multiple and often extremely complex (see § II). It is sometimes possible to define, in spite of the wide variety of structural and hydrogeological configurations, a typical aquifer system that is divided into an intake area with the infiltration of meteoric water, a generally slow water flow area and a collection area that acts as a drain and enables the rapid upflow of natural mineral water (Lopoukhine, 1994).

The infiltration of water in the decompression zone (down to a depth of around 200 m) of terrains and its deep circulation (down to several thousand metres) in low-permeability terrains (granite) result from the high hydraulic gradient between the intake area, which is often at an altitude, and the discharge area, which is generally in a valley.

The conditions favourable to the emergence of water are mainly structural and there needs to be a high-permeability ascending channel, but they can also be related to a waterflow obstacle or the disappearance of an impermeable screen under which the water was confined.

Furthermore, natural mineral water's low density, due to its temperature, also promotes its upflow to the surface, which may be helped by a 'gas lift' effect when carbon dioxide is present (carbogaseous waters).

When nearing the surface, the mineral system tends to divide up because the terrains are more fractured and generally altered. There may consequently be a mixing zone between inflows of natural mineral waters and groundwater contained in the altered rock or in surface formations (e.g. alluvia) which frequently means that waters of the same facies are present but with different mixing proportions.

II- TYPOLOGY OF AQUIFER SYSTEMS

According to their complexity, the aquifer systems that produce natural mineral waters can be divided into two main categories of unequal frequency:

1. Systems consisting of an aquifer whose geometry can fairly easily be defined. A minority, located in sedimentary basins and sometimes in hard-rock (Plancoët), the aquifers may be relatively superficial (Enghien les Bains, Larivière Arnoncourt, Saint Amand les Eaux, etc.) or very deep (Jonzac, Barbotan, Lectoure, etc.).

   These are single-layer (Chambon) or multi-layer (Vittel, Contrexéville, Chaponnay, Plancoët) aquifers with semi-confined or confined groundwater[8]. The natural emergence[9] of these waters, which sometimes entails only seepages or discrete transfers to other aquifers, occurs when the impermeable screen confining the groundwater disappears or when there are fractures.

   For these systems whose waters are comparable to the groundwater used for the drinking water supply, it is generally possible to define the intake area[10] and the resource's potential by implementing traditional hydrogeological tools (lithological, structural, geophysical studies, sampling, pumping, water balances and tracing).

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[8] see meaning and discussion in Annex 1, § 1.3.3
[9] see meaning and discussion in Annex 1, § 1.6.
[10] see meaning and discussion in Annex 1, § 1.6.1

2. Systems linked to tectonically active zones (Massif Central, Vosges, Alps and Pyrenees), which represent the vast majority and are located south of a Bordeaux-Sedan line (Pomerol and Ricour, 1992). Their waters usually come from complex aquifer systems that may combine terrains of different facies (metamorphic or magmatic terrains and sedimentary terrains) with folded and faulted structures.

For this type of spring, the geometry of the geological structure crossed by the water is rarely completely known. In some cases, the altitude, and consequently the location, of the spring's[11] intake area can be obtained, given the water's transit time, by using the isotopes of oxygen ($^{16}O/^{18}O$) and/or water dating with isotopes with long half-lives (^{3}H, ^{14}C), which can remove uncertainties about the intake area's location.

As for the depth that the water reaches in its underground circuit, it can be determined with the use of chemical geothermometers (Michard, 1979) such as SiO_2, Na/K and Na/K/Ca, which give a maximum temperature value reached by the water according to the local geothermal gradient.

III – VULNERABILITY OF AQUIFER SYSTEMS

The risk of an aquifer system's water becoming contaminated depends on the conjunction of a hazard, related to a potential contamination source likely to alter the resource's quality, and a vulnerability[12] that depends not only on the aquifer system itself (intrinsic vulnerability) but also on the behaviour of contaminating products and agents (specific vulnerability).

Given that the intake area is a system's initial vulnerable sector, it is important to attempt to define it as precisely as possible:
- with fissural aquifer systems, this area may correspond to a sector where the terrain's fractures are particularly numerous and open. Its specific location and, even more so, its delineation are often difficult to establish, but a hilly location, in sectors with few activities, is common and represents a sign of natural protection.
- when the aquifers are located in sedimentary basins or hard-rock, the intake area is generally easier to define, but is often highly exposed to urban and/or agricultural and industrial pollution.

The percolation area, contained between the intake area and the discharge area, which is rarely clearly delineated, offers the best protection because the water circulates slowly under levels ensuring its confinement. The natural mineral water, in contact with a component from karstic limestone formations at certain periods of the year, can be very mediocre in quality.

In the discharge area where the water rises to the surface, protection decreases. As the fractures are generally open and the rock is altered, this is the aquifer system's most vulnerable area, especially since its exits and catchment areas are frequently located in urban sectors. Agricultural practices can also cause the water's quality to deteriorate.

Moreover, in this same discharge area, the difference in head between the deep water and the groundwater is often small and if this difference is even slightly modified, it can heavily impact the quality of the natural mineral water. Pumping can stop spontaneous artesian flow and cause exchanges to reverse, as the groundwater flows downward toward the deep water.

In addition, regardless of the aquifer system, natural mineral waters are renewable and sustainable resources if the balance between water inflows (meteoric inflows measured annually) and the spring's operating flow is maintained.

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[11] **See Annex 1, § 1.6.2.**

[12] **Risks, hazards and vulnerabilities: for explanations, see Annex 1, § 1.7**

IV - RESEARCH NEEDED TO UNDERSTAND THE ORIGIN AND VULNERABILITY OF NATURAL MINERAL WATERS FOR A HEALTH RISK ASSESSMENT

Hydrogeological information about the origin and vulnerability of natural mineral waters is necessary in order to conduct a health risk assessment.

Like all groundwaters, natural mineral waters come from an aquifer system, which is a spatial and dynamic concept. They are waters that flow through a unique underground environment, under specific hydrological and hydrochemical conditions.

Since the regulations in force acknowledge the possibility of exploiting natural mineral water at "several natural or bore exits", the <u>aquifer system's unity</u> should be verified. The composition of the water itself (physico-chemical and isotopic characteristics) provides information about this unity. Nevertheless, natural or bore exits, located in different areas of the same aquifer system, can produce waters with different characteristics, insofar as they express the specificity of a particular sub-system (a system with successive reservoirs, for example).

Applications for authorisation to exploit a natural mineral water spring require the submission of a dossier (Order of 5 March 2007) that includes (Annex II-A)[13] **essential geological, hydrogeological and physico-chemical information** about the deposit (Annex II-A-2.1)[13], at catchment or exit (Annex II-A-2.2), and at the spring (Annex II-A-2.3)[13]. The goal is to have:

- a **detailed summary of the geological context** (Annex II-A-2.1.1): a detailed, accurate and updated description of the aquifer system (the geological and technical section of the catchment(s) - requested in Annex II-A-2.3.2 - generally enables an initial approach to the tapped aquifer) and its regional geological setting:
  - lithostratigraphy (nature, thickness and original succession of terrains, lateral facies variations), aquifer properties (micro- and/or macro-permeability),
  - state of fissuration, alteration or karstification (karst topography in particular) that may or may not locally modify the aquifer's characteristics,
  - the region's geological structure (overall charts and sections), highlighting the organisation of layers (folds, overlaps, inversion of sequences) and fracturing (major faults, gouge zones, secondary fracturing) as well as post-tectonic overlap (sedimentary or volcanic),
  - summary of the region's sedimentary, tectonic, and possibly magmatic and volcanic history,
  - geological overview of the aquifer system, placed in its regional context: structure (detailed charts and sections), nature (lithology and minerals susceptible to leaching) and geometry of the aquifer(s) (wall and roof), role of faults (screen or drainage), possible relationships between aquifers (stratigraphic or tectonic contact, leakage) and the surface (determination of the intake area, recharge possibilities from groundwater or a river, preferential drains, determination of the natural discharge area(s));

- a satisfactory understanding of **the hydromineral system from a hydrogeological viewpoint** (Annex II-A-2.1.2)[13], which requires the compilation or further assessment of the following information:
  - the sector's hydrological context: regimen of streams, proven or suspected losses, physico-chemical characteristics of this surface water,
  - existence of aquifers and groundwater, apparently independent of the presupposed aquifer system, piezometric levels in the sector with their fluctuations, physico-chemical and isotopic characteristics of this groundwater,
  - compilation of all one-off data or time series of piezometric (or pressure) levels and flow related to the aquifer system's groundwater,
  - analysis of hydrographs at the outlet (flow duration curves, recession curves, etc.),
  - compilation of existing data (and more importantly of time series) related to the physico-chemical and isotopic characteristics of natural mineral water that has been extracted or borehole surveyed,
  - testing for correspondence between piezometric (or pressure) fluctuations, flow variations and modifications in physico-chemical and isotopic characteristics:

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[13] **Annex of the order of 5 march 2007**

- for natural mineral water at the outlet (and where applicable, at any observation point upstream),
- with climate data (precipitation, air temperature and barometric pressure),
- with the corresponding parameters of other nearby surface and groundwater,
  ▪ summary of the results of all surveys undertaken on the entire aquifer system and at its outlet (natural or drilled): mechanical drilling, geophysical campaigns, natural and artificial tracing, dating, geothermometry, borehole logging (particularly with a micro-flow meter), pumping tests,
  ▪ numerical modelling results,
  ▪ summary of the exploitation regimen and its potential effects on piezometric (or pressure) levels and the extracted water's physico-chemical quality,
  ▪ quantitative and qualitative diagram of the aquifer system from the recharge (or intake) area to the outlets (tapped or not);

● the establishment of a **relationship between the nature of the terrains and the natural mineral water's constituents** (Annex II-A-2.1.3)[14]. This will depend on the solid knowledge that will be acquired of the aquifer system's nature, geometry and functioning: the essential characteristics of the water's mineral content should be compared with the mineralogical nature of the aquifer reservoirs and/or conduits. The relationship may be obvious when soluble minerals, such as gypsum, come into contact with the water. The flow of groundwater through terrains with different mineralogical properties, particularly in the case of successive reservoirs, can explain a degree of spatial variability in natural mineral water from the same 'deposit' collected from geographically scattered drilling, but also sometimes temporal variability, related to a variable distribution of each reservoir's contributions, between high and low water;

● **an assessment of the resource's intrinsic vulnerability** (Annex II-A-2.1.4), i.e. the ease with which the water flows from its infiltration in the soil and sub-soil (the aquifer's intake or recharge area) to the natural or bore exit. This is a property of the geological and hydrogeological environment that does not take into account the phenomena of time lag and attenuation. It essentially depends on the rainfall regime and factors specific to the geological environment, i.e.:
  ▪ modes of infiltration: diffuse, organised around a point (e.g. local run-off toward a fault) or concentrated (occasional loss),
  ▪ the presence or absence of a protective cover (with low or mediocre permeability) whose thickness variations need to be specified and mapped,
  ▪ the duration of the underground water course, which may be estimated through dating[15] with radioactive isotopes (tritium, carbon 14, etc.) in the event of a slow and deep flow. In some cases, depth may be estimated with geothermometry measurements[16],
  ▪ drainage organisation, which may be approached, in the very specific cases of fissural or karstic rapid flow systems, with the residence time distribution curve obtained from trial tracing, which can then give the total transit time.

The two most vulnerable areas of a hydromineral aquifer system are:

▪ the intake area, which must be delineated as accurately as possible, either using water balances when the aquifer system is relatively simple, or oxygen isotope measurements that can estimate the altitude of infiltrated meteoric water, or dating, which can also resolve uncertainties about the intake area's location (see § II.2); the mapping of a protective cover (nature and thickness), when one exists, is essential, as is a breakdown of the geological (alterations, fissuration, lapies, sinkholes, losing streams), topographical (slopes) and vegetal (forest cover, grassland or pasture, humid zones, bare soil, etc.) natural environment;

▪ the discharge area, where the fractures are generally more open and the rock is altered, which is often the most vulnerable area as it is frequently located in an urbanised sector, sometimes close to industries, or in an agricultural environment. An alluvial sheet or a stream may cause their more or less polluted waters to mix with the deep mineral water, insofar as the latter's

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[14] **Annex of the order of 5 march 2007**
[15] **see Annex 1, § II-11**
[16] **see Annex 1, § II-12**

hydraulic potential would become smaller than that of the surface water (particularly in the event of pumping that stops the natural artesian flow);

● an **assessment of hazards** likely to alter the water's quality: **inventory of pollution sources** (Annex II-A-2.1.5), and particularly of risks related to land use: at-risk activities, classified facilities for the protection of the environment, farms, sanitation and effluent discharge, places used to store pollutants or hazardous products, including waste, etc. This study shall be undertaken both in the intake area and in the discharge area, in the case of aquifers in sedimentary basins or in hard-rock areas, in low- or medium-altitude regions. However, in fissural aquifers located in tectonically active zones, this inventory of pollution sources will mainly focus on the discharge area, as the intake area is often located at an altitude with few human activities, although it nevertheless remains at risk of microbiological contamination, particularly from animal faeces.

● a **proposal of protection** (Annex II-A-2.1.6), **monitoring and alert measures** to be implemented (Annex II-A-2.1.7). Technical and environmental protective measures must be fully tailored to the aquifer system's recognised characteristics (geometry, geology and functioning) and to its intrinsic vulnerability (primarily in its discharge and intake areas). But since the exploitation of natural mineral waters generally falls under the private domain, it remains more difficult to protect the resource through regulations.

From a technical viewpoint, improving the catchworks themselves (see § V) is certainly the first measure that should be implemented.
Monitoring and alert measures should also be tailored to the aquifer system's specific characteristics, and particularly to transit times and the characteristics of hazards and risks recorded in the discharge and intake areas.

All of the **geological and hydrogeological information** requested for authorisations to exploit a natural mineral water spring, and primarily the information **related to the deposit** (Annex II-A-2.1)[17] described above (but explained in greater detail in Annex 1 of this report), requires at least an exhaustive compilation of existing data followed by a meticulous summary, and sometimes, if there have been no serious investigations into the origin of the extracted water, an in-depth preliminary study of the 'deposit' and the 'resource', i.e. of the aquifer system (geometry, functioning, vulnerability) and its exploitation possibilities; this type of study should only be entrusted to a sufficiently specialised organisation that is competent in the field of quantitative and qualitative hydrogeology.

To conclude, the geological and hydrogeological information in the guidelines aims to ensure knowledge of the resource, its functioning and its protection to control any health risks related to the infiltration of contaminated surface water or poor exploitation conditions.

V- CATCHMENT OF NATURAL MINERAL WATER

V.1 - CATCHMENT

V.1.1 - Catchment of natural discharge

Natural mineral water spring discharge is related to:
  - either the existence of faults or rock joints that affect the terrain,
  - or the disappearance of impermeable screens. These enable the water flowing underground to reach the soil's surface.

Natural springs may be:
  - point to point: water reaches the soil's surface under pressure through distinct cracks,
  - diffuse: water intakes are scattered along the overlying surface.

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[17] **Annex of the order of 5 march 2007**

In all situations, the catchment of natural discharge requires clearing, if possible, of the spring's discharge point[18] since deep water frequently mixes with surface water, and even run-off water.

Inflowing water is captured through the construction of structures that collect water. These are usually wells but, in the past and in hilly areas, horizontal and oblique galleries have been used.

The well should be dug, if possible, until it hits fresh rock and, to eliminate the risk of parasite water infiltrating the upper steening, the annulus[19] should be sealed with a clayish material and/or with cement.

V.1.2 - Drilling

In order to prevent deep water and surface water from mixing, catchment at natural springs is increasingly being abandoned for drilling.

While drilling techniques differ according to the type of terrain and the degree of fracturing (MINEFI-DNEMT, 1995 [b]), borehole equipment must have a certain number of shared characteristics to guarantee the quality of the extracted water in terms of its safety.

To that end:
- the material used in the drilling rig must be suited to water's characteristics in order to prevent corrosion and the premature ageing of the structure.
- the annular spaces (spaces between the hole and the upper casing when they exist and between the upper casing and the casing) must be cemented. The cement must be at least 5 cm thick and be applied, if possible, through pressurised injection, from the bottom, using a rod and at a sufficient height to prevent water from other aquifers from penetrating.
- for sulphate, chloride, carbogaseous and hot water, cementation must be performed with cements that are authorised to be in contact with natural mineral water and whose additives must not be harmful to the borehole environment or to the health of consumers of the exploited natural mineral water.
- the head of the structure must be designed to shelter it from risks of flooding, penetration of run-off water and the infiltration of extraneous water along the pump's electrical supply cables.

Even more than for boreholes used to supply drinking water, strict hygiene rules must be followed on the worksite because there is no subsequent disinfection stage (MINEFI-DNEMT, 1995 [c]). Drilling equipment must not have leakage on the water and supply pipes, greasing must be performed only when necessary and, before they are put in the borehole, casings, intake screens, drill rods and gravel must not be placed directly on the ground.

V.1.3 - Catchment abandonment

When the exploitation of a catchwork is abandoned, some technical requirements must be satisfied to prevent the deposit's water from being contaminated (e.g. filling with bentonite slurry or cement slurry) (MINEFI-DNEMT, 1997).

To that end, the solid and slotted parts of the casing or the bare hole (for an unequipped structure or after pulling of tubes) must be filled with, from bottom to top:
- an inert material (coarse silica sand, silica gravel), which is clean and has been disinfected beforehand, to around ten metres below the soil surface,
- a well-compacted clay or Sobranite plug for around five metres.
- cement slurry in the remaining part (to the soil's surface).

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[18] **See Annex 1, point 1.6.2**
[19] **Space between the casing and the walls of the borehole (Detay, 1993)**

V.2 - EXPLOITATION OF CATCHWORKS

Catchworks can be exploited via either artesian flow or pumping. The two methods can be used alternately.

V.2.1 - Artesian flow

When the structure is spouting and the emerging deep water has a significantly greater head than the groundwater, mixing with cold surface water is not problematic thanks to this significant difference in hydraulic head: it contributes to the stability of water quality.

The artesian flow of a mineral spring is never exactly constant and its natural variations can have several origins:
- local weather influence (atmospheric pressure in particular),
- variations in pressure on the hydrothermal reservoir due to variations in the groundwater level particularly in alluvial zones where numerous outlets are located,
- Earth tides,
- deposits of scale-forming substances on the discharge points or in the transport pipes,
- recharge of groundwater,
- etc.

V.2.2 - Pumping

When pumping is used, the depression that is created can promote the intake of water having different characteristics: cold surface water or high-mineral deep water.

Respecting the exploitation rate determined for the structure further to pumping tests contributes to its sustainability and the long-term stability of the extracted water's composition.

V.3 – CATCHMENT EQUIPMENT

So that natural mineral waters may be exploited under good conditions, catchworks must be equipped and the materials and equipment used to that end must be approved for food contact and not alter the organoleptic properties of natural mineral water.

Most of the materials used for the catchment of drinking water (tubes, pumps, cements, etc.) are acceptable but it is however necessary to check that they are suited not only to natural mineral water's characteristics (risk of corrosion from metallic materials according to the water's mineral content, etc.), but also to the boring fluids and products used for cleaning and disinfecting during exploitation and after boring, as there must be no residual traces.

To respect the set exploitation flow and to limit drawdown, the structure should be equipped with low and high electrodes and a control system including a flow meter, a temperature probe and possibly a conductivity meter.

Moreover, the compatibility of the various materials that make up the casing and intake screen should be checked to avoid electro-chemical coupling (battery effect).

All items introduced into the borehole (string, pump, gravel, etc.) must be cleaned and disinfected beforehand according to a pre-defined procedure.

Site personnel must be trained to apply these specific hygiene measures.

V.4 - CATCHMENT PROTECTION: REGULATORY ASPECTS

V.4.1 – Sanitary perimeter of emergence

Under Article R. 1322-16 of the Public Health Code, *"the order giving authorisation to exploit a natural mineral water spring determines a sanitary perimeter of emergence for which the owner shall enjoy, for each outlet, full ownership or acquire easements guaranteeing protection against occasional or accidental pollution".*

This sanitary perimeter of emergence, which much be closed off, is essential to block out intrusion and prevent pollutants from being spilled immediately next to the catchment. Its purpose is to guarantee the <u>physical protection</u> of the catchwork and the <u>health protection</u> of its immediate surroundings.

The MINEFI-DNEMT technical note no. 6 of 1996 entitled "Périmètre sanitaire d'émergence" (Sanitary perimeter of emergence) gives examples of prefectural orders.

V.4.2 – Perimeter of protection

Article R. 1322-17 of the Public Health Code stipulates that the owner of a spring can apply to the prefect to obtain a declaration of public interest (DIP) for a natural mineral water spring and assign it a perimeter of protection. In this case, the prefect obtains the opinion of the hydrogeologist certified in public health, specifically appointed to that end, particularly regarding the exploitation flow, the perimeter's rationale and determination, and protective measures to be implemented.

This application, once deemed proper and complete, is subject to a public hearing that takes place under the conditions set forth in Articles R. 11.4 to R.11.14 of the Code of Compulsory Purchase in the Public Interest. After this hearing and consultation of the departmental council for the environment and health and technological risks, a decision on the request is rendered by a Decree of the Council of State, issued upon recommendation by the Minister of Health.
Inside this perimeter of protection, some activities, deposits or facilities may be prohibited or regulated if they present a direct or indirect risk to the quality of water.

V.4.3 – Work in the perimeter of protection

Article R. 1322-23 of the Public Health Code stipulates that all drilling or underground work in the perimeter of protection is subject to prior authorisation and that requests shall be submitted for the opinion of the hydrogeologist certified in public health appointed to that end, then to the departmental council for the environment and health and technological risks.

Furthermore, Article R. 1322-25 stipulates that the owner of a natural mineral water spring can request the prefect to prohibit work in the perimeter of protection. In this case, the prefect has a hydrogeologist certified in public health assess, at the requesting party's expense, the risk that the work may alter the spring or reduce its flow.

Upon receipt from the owner of a natural mineral water spring, under Article L. 1322-5 of the Public Health Code, of a request to prohibit work in the perimeter of protection, the prefect has a hydrogeologist certified in public health assess, at the requesting party's expense, the risk that the work may alter the spring or reduce its flow (Article R. 1322-25 of the Public Health Code).

Concerning excavations, trenches for the extraction of materials or any other object, foundations of houses, cellars or other open work, the Decree mentioned in Article L. 1322-13 of the Public Health Code that establishes the perimeter of protection can require that owners send, at least one month in advance, a declaration to the State representative in the département, who issues a receipt.

Other activities, deposits or facilities that pose a direct or indirect risk to the quality of water may also be subject to authorisation or declaration by the Decree mentioned in Article L. 1322-13 of the Public Health Code establishing the perimeter of protection.

V.4.4 – Work outside of the perimeter of protection

Article 1332-27 states that, as above, the owner of a natural mineral water spring with a declaration of public interest can request that the prefect *"temporarily order, under Article L. 1322-6, the suspension of drilling or underground work undertaken outside the perimeter of protection and reported as being likely to alter the spring or reduce its flow"*.

In conclusion, the creation of a sanitary perimeter of emergence aims to protect the catchwork from pollutants that may intrude or be spilled in its immediate environment, to prevent the water from being contaminated at the exit point where it is the most vulnerable.

The declaration of public interest (DIP) for a natural mineral water spring, with assignment of a perimeter of protection, is highly recommended because it reinforces the protection of the catchwork(s).

PART THREE:
PHYSICO-CHEMICAL CHARACTERISTICS, STABILITY AND PURITY OF NATURAL MINERAL WATERS

REFERENCE TEXTS
- European Council Directive 80/777/EEC of 15 July 1980 on the approximation of the laws of the Member States relating to the exploitation and marketing of natural mineral waters, amended version: Article 7 and Annex III - Articles L. 1322-1, R. 1322-2, R. 1322-44-9 and following of the Public Health Code - Order of 14 March 2007 on quality criteria for packaged water, treatment and special labelling requirements for packaged natural mineral and spring waters and natural mineral water distributed in public drinking fountains

I - CHARACTERISTICS

I.1 - ESSENTIAL CHARACTERISTICS

The essential characteristics of a natural mineral water are represented by:

- global physico-chemical parameters: temperature, pH, conductivity, dry residue and oxidation-reduction potential,
- major essential anions (hydrogen carbonates, sulphates, chlorides, fluorides) and cations (calcium, magnesium, sodium, potassium),
- and, in some cases:
  - a carbon dioxide content that can vary from a few hundred milligrams per litre to a few grams per litre for carbogaseous waters,
  - a concentration of specific minor elements, naturally found in water, which indicate the facies of some waters: sulphides, arsenic, lithium, etc.

These essential characteristics are acquired when water comes into contact with the geological formations it flows through and depend on pressure, temperature, the water's residence time in the aquifer and the oxidation-reduction potential.

I.2 - CLASSIFICATION

Natural mineral waters can be classified according to various criteria, namely:

I.2.1 - Mineral content

A water's mineral content refers to the total amount of dissolved salts expressed in milligrams per litre of water. The dry residue at 180°C[20] is a good indicator of the concentration of mineral salts. Mineral content can range from a few milligrams to a few grams per litre.
It should be constant over time but can range from a few milligrams per litre to several tens or, exceptionally, around one hundred milligrams per litre. On the basis of this criterion, five categories can be defined:

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[20] **name for the analysis: dry residue at 180°C. Regulatory name for labelling: fixed residue**

- very low-mineral waters	:	mineral content less than 50 mg/L,
- low-mineral waters	:	mineral content between 50 and 500 mg/L,
- moderate-mineral waters	:	mineral content between 500 and 1,000 mg/L,
- mineral waters	:	mineral content between 1,000 and 1,500 mg/L,
- high-mineral waters	:	mineral content greater than 1,500 mg/L.

I.2.2 - The physico-chemical composition of water

To characterise natural mineral waters and distinguish them from one other, it is necessary to take into account not only their physico-chemical profiles but also their by-products which may be, for example, gases.

Classification therefore takes into consideration some original parameters likely to play a specific role or have a specific effect (Popoff, Honegger, 1990), such as:
- temperature,
- pH,
- ions: Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, HS^-, Fe^{2+}, Mn^{2+}, etc.,
- soluble silica H_4SiO_4, expressed as SiO_2,
- dissolved gases: H_2S, CO_2, O_2,
- deposits or solid phases in suspension.

According to the dominant presence of one or more of these parameters, the following specific categories can be defined (Popoff, 1992):

I.2.2.1 – Sulphide waters

These are waters rich in sulphides that are used solely for therapeutic purposes in spas. They are therefore not packaged.

Sulphur-based compounds often give these waters a highly negative oxidation-reduction potential that promotes oxidation-reduction reactions, making these waters very unstable.

Sulphide waters are divided into two categories:

- **'Pyrenean' sodium sulphide waters** (Ohayon-Courtes, 1992)
  These are sulphide-rich waters whose dominant cation is sodium. They have a low mineral content (less than 400 mg/L), are hot to very hot ($30°C \leq T \leq 65°C$), have an alkaline pH ($8 \leq pH \leq 10$) and contain often large quantities of soluble silica and fluoride.

- **Calcium sulphide waters** (Tisserand, 1998)
  These are sulphide-rich waters whose dominant cation is calcium. They have a wide variety of temperatures and mineral concentrations and are unique in that their pH is between 7 and 8, which promotes the release of hydrogen sulphide (H_2S).

I.2.2.2 – Sulphate waters

They mainly contain SO_4^{2-} sulphate ions combined with calcium and magnesium ions. Their mineralisation results from the leaching of gypsum or anhydrite, which can be found in the evaporitic formations with which they were in contact.

According to the nature and relative abundance of their cations, these waters are known as ***calcium sulphate*** waters when their calcium content is higher than their sodium content, ***sodium sulphate*** waters when their sodium content is dominant and ***mixed sulphate*** waters when their mineralisation results from a simultaneous intake of sulphates, sodium and calcium.

In general, magnesium and strontium ions are also found, with the latter reaching concentrations of 10 to 15 mg/L.

I.2.2.3 – Sodium chloride waters

In these waters that are not packaged, the dominant ions are chloride and sodium ions.
Sodium chloride natural mineral waters are divided into two categories:

- **cold high-sodium waters**

  They result from the dissolution of common salt (halite) and have mineral concentrations that can reach the saturation threshold (300 g/L). These waters are highly corrosive when in contact with metallic materials.

- **hot low-sodium waters**

  Their total mineral content is only a few grams per litre and they are highly corrosive when in contact with metallic materials.
  These waters, whose dominant ion is sodium, always have an acid pH. In some cases, the sodium ion can be combined with the calcium ion but in a smaller quantity.

I.2.2.4 – Low-mineral waters

The majority of packaged waters fall under this category. The dry residue of these waters is lower than 500 mg/L and they do not contain sufficiently high quantities of elements to rank them in one of the previous groups. They usually have a low or very low mineral content (tens of milligrams of dry residue per litre).

This category includes so-called '**trace mineral**' waters that contain trace amounts (around one microgram per litre) of elements such as copper, arsenic, selenium, zinc, lithium, boron, uranium, radium, beryllium or vanadium.
Most of the time, the physico-chemical composition of these waters is not distinctive and therefore the very rationale behind the name 'trace mineral' may be called into question.

I.2.2.5 – Ferruginous waters

They contain the soluble form of iron, Fe^{2+}, at concentrations ranging from 0.5 to 20 mg/L. This element is mainly found in low-oxygen groundwater, often in combination with a small amount of soluble manganese in the form Mn^{2+}. These elements can directly precipitate in the form of carbonates. Under the effect of oxygen from the water's aeration during transport or storage, the ferrous iron can convert into ferric iron and precipitate in the form of ferric hydroxide, which can catalyse the oxidation of manganese in the form of manganese dioxide.

It is not a separate category strictly speaking because soluble iron is never the dominant element and can be found in waters in other categories.

In anticipation of their bottling, these waters must be treated to remove the iron (unstable element).

I.2.2.6 – Sparkling "bicarbonate" waters

When mineral waters have particularly high concentrations of hydrogen carbonate ions (more than 600 mg of HCO_3/L) and they contain excess free carbon dioxide (more than 250 mg/L), they are called 'sparkling bicarbonate waters'. These waters may be sodium, calcium or mixed 'bicarbonate' waters. Sodium bicarbonate waters often contain non-negligible quantities of fluoride, silica and arsenic.

I.3 LABELLING REQUIREMENTS REGARDING WATER'S COMPOSITION ESTABLISHED BY THE PUBLIC HEALTH CODE

Article R. 1322-44-12 of the Public Health Code and the Order of 14 March 2007 on quality criteria for packaged water, treatment and special labelling requirements for packaged natural mineral waters and spring waters and natural mineral water distributed in public drinking fountains (Annex III of the aforementioned Order) distinguish between, according to their physico-chemical composition, the following thirteen categories of natural mineral waters:

- 'very low-mineral' waters whose mineral salt content (expressed in fixed residue at 180°C) is not greater than 50 mg/L,
- 'trace-mineral' or 'low-mineral' waters whose mineral salt content (expressed in fixed residue at 180°C) is not greater than 500 mg/L,
- 'rich in mineral salt' waters whose mineral salt content (expressed in fixed residue at 180°C) is greater than 1,500 mg/L.
- 'bicarbonate' waters whose bicarbonate content is greater than 600 mg/L (in HCO_3^-).
- 'sulphate' waters whose sulphate content is greater than 200 mg/L (in SO_4^{2-}).
- 'chloride' waters whose chloride content is greater than 200 mg/L (in Cl^-).
- 'calcium' waters whose calcium content is greater than 150 mg/L (in Ca^{2+}).
- 'magnesium' waters whose magnesium content is greater than 50 mg/L (in Mg^{2+}).
- 'fluoride' waters whose fluoride content is greater than 1 mg/L (in F^-).
- 'ferruginous'[21] waters whose ferrous-iron content is greater than 1 mg/L (in Fe^{2+}).
- 'acidulous' waters whose free carbon dioxide content is greater than 250 mg/L (in CO_2).
- 'sodium' waters whose sodium content is greater than 200 mg/L (in Na^+).
- 'low-sodium' waters whose sodium content is less than 20 mg/L (in Na^+).

II - RADIOACTIVITY

II.1 - RADIOACTIVITY AND WATER[22]

As natural mineral waters come from under the ground, it is not rare for them to be naturally radioactive.

Concentrations of radioactive elements vary, particularly according to the geological nature of the terrains that the water flows through, the time the water is in contact with these terrains, temperature and the radioactive element's solubility. This is primarily seen in carbogaseous and chloride waters.

The most frequent radionuclides are as follows:

- potassium-40: the potassium ions contained in waters have concentrations ranging from 1 to 200 mg/L. There is 1 atom of potassium-40 per 10,000 atoms of potassium-39 [proportions: ^{39}K (93.26%), ^{40}K (0.01167%) and ^{41}K (6.73%)],
- natural uranium whose concentration is generally low (< 2 µg/L) but can sometimes exceed 10 µg/L at the source [proportions: ^{238}U: 99.28%; ^{235}U: 0.71%; ^{234}U: 0.0054%)].
- radium 226 whose concentrations expressed in Bq/L remain very low.
- radon-222: often abundant, it escapes from water when placed in the open air, which means there is a risk it will accumulate in water storage reservoirs or in catchment buildings (expressed in Bq/L).
- thorium-230 and thorium-232 expressed in Bq/L,
- tritium, whose concentration in water, expressed in Bq/L, has increased after thermonuclear tests in the atmosphere, and whose assaying is used to assess water's age because it is an indicator of its transit time. It is a β emitter whose concentrations are expressed in tritium units[23] (TUs). In 'old'

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[21] **Ferruginous waters are waters that have more than 1 mg ferrous iron/L at the time of extraction. They cannot be packaged as is, and after iron removal treatment are no longer ferruginous.**

[22] **Fundamental notions related to radioactivity and particularly the definition of radiological indicators for water are presented in the Note by the Nuclear Safety Authority (ANS) attached to Circular no. DGS/EA4/2007/232 of 13 June 2007.**

[23] **1 tritium unit corresponds to 1 tritium atom per 10^{18} hydrogen atoms.**

natural mineral waters, the tritium concentration is 1 to 2 TUs whereas it is higher in 'young' natural mineral waters (after 1950),
- <u>carbon-14</u>, which is also a β emitter (expressed in Bq/L).

II.2 - REGULATORY TEXTS

The European regulations require the establishment of radio-actinological properties[24] at source but do not set any regulatory quality limit for radioactivity in natural mineral waters.

On 20 December 2001, AFSSA issued a favourable Opinion of the radio-actinology analysis strategy established in reference to the recommendations published by the World Health Organization (WHO) and based on the measurement of global alpha and beta activities (Figure 1).
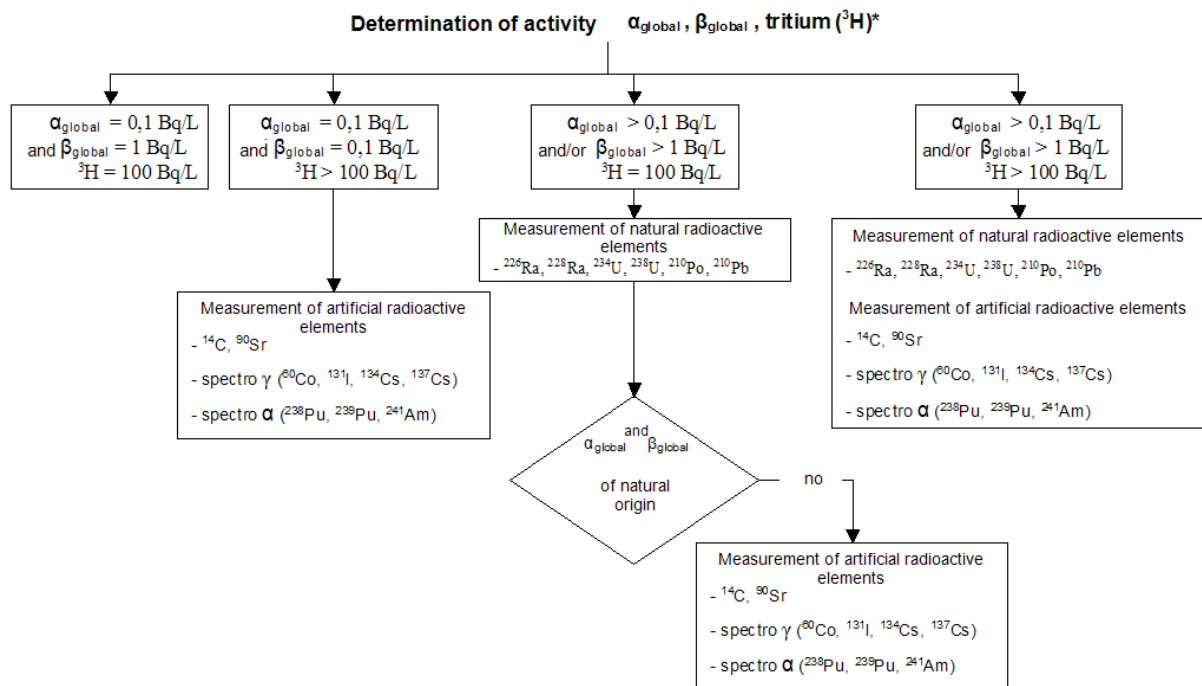
Figure 1: Procedure for the determination of water's radioactivity

On 2 December 2003, AFSSA recommended that natural mineral water used to feed infants should comply with the criteria set forth in the European drinking water directive 98/83, i.e.:

- global alpha (α) activity ≤ 0.1 Bq/L
- global beta (β) activity ≤ 1 Bq/L
- total indicative dose (TID) ≤ 0,1 mSv/year
- tritium content ≤ 100 Bq/L,

Since that time, these criteria have been revised by regulations specifically related to natural mineral waters such as:
- the Order of 5 March 2007, which requires the determination of global α and β activity, and the concentration of tritium and other radionuclides, to calculate the Total Indicative Dose (TID),
- **the Order of 14 March 2007, whose Annex IV sets quality and labelling requirements for infant foods.**

III - STABILITY

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[24] **analytical testing for radioactivity**

Stability is monitored to highlight changes in natural mineral water's characteristics which could lower its quality and have health consequences (mixing with waters of other origins, for example). Variations in stability indicate the resource's degradation and should be considered as health alert signals.

III.1 - ASSESSMENT OF COMPOSITION STABILITY

According to Article R. 1322-2 of the Public Health Code, for natural mineral water, "*within the limits of known natural fluctuation, its composition, temperature and other essential characteristics must remain stable; in particular, they must not be affected by possible variations in the rate of flow*".

The notion of the stability of a water's physico-chemical composition is an important criterion when defining a natural mineral water and it is therefore useful and necessary to define a methodology to quantify this notion of stability. The following questions are relevant:

- Is it possible to define objective criteria to intrinsically assess the stability of a natural mineral water's composition?

- What is the relationship between the variability of a water's composition in terms of seasonal or sudden fluctuation and a water's stability?

- What is the relationship between a water's stability (short- and medium-term) and its long-term drift?

- What is the degree of uncertainty when analytically measuring fluctuations in water's composition?

III.2- ORIGIN OF VARIATIONS IN WATER QUALITY

The physico-chemical composition of all extracted groundwater, regardless of the exploitation method used (artesian flow or pumping), fluctuates more or less significantly. These fluctuations may have a geological origin or be related to the exploitation regimen. Composition variations do not directly impact the safety of natural mineral waters but indicate the occurrence of an event that is likely to have health consequences.

III.2.1 - A geological origin

As was explained above (see Part 2, § I), natural mineral waters can have different mineral contents related to the location of natural or bore exits in relation to the water's natural path of flow in an often complex aquifer system, which may have a series of different reservoirs that transfer their own physico-chemical characteristics to the water. Moreover, recharge conditions, which are subject to mostly seasonal weather variations, can cause these reservoirs' relative contributions to vary, which can then lead to temporary modifications in the resulting mineralisation at the source.

In the discharge area, waters can mix with groundwater or water from infiltrating atmospheric precipitation. In this case, the ratio of the hydraulic head of deep intakes to that of the surface water determines the mixing conditions that will vary over time, increasing the risk of pollutant contamination.

III.2.2 – An origin related to the exploitation regimen

The catchment method used can also influence the extracted water's mineral content.

When artesian flow is used alone, water variations are completely natural. However, pumping can cause mineral fluctuations because according to the dynamic pumping level reached in the structure, the various aquifer intakes do not contribute equally to the flow, which leads to variations in the water's composition that are particularly sensitive for structures located in unproductive aquifers, for which drawdown during exploitation can be significant.

On this topic, it should be noted that excess sampling in terms of the aquifer's potential can cause an inflow of water from remote sectors, and possibly from surface resources, which increases the instability of the extracted water's mineralisation.

Furthermore, it is important to point out that the exploitation of a resource through pumping reduces the water's residence time in the aquifer reservoir and causes a turnover that will almost inevitably cause variations in mineral content.

III.3 - ANALYTICAL UNCERTAINTIES

Parameter variations observed at the source are due to:

- firstly, the natural variability of the water composition and the exploitation regimen;

- secondly, uncertainty related to sampling and analytical conditions.

The concept of a natural mineral water's stability cannot be addressed without first having characterised the analytical uncertainty surrounding each parameter's concentration in the water.

This analytical uncertainty corresponds to the confidence interval for the statistical measurement, under the assumption that the parameter is normally distributed. It characterises the dispersion of values that could reasonably be attributed to a measurement.

Analytical uncertainties are closely related to:

- *the concentration of elements*: in the method's linearity range, the higher the concentration of an element, the lower the uncertainty. However, for waters with very high concentrations, the analytical uncertainty increases due to the significant dilutions needed for analysis,

- *the analytical technique used*,

- *the nature of the element, its stability over time and the matrix studied*: lack of standardised analytical methods for carbogaseous waters.

It is necessary here to distinguish between:

- *intra-laboratory uncertainty*, which corresponds to the laboratory's uncertainty concerning the assay of a given element at a given concentration performed by personnel working in a team,

- *inter-laboratory uncertainty*, which is uncertainty concerning an assay performed by various laboratories with different teams and devices.

The calculation methods used to estimate analytical uncertainty are defined in the standard XP T 90-220 'Protocol for estimating measurement uncertainty related to an analysis result for physico-chemical analysis methods'.

III.4 – COMPOSITION: STABILITY, DRIFT OR FLUCTUATION

In light of the preceding data, it is clear that the arbitrary tolerance of 10%, set forth in some ministerial authorisation orders, does not rely on any reliable scientific base and therefore is of very limited interest since tolerance should depend only on the parameter in question and changes in its concentration over time.

For example, a 10% calcium tolerance, which is acceptable for a high-mineral water, is not acceptable for a low-mineral water. For elements having a concentration of around one mg/L or for dissolved gases (CO_2 for example) whose measurement is particularly delicate, this 10% tolerance is sometimes lower than analytical uncertainties.

A BRGM[25] study of five natural mineral water springs exploited at a constant flow showed that with a 10% tolerance, none of them could be considered stable.

Special case of sparkling natural mineral waters:

EEC Directive no. 80/777 states that "*at source or after bottling, effervescent natural mineral waters give off carbon dioxide spontaneously and in a clearly visible manner under normal conditions of temperature and pressure*".

The carbon dioxide found in natural mineral waters can have several origins:
   - a magmatic origin,
   - a metamorphic origin (metamorphism of carbonate formations),
   - a biogenic origin in surface horizons.

Sparkling natural mineral waters are complex and their equilibrium is fragile, which is why sampling conditions and measurement conditions should be taken into account when interpreting analysis results. In fact, the carbon dioxide release that characterises them modifies the water's pH, causing more or less significant variations in other parameters (carbonates, calcium, etc.), which explains why it is difficult to evaluate the stability of such waters.

III.5 - PROPOSAL OF NEW STABILITY ASSESSMENT CRITERIA

A study was undertaken to evaluate the stability of selected parameters regardless of their concentration levels. It led to the following result:

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[25] **BRGM study 1998R40136 - 1998 -** *"Critères d'évaluation de la stabilité des eaux minérales"* **["Assessment criteria for the stability of mineral waters"].**

III.5.1 - Proposal of a stability characterisation methodology

1. among the essential characteristics of natural mineral water, pH and carbon dioxide (CO_2) should not be taken into consideration,

2. compilation of as many available analytical data as possible concerning these elements, from the same laboratory, with indication of the corresponding measurement method,

3. graphic representation of data over time[26],

4. calculation of the coefficient of variation (CV) of the data,

5. for the concentration level of a given element, comparison of that element's concentration variation with the analytical uncertainty determined by the laboratory,

6. the stability criterion S for each parameter would be given by the following formula:

$$S = 2 \times CV / Ip$$

in which CV is the coefficient of variation expressed as a percentage, 2 x CV the 95% confidence interval and Ip the laboratory's coefficient of analytical uncertainty for the parameter at the measured concentration level (intra-laboratory variability),

7. for each essential characteristic element, the following stability assessment criterion is proposed:

    - If S < 2: the parameter is stable over time, which means that analytical uncertainty explains at least half of the observed variation,

    - If S > 2: the parameter has significant instability or drift over time,

8. the interpretation is as follows:

    i. if two essential characteristic elements have an S value slightly greater than 2, the drift may be slow and, in this case, a comparison should be made with the graphic representation of these parameters' evolution over time,

    ii. if over half of the essential characteristic elements have S values greater than 2, it means that the fluctuations are abnormal and that consequently, the water clearly shows signs of instability over time.

III.5.2- Validation of the stability criterion

This methodology was applied to thirteen natural mineral waters of various facies, taken from the national register of natural mineral water springs managed by the AFSSA Laboratory for study and research in hydrology for the 1992 to 2003 period inclusive.

For example, this approach applied to TAC is broken down as follows:

Reference period: February 1992 to October 2003
Number of data: 38
Average TAC: 9.1 °f (French degrees)
Standard deviation: 0.32
Coefficient of variation: 3.5%
TAC measurement uncertainty: 5%
Stability criterion: $\boxed{S = 2 \times 3.5 / 5 = 1.4}$

---

[26]   **if the analytical method changes, this curve should be marked by distinct sub-sets related to each method**

The graphic representation in various natural mineral waters leads to the following results:

a. Example of an <u>unstable</u> composition
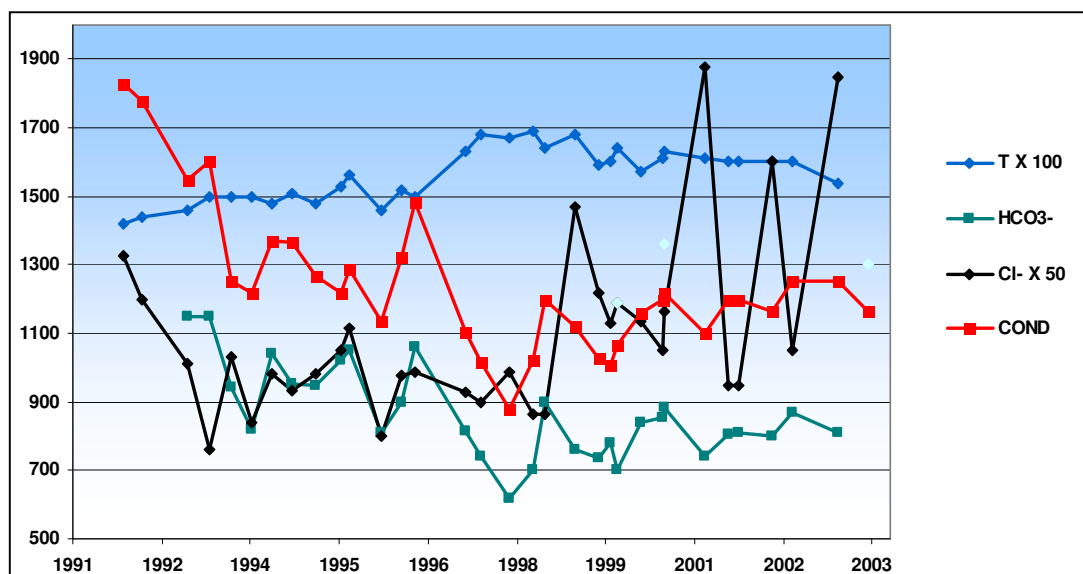
Figure 2: Application of the stability criterion to various parameters of a natural mineral water with an unstable composition
T = Temperature in °C, values x 100;
HCO_3 = Hydrogen carbonates in mg/L;
Chlorides in mg/L, values x 50;
COND = conductivity in µS/cm² at 20 °C.
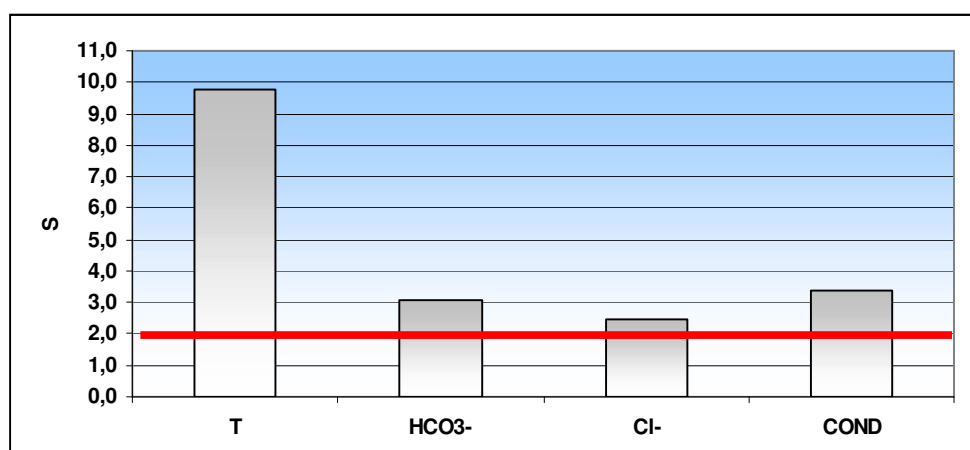
Figure 3: Evolution of various parameters of a natural mineral water with an unstable composition

b. Example of a <u>stable</u> composition
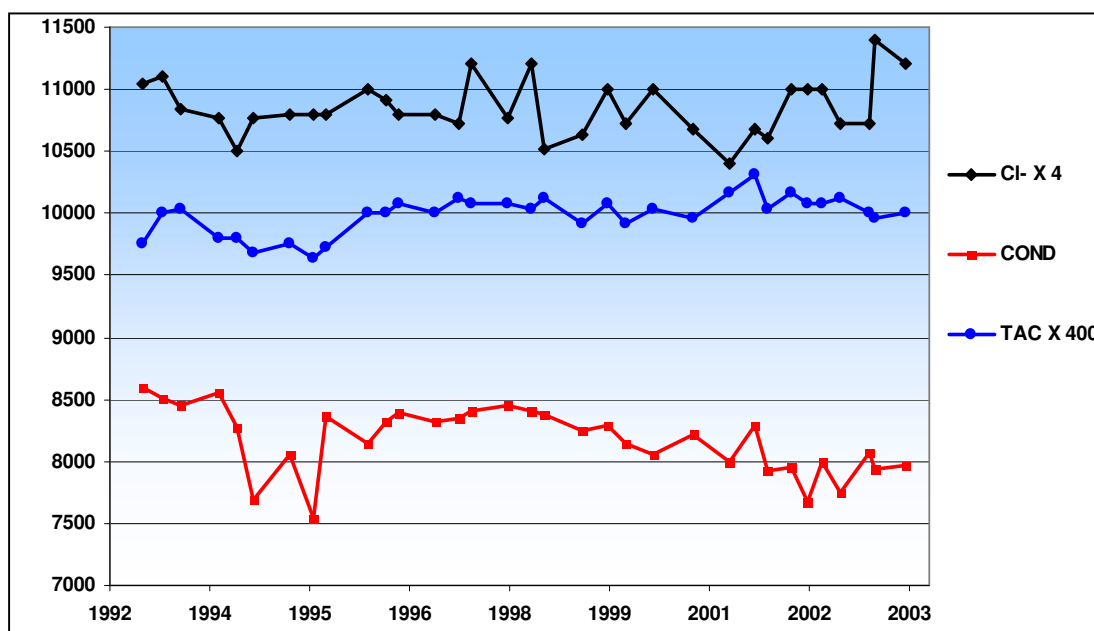
Figure 4: Evolution of various parameters of a natural mineral water with a stable composition

Cl⁻ = Chlorides in mg/L, values x 4;
COND = conductivity in µS/cm² at 20 °C;
TAC = Complete alkalinity titration in °f, values x 400.
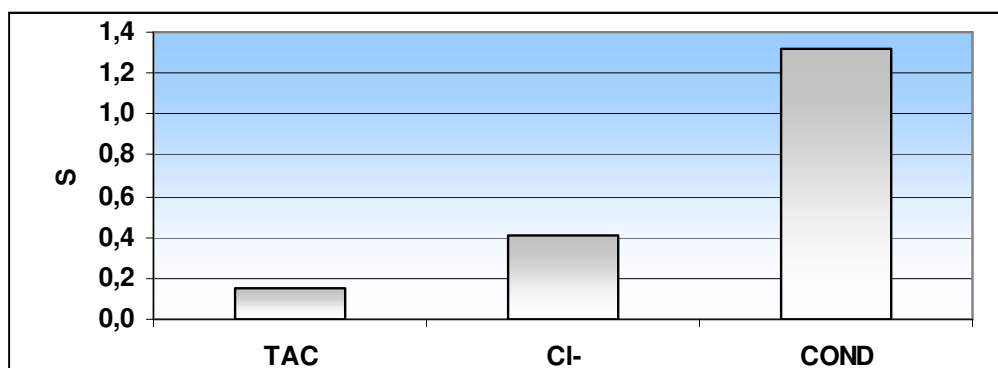
Figure 5: Application of the stability criterion to various parameters of a natural mineral water with a stable composition

c. Example of an <u>intermediary case</u>
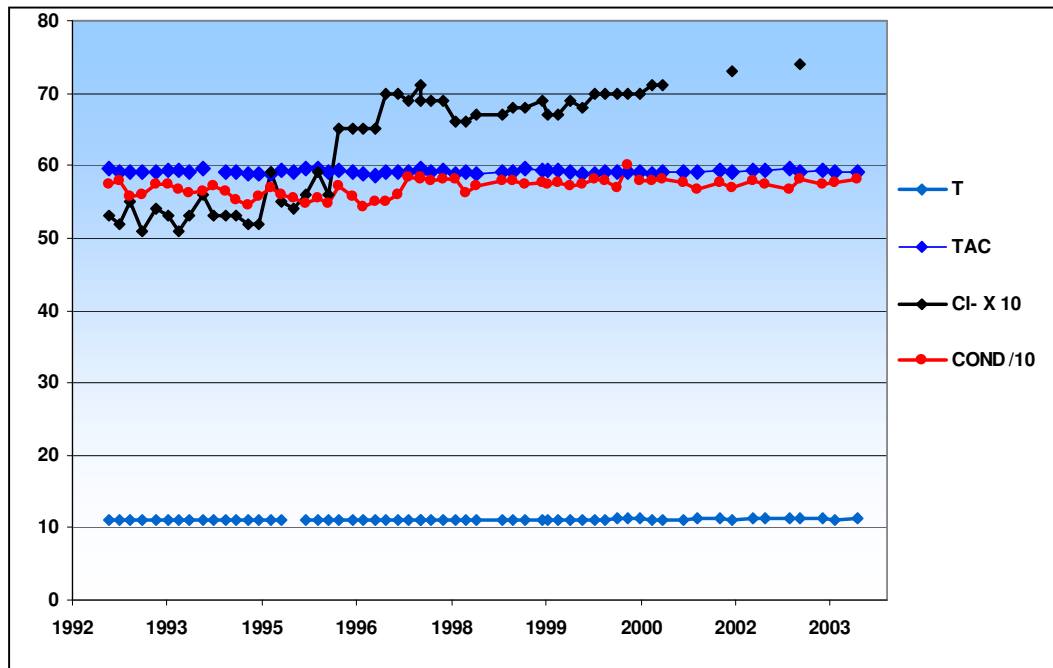
Figure 6: Evolution of various parameters of a natural mineral water with an intermediary composition
T = Temperature in °C;
TAC = Complete alkalinity titration in °f;
Chlorides in mg/L, values x 10;
COND = conductivity in µS/cm² at 20°C, values/10.
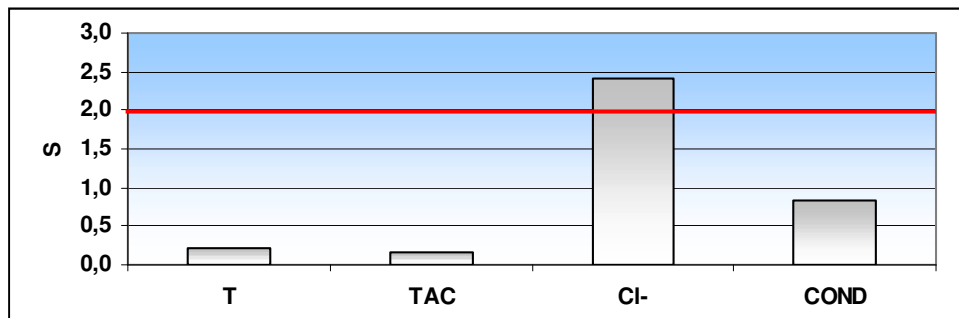
Figure 7: Application of the stability criterion to various parameters of a natural mineral water with an intermediary composition

III.6 - CONCLUSION AND RECOMMENDATIONS

This tool can be used to highlight not only fluctuations in water's composition but also a drift that should undergo additional investigations that take the site's hydrodynamic context into account.

It should be considered a decision-support tool and not a strict judgment criterion, since a natural mineral water's stability needs to be evaluated in its global context. For carbogaseous waters and when there are no data available concerning analytical uncertainties, this model cannot be applied as is.

The assessment of a natural mineral water's stability is important in that observed fluctuations and/or drift in the water's composition could imply a risk of contamination via dilution and mixing with more vulnerable waters.

Various comments may be made in light of the above points:

- the essential characteristics of a natural mineral water concern general (temperature, pH, conductivity, dry residue) and specific parameters (dominant anions and cations, specific elements),

- in practice and regardless of the water's facies, in the framework of the health control of natural mineral waters, the following parameters at least should be periodically monitored: temperature, pH, conductivity, complete alkalinity titration (TAC), major anions and cations,

- analytical uncertainty is a parameter that can change over time according to the analytical techniques, which means that, for each result, the method and analytical uncertainty should be specified,

- for low-mineral waters, only the general parameters listed above should be taken into account, since there may be extremely high analytical uncertainty with low concentrations of anions and cations,

- for carbogaseous waters, the start of exploitation or modified exploitation conditions (increased pumping speed for example) disrupts the water's physico-chemical balance. A new balance is often not restored until after six months or more[27]. The only cases of observed stability involve springs exploited via artesian flow,

- in order to assess possible seasonal variations in water composition and identify their origins, at least twelve analyses would need to be conducted on a monthly basis (annual hydrological cycle) by the same laboratory and under the same conditions, at the requested exploitation rate. However, it is important to note that this monitoring will not lead to a conclusion on a natural mineral water's stability,

- a tool could be defined to assess water's stability over several years. It would be based on the following principles:

  ➢ for a given spring:

    - preparation of control charts used in quality assurance, by copying the monthly monitoring results on a graph for the characteristic elements and tolerance levels used. Such a representation would make it possible to track upward or downward trends, sudden deviations from the set tolerance levels or systematic lag versus the calculated average value,
    - a water will only be deemed stable over time if all of the parameters that represent its essential characteristic elements are stable,

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[27] **BRGM study 2000R40863: Study of stabilisation conditions for sparkling mineral waters**

> for a spring combining water from several catchments and in order not to conceal a drift in the composition of one of the resources:
> - application of stability criteria at each catchment,
> - mixing of waters in relative proportions defined during the authorisation process and not controlled based on conductivity for example.

In conclusion, stability criteria are used to ensure that the water's quality does not drift and therefore that no anomaly that could have health consequences has appeared or could appear.

IV – PURITY OF NATURAL MINERAL WATERS

A natural mineral water is characterised not only by the stability of its physico-chemical composition, but also by its original purity, assessed on the basis of three criteria:

- microbiological purity with respect to pathogenic germs, the criteria for which are set in European texts;
- physico-chemical parameters such as toxic mineral elements and some by-products of ozonation for which criteria are also defined in European texts;
- organic substances, although there are presently no corresponding criteria for assessing original purity, with the exception of the substances mentioned in the Codex standard on 'Natural mineral water'. When Directive 80/777/EEC was written, laboratories did not have the analytical means to screen for and assay trace organic elements at concentrations smaller than one microgram per litre of water.

IV.1 - REGULATORY MICROBIOLOGICAL CRITERIA

Article R. 1322-3 of the Public Health Code states that "*a natural mineral water must not contain a number or a concentration of microorganisms, parasites or any other substance that constitutes a hazard to public health*".

Article 1 of the Order of 14 March 2007 specifies that at source and on the market, natural mineral waters must be exempt of germs indicating faecal contamination, parasites and pathogenic microorganisms.

Annex I of the aforementioned Order:
> establishes quality criteria for:
> - *Escherichia coli*, total coliforms, enterococci, *Pseudomonas aeruginosa* to be screened for in 250-mL water samples taken at source and on the market;
> - Sulphite-reducing bacteria including spores to be screened for in 50-mL water samples taken at source and on the market;
> - Revivable aerobic germs at 22 and 37°C to be screened for in 1-mL water samples taken at source and on the market;
> specifies that if contamination is suspected, *Cryptosporidium sp.*, *Giardia*, *Legionella sp.* and *Legionella pneumophila* must be screened for.

As natural mineral waters come from under the ground, they should not contain elements such as algae or mildew.

It should be noted that enumerations of revivable aerobic germs take into account common aerobic bacteria and some mildew and yeast but never their totality.

Revivable aerobic flora can be an indicator of other elements or organisms that could have a direct impact on consumer health. As a result, algae and mildew must not be tolerated in natural mineral waters, at any stage of their marketing, because they imply a breach of hygiene rules.

IV.2 - REGULATORY PHYSICO-CHEMICAL CRITERIA

> **The Order of 14 March 2007 establishes the list, concentration limits and labelling requirements for the constituents of natural mineral waters. These are elements for which a guideline value has been set by the World Health Organization.**

IV.2.1 - Regulated mineral elements

These are primarily elements such as arsenic, selenium, nickel, antimony, fluoride, etc.

For some of this category's elements, quality limits have been set by the European Union, and on this report's publication date, treatment methods have been approved or are undergoing approval for:

- the removal of fluoride by selective adsorption on activated alumina, which was the subject of a favourable Opinion issued by the European Food Safety Authority (EFSA, 2006).

- the removal of arsenic, selenium, antimony, uranium, radium and nickel by selective adsorption on manganese dioxide or iron oxyhydroxide, which are undergoing evaluation.

IV.2.2 - Impurities and secondary reactions related to ozone

Compounds and substances can form via secondary reaction after ozone is used to treat natural mineral waters (for the removal of manganese).

> **Annex II of the 14 March 2007 Order establishes maximum limits for residues of ozone-enriched air treatment in natural mineral waters:**
> - **50 µg/L for dissolved ozone,**
> - **3 µg/L for bromates**
> - **1 µg/L for bromoform**
>
> **as larger concentrations would indicate the use of ozone for disinfection purposes, which is prohibited.**

IV.3 – NON-REGULATED PHYSICO-CHEMICAL CRITERIA

Natural mineral waters can, in some cases, contain mineral or organic compounds, in dissolved or particle state, which indicate contamination related to treatments or anthropogenic activity.

Since there are no relevant regulations, an analysis to assess purity was undertaken. It took the following into account:
- the sole international reference, *Codex Alimentarius*,
- the aim of recommending threshold values independent of laboratories' analytical performance.

First, it is important to remember that for water intended for human consumption, the regulations have long determined quality criteria, particularly regarding organic substances, and that recent analytical methods can detect micropollutants at concentrations much lower than the limits which present no health risk. The application of these analytical methods to natural mineral waters has highlighted very low levels of impurities, hence the question: if micropollutants are detected, can natural mineral waters be considered pure or is it necessary to define contamination limits that will need to be harmonised at the European level?

According to the recommendations of the WHO, which sets guideline values for each element, and the values in Directive 98/83/EC, which sets quality limits for each element in relation to water intended for human consumption, the organic substances measured in a natural mineral water, at values lower than these limits, present no health risk.

IV.4 - CODEX STANDARD REQUIREMENTS

The only international reference related to the purity of natural mineral waters can be found in the *Codex Alimentarius* standard (Codex STAN 108-1981), which sets a limit for parameters that result from contamination:

"*The following substances shall be below the limit of quantification[28] when tested, in accordance with the methods prescribed in Section 7 (see Methods of analysis and sampling, Codex Alimentarius, Volume 13):*
  - *surface active agents,*
  - *pesticides and PCBs,*
  - *mineral oil,*
  - *polynuclear aromatic hydrocarbons".*

The *Codex Alimentarius* states that, for natural mineral waters, purity can be considered good when the concentration of a given element is lower than the limit of quantitation in the method proposed by the WHO.

In 1992, the WHO decided to set guideline values (or parametric values) for toxic micropollutants contained in water for human consumption and, to keep them independent of laboratory performance and the analytical methods used, it defined guideline values not based on analytical criteria but based on toxicological criteria.

Traditionally it is considered that an analysis method's performance should reach at least **10% of the guideline value and the limit of detection (LOD) should therefore be one-tenth of the parametric value (PV) or the quality limit of the element to be assayed:**

$$LOD = PV / 10$$

IV.5 - PROPOSAL FOR ITS APPLICATION TO NATURAL MINERAL WATERS

The *Codex Alimentarius* standard on natural mineral waters states that the concentration (C) of organic micropollutants must be lower than the limit of quantitation (LOQ) as defined in the standardised method based on the WHO rule:

$$C < LOQ$$

According to the AFNOR XP T 90-210 standard of December 1999, the limit of detection is obtained by dividing the limit of quantitation by 3:

$$LOD = LOQ / 3 \quad \text{or} \quad LOQ = 3 \times LOD$$

$$\text{while} \qquad LOD = PV / 10$$

where PV is the parametric value (or quality limit) set for water intended for human consumption.

It could therefore be considered that the purity objective for an organic substance in a natural mineral water corresponds to a concentration (C) calculated as follows:

$$C < 3 \times PV / 10, \text{ i.e. } C < 30\% PV$$

According to these criteria, trace organic substances do not indicate that water presents a health risk insofar as these values are lower than the quality limits set for water intended for human consumption (established based on the acceptable daily intake (ADI)).

They are simply an indicator of pollution risk, which requires the implementation of appropriate monitoring and protective measures.

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[28] **As stated in the relevant ISO methods**

Furthermore, when haloforms other than bromoform are found in water at a concentration greater than 1 µg/L per molecule, it indicates the persistence of chlorine in plants after a disinfection operation.

Note that the disinfection of plants is authorised but that the disinfection of natural mineral water is prohibited.

IV.6 - CONCLUSION AND RECOMMENDATIONS

For a natural mineral water to be considered pure, it must fulfil specific criteria set by European texts:
- related to microbiology,
- for toxic mineral elements and regulated by-products of ozonation.

Concerning organic micropollutants, there are three types of values used to guarantee the safety of natural mineral water:
- the guideline values set by the WHO, for each organic substance, on the basis of toxicological considerations. These values are generally higher than those set for water intended for human consumption because they do not take protection of water resources into consideration,
- the quality limits established by Directive 98/83/EC for drinking water,
- the *Codex* standard on 'Natural mineral water', i.e.: concentrations lower than the limits of quantitation in accordance with the applied method. These values are the most stringent for the protection of resources and should be considered purity objectives.

If a concentration exceeds the Codex values and still falls within the WHO's guideline values, it does not mean that the water is unfit for consumption but that a resource is inadequately protected and that investigations need to be undertaken to identify the origin.

AFSSA experts, after applying the Codex method, concluded that the following purity objectives could be applied to natural mineral waters:

   a. ***for the organic substances listed in Table B2 of Annex I of the 14 March 2007 Order*** (with the exception of trihalomethanes [THMs], tetrachloroethylene and trichloroethylene), ***concentrations must be lower than <u>30% of the quality limit for water intended for human consumption</u>*** set in the Annexes of the 11 January 2007 Order,

   b. ***for emerging organic products and compounds not listed in the European regulations, concentrations must be lower than <u>0.03 µg/L</u> per individual substance,***

   c. ***for chlorine by-products*** (trihalomethanes [THMs]), ***<u>concentrations must be lower than 1 µg/L</u> for each identified substance***.

Although organic micropollutant testing gives a value between the quality limit set for water intended for human consumption and the Codex values, a study should be undertaken in order to determine the origin of the pollution and take requisite measures.

The AFSSA Laboratory for study and research in hydrology assessed the applicability of this proposal (see Annex 2). For the 14 tested natural mineral water production sites, the results indicate that all natural mineral waters can be consumed with no health risk. For three of these sites, the results are lower than the health limits but higher than the quality objectives and a study should be undertaken to determine the origin of the pollution and take measures to eliminate the pollution and achieve the defined purity objectives.

PART FOUR:
TREATMENTS AND ADDITIONS

Treatments and additions represent a significant and specific part of the exploitation process and are therefore covered by a separate section. The other exploitation stages (mixing, transport, packaging and monitoring) are addressed in the 5th part of this report.

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REFERENCE TEXTS

- European Parliament and Council Directive 96/70/EC of 28 October 1996 amending Council Directive 80/777/EEC on the approximation of the laws of the Member States relating to the exploitation and marketing of natural mineral waters.
- Commission Directive 2003/40/EC of 16 May 2003 establishing the list, concentration limits and labelling requirements for the constituents of natural mineral waters and the conditions for using ozone-enriched air for the treatment of natural mineral waters and spring waters.
- Article R. 1322-32 of the Public Health Code.
- Order of 14 March 2007 on quality criteria for packaged water, treatment and special labelling requirements for packaged natural mineral and spring waters and natural mineral water distributed in public drinking fountains.

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I - REVIEW OF THE REGULATIONS

On the European level, Directive 80/777/EEC amended by Directive 96/70/EC on natural mineral waters addresses the issue of applicable treatments. These provisions have been transposed in the Public Health Code (Article R. 1322-32) and in the implementation Order of 14 March 2007 (Article 5). Moreover, Directive 2003/40/EC establishes the list of elements that, in excess concentrations, can present a public health risk and also lays down conditions for using ozone-enriched air for the treatment of natural mineral waters and spring waters (provision transposed in Article 2 of the 14 March 2007 Order).

It should be noted that treatments applicable to natural mineral waters and spring waters must undergo an assessment by the European Food Safety Authority (EFSA) and then obtain a European Community authorisation. Some, such as ozone, are already authorised and others are under evaluation (for fluoride and arsenic removal).

To satisfy the European Community's health requirements, treatments that may be applied for the removal of certain parameters must fulfil the following conditions:

- be suited to the composition of water;
- not alter the composition of natural mineral waters as regards the essential constituents which give them their properties;
- apply only to the removal of constituents naturally found in water and not resulting from the spring's contamination;
- not cause the formation of treatment residues that could present a risk to public health.

On the national level, Article 5 of the 14 March 2007 Order specifies that "*a natural mineral water cannot be subject to any treatment or addition other than those related to:*
1. *the separation of unstable elements, by decanting or filtration, possibly preceded by oxygenation, insofar as this treatment does not alter the composition of the water as regards its essential constituents;*
2. *the removal of free carbon dioxide by exclusively physical methods;*
3. *the introduction or reintroduction of carbon dioxide;*
4. *the separation of iron, manganese, sulphur and arsenic compounds, using ozone-enriched air;*
5. *the separation of undesirable constituents.*

These treatments or additions must not alter the composition of the natural mineral water as regards its essential constituents or aim to alter the water's microbiological characteristics".

It should be noted that this refers to a 'positive' list of treatments that may be applied to natural mineral waters for the removal of a specific element; it is therefore not the treatment itself that is authorised, but the removal of a specific element (e.g. iron or arsenic) using a specified treatment.

This approach is very different to the one adopted for publicly distributed water for which any treatment is possible as long as it is evaluated and authorised.

The aforementioned constraints and requirements show that not all treatments usable for water intended for human consumption can be applied to natural mineral waters and that those based on the addition of residual chemical reagents and those that significantly impact the water's mineral content (treatments via coagulation/flocculation using chemical reagents and membrane techniques such as reverse osmosis, nanofiltration, electrodialysis and ion exchange) must be immediately ruled out.

Table B-1 of Annex I of the 14 March 2007 Order establishes the list of undesirable constituents that have a quality limit (antimony, arsenic, barium, boron, cadmium, chromium, copper, cyanides, fluorides, lead, manganese, mercury, nickel, nitrates, nitrites and selenium) and Annex II sets forth maximum limits for residues of ozone-enriched air treatment (dissolved ozone, bromates, bromoforms).

To improve legibility, the authors of this section found it preferable to describe the treatments applicable to natural mineral waters in the same order as that used in Article 5 of the 14 March 2007 Order.

II - CURRENTLY AUTHORISED TREATMENTS AND ADDITIONS

Treatment processes applied to natural mineral waters are assessed at the European level, under a two-part process:
 - assessment of their efficacy,
 - assessment of their safety.

II.1 - SEPARATION OF UNSTABLE ELEMENTS, BY DECANTING OR FILTRATION, POSSIBLY PRECEDED BY OXYGENATION

II.1.1 - Goal

The goal is to remove, via aeration followed by decanting or filtration, and possibly preceded by degassing, unstable elements such as iron, manganese and arsenic compounds and volatile sulphur compounds (H_2S) contained in a natural mineral water.

In order to accelerate firstly the oxidation of some unstable elements such as iron in the form Fe^{2+}, manganese in the form Mn^{+2} and arsenic, and secondly, the precipitation of oxidised compounds in the form Fe^{3+} and/or the co-precipitation of manganese and arsenic, it is necessary to increase the redox potential and the water's pH, which must be brought to a value greater than 7. For naturally sparkling mineral waters, this oxidation can occur only by removing (completely or partially) the carbon dioxide beforehand. Oxidation then takes place, particularly for iron, using compressed air.

The removal of iron and manganese from a sparkling natural mineral water involves four successive steps:

 - degassing (where applicable),
 - oxidation of iron and/or manganese salts with a more or less strong oxidising agent (generally compressed air or sometimes ozone-enriched air),

- separation of insoluble particles by decanting-filtration,
- possible regassing of the water.

II.1.2 - Aeration/oxygenation treatments

Oxidation takes place in a specific column, possibly with added pozzolan, using sterile compressed air or oxygen. The air is sometimes ozone-enriched (see § II.4).

II.1.2.1 - Effects

In the presence of air or oxygen, ferrous iron is converted into ferric iron and precipitates if the pH is greater than 7. For manganese, treatment may prove inefficacious if this element is alone or at a concentration much higher than that of iron.

Furthermore, other trace elements co-precipitate with ferric iron: this is the case of pentavalent arsenic, which reacts with iron to form ferric arsenate, which can then co-precipitate with ferric hydroxide.

II.1.2.2 - Indirect risks

While these treatments can, <u>without additives</u>, remove iron, manganese and arsenic from water and nitrify it, they may however be responsible for:

- post-bacterial proliferation and a denitrification of the water with production of nitrites during the water's stagnation following, for example, a temporary filter stoppage,
- the production of nitrites if the water's nitrification is incomplete when the temperature is too low (< 6 °C) or the concentration of dissolved oxygen is too low,
- departure of the carbon dioxide found in natural mineral water,
- a shift in the calcium-carbonate equilibrium with precipitation of calcium carbonate and, consequently, a change in the water's total mineral content,
- microbiological and chemical contamination of the treated water, if the air that is used has not been filtered at 0.2 µm then purified with activated carbon to remove any organic pollutants.

To offset these effects and increase the redox potential without introducing a significant amount of air, the air is often replaced with oxygen.

II.1.3 - Decanting or filtration treatments

Decanting generally takes place in concrete basins or, exceptionally, in stainless steel basins, which are compartmentalised and fitted with baffles to promote the sedimentation of ferric salts. Before being directed to storage vats, the water passes through sand filters or sometimes membrane filters to remove the last suspended particles.

II.1.3.1 - Effects

These treatments effectively separate suspended materials, comprised mainly of iron and manganese hydroxides and oxides.

In the beginning, their sole goal was to retain particles formed from the oxidation of unstable elements such as $Fe(OH)_3$, $FeO(OH)$ and MnO_2, S_8 (colloidal sulphur) that could precipitate in bottles, but it is now known that filters are also biological reactors capable of oxidising manganese (role of mangano-bacteria) and ammonium ions when the pH is near or greater than 7 (nitrification).
Note that the filtration of natural mineral water whose cut-off is lower than 0.8 µm tends to retain the microbial flora.

II.1.3.2 - Indirect risks

If filtration stops and when the water contains nitrates, nitrites are likely to form and the problem arises of filter rinsing time before the plants restart.

After the filtering materials are disinfected, the filters need to be matured to enable the effective removal of manganese and ammonium ions.

If biological phenomena are involved and the water no longer has its initial pH, the microbial flora may undergo quantitative and qualitative modifications.

These treatments are necessary in the case of natural mineral waters; however, they are difficult to control and manufacturers need to optimise them and adapt them to each natural mineral water.

II.2 - REMOVAL OF FREE CARBON DIOXIDE USING EXCLUSIVELY PHYSICAL METHODS

The removal of free carbon dioxide (Point 2 of Article 5 of the 14 March 2007 Order) is an authorised treatment that is part of a comprehensive treatment described in Points 1, 4 and 5 of Article 5 of the aforementioned Order.

Degassing occurs either through the vacuum created in an extraction tower fitted with Raschig rings that increase the exchange surface areas, or through runoff on sloping steps in a tower releasing the over-saturated gas. The CO_2 extraction level is kept below the critical value for carbonate precipitation.

Less frequently, it can also be a simple degassing operation intended to market a naturally sparkling water as a still natural mineral water.

II.3 - ADDITION OR REINTRODUCTION OF CARBON DIOXIDE

Carbon dioxide is added or reintroduced just before a water is bottled.

When it is added, the carbon dioxide's quality must comply with the regulations in force.

If it is reintroduced, the natural gas collected in the first stage is added to the natural mineral water in the carbonator placed just before the bottling line when it is not directly built-in. This operation restores (and may even increase) the natural mineral water's initial CO_2 content. When the amount of CO_2 added is significantly higher than the water's CO_2 level at the source, the water is marketed as a 'natural mineral water fortified with gas from the spring'.

Moreover, natural carbon dioxide that does not come from the groundwater or deposit can be introduced to carbonate still waters and the carbonator used to dissolve varying quantities of natural or synthetic carbon dioxide in the water is generally the same as the one described above.

The resulting water is marketed under the name 'carbonated natural mineral water'.

II.4 - SEPARATION OF IRON, MANGANESE, SULPHUR AND ARSENIC COMPOUNDS, USING OZONE-ENRICHED AIR

II.4.1 - Principle

Ozone is a highly powerful oxidising agent that is authorised for the removal of iron, manganese, sulphur and arsenic compounds. Mixed with air, it converts ferrous and manganous salts into ferric and manganic salts.

This type of treatment is of no use when applied to arsenic-rich waters containing no iron and/or manganese.

In practice, the four stages and the corresponding facilities are the same as those used for the removal of unstable elements, with ozone replacing the air.

II.4.2 - Indirect risks

II.4.2.1 - Related to the quantity of ozone used

When the quantity of ozone added is slightly lower than the stoichiometry, manganese that is not directly oxidised may, via adsorption on MnO_2, be oxidised via catalysis.

However, if the quantity of ozone is higher than the stoichiometry and residual ozone subsists in the water, hazardous and possibly even carcinogenic by-products may form, and particularly:
- bromates through the oxidation of bromides in the water,
- iodates through the oxidation of iodides in the water.

II.4.2.2 - Other

Ozone, when added to natural mineral waters, can also:
- disinfect the water even though this is not the goal since disinfection treatments are not authorised for natural mineral waters,
- complicate compliance with the regulatory limit of 50 µg residual ozone/L at bottling, because of an ozonizer's operating conditions,
- be efficacious for arsenic removal only if the water contains iron and/or manganese with the salts from which this element precipitates and thus complicate compliance with this element's regulatory limit of 10 µg/L,
- cause the formation of unknown by-products that are not yet detectable using traditional analytical methods if the water is rich in organic materials.

In light of some of these risks, maximum concentration limits in natural mineral waters have been established for residual ozone at 50 µg/L, for bromates at 3 µg/L and for bromoform at 1 µg/L but, to date, no value has been set for iodates, which may form during this oxidation.

The above points therefore show that the use of ozone to reduce or remove some undesirable elements naturally found in water has more disadvantages than advantages.

II.5 - SEPARATION OF UNDESIRABLE ELEMENTS

Regulatory texts introduce the possibility of removing undesirable elements but do not give a list of such elements. The new elements that could undergo removal treatment are established by the European Commission and the element-treatment pair must undergo an assessment at the European Community level by the European Food Safety Authority (EFSA).

II.5.1 - Nature of selective adsorption treatments

Commonly used for publicly distributed water, these treatments implement filtering media with manganese oxide, iron oxyhydroxide or activated alumina to remove arsenic, fluoride, selenium, antimony, nickel, uranium and radium. They are currently undergoing appraisal on the European level and, for activated alumina, the EFSA recently issued a favourable Opinion.

The following documents provide more information about their nature and efficacy:

- the bibliographic review attached to the AFSSA 17 March 2005 Opinion entitled "Assessment of the use of sand coated with metal oxides for the treatment of water intended for human consumption and natural mineral waters: filtration materials coated with metal oxides" (Request no. 2004-SA-0236).

- the report attached to the AFSSA 17 March 2005 Opinion entitled "Assessment of treatments to remove some mineral elements found in natural mineral waters and spring waters" concerning the safety and efficacy of such treatments in consideration of special constraints related to natural mineral waters (Request no. 2005-SA-0005).

The conditions for using adsorption-filtration treatments on sand coated with metal oxides for water intended for human consumption were the subject of an AFSSA Opinion and Report on 25 April 2005 (Request no. 2004-SA-0236).

Below are a few reminders concerning treatments that use activated alumina, apatite, MnO_2 sand and sand coated with metal oxide (MnO_2):
- They involve not only filtration but also a selective adsorption of some water-soluble compounds;
- The filtering media used must, in the majority of cases, undergo regeneration implementing acid or basic reagents to remove the adsorbed compounds or using oxidation for the redeposition of oxides and hydroxides, which requires treatment of the regenerates in accordance with environmental protection rules,
- They are not yet authorised for the treatment of natural mineral waters except for arsenic removal which has a provisional authorisation.

II.5.2 - Authorised filtering media

II.5.2.1 - Nature

- **Synthetic activated alumina:** it removes 'fluoride' ions, arsenic V, zinc, selenium, antimony, phosphate ions, humic and fulvic acids and, to a lesser extent, silicic acid (silica). EFSA has issued a favourable Opinion of its use for the treatment of natural mineral waters.

- **Akaganeite or synthetic β Fe(OH,Cl):** this material has a high selective adsorption capacity for arsenic, selenium, antimony, uranium, radium and nickel and does not require regeneration since it must be replaced when it is saturated.

- **Natural or synthetic manganese oxide sand:** it adsorbs arsenic, selenium, antimony, uranium, radium and nickel but there are fewer adsorption sites than for akaganeite.

- **Synthetic apatite $Ca_{10}(PO_4)_6(OH)_2$:** it has three exchange sites: OH^- for Cl^-, Br^-, F^-, I^-, PO_4^{3-} for arsenic, antimony and Ca for nickel, barium and lead. This material however has a degree of water solubility, which limits its use.

- **Sand or other media coated with metal oxides or hydroxides.**

It should be noted that the implementation of all of these media requires a final filtration operation, called polishing, on a sand filter or membrane. This operation is taken into account in the assessment of these treatments' safety and efficacy.

There are French standards (taken from the European standards) related to these media. They are divided into two categories:

- the first concerns definitions (NF EN 12901) and leaching test methods (NF EN 12902),

- the second category is specific to the various categories of media:
    - manganese dioxide (NF EN 13752),
    - calcium carbonate coated with manganese dioxide (NF EN 14368),
    - activated alumina beads coated with iron (NF EN 14369),
    - iron oxide-hydroxide (NF EN 15029),
    - manganese greensand (NF EN 12911).

These standards establish numerous physical specifications particularly in terms of mass density, grain size, chemical composition, loss on ignition, production origin, etc. Some of them (NF EN 15029 and NF EN 12911) establish purity criteria (maximum limits for heavy metals). The others, which are older, do not establish purity criteria but draw users' attention to the possible release of impurities contained in the media.

II.5.2.2 - Advantages of these treatments

Not only do they circumvent the disadvantages related to ozone use in some cases but they also have the following advantages:

- separation of various undesirable elements (manganese, iron, etc.) due to the filtering medium's highly selective oxidising capacity,
- no formation of residues (called by-products),
- no addition of chemical products,
- reduced bacterial loading where no comparable efficacy in a disinfection stage can be claimed,
- negligible, or even null, modifications in the concentrations of characteristic mineral elements (calcium, magnesium, potassium, sodium, chlorides, sulphates, hydrogen carbonates),
- a much lesser dependence on the pH of the water to be treated which, particularly for iron and/or manganese removal, means that the water does not need to be degassed to remove excess carbon dioxide.

II.5.2.3 - Disadvantages of these treatments

Besides the fact that the use of some filtering media, and particularly those coated with manganese dioxide, generally requires a regeneration of sites with a strong base followed by neutralisation with hydrochloric acid and then appropriate rinsing, the application of this type of treatment can:

- promote bacterial growth and the formation of biofilms since the media behave like biological reactors,
- if the water contains ammonium ions, cause the formation of nitrates and/or nitrites when the pH is close to 7,
- promote the adsorption of some trace metal ions (co-removal).

> These filtering media are highly useful treatments for natural mineral waters; however, like separation treatments, they are difficult to control and manufacturers need to optimise them and adapt them to each natural mineral water.

II.5.2.4 - Treatments undergoing assessment by EFSA

A working group from the European Commission drew up a first report[29] concerning the assessment of fluoride treatment using activated alumina. This report was submitted to EFSA for approval. It issued a favourable Opinion on 27 September 2006 on the safety of using activated alumina to remove fluoride from natural mineral waters. It was published in The EFSA Journal (2006).

A second request for the treatment of manganese, iron and arsenic on a filtering medium with iron oxyhydroxide or manganese is under assessment by EFSA.

II.6 - SEPARATION OF SOLID PARTICLES USING FILTERS

Bottling plants all contain filters intended to protect sensitive parts such as pumps, electrical valves and spouts of bottling machines from fine particles that are the result of extraction (clay, for example) or iron removal treatment (iron or manganese hydroxide).

These filters are often sand filters (called quartz) but may also be porous-cartridge filters (porcelain) or membrane filters. In the latter case, cross-flow filtration may also be applied. The use of such membrane filters is problematic since, depending on the cut-off, they can end up disinfecting the water which is not authorised for natural mineral waters.

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[29] **30 March 2006: "Report of the ad hoc working group on the technological assessment of natural mineral water treatments on the evaluation of treatment by aluminium oxide for the removal of fluoride from natural mineral waters and spring waters"**

When questioned about this case, AFSSA considered – in an Opinion of 29 November 2001- that the cross-flow filtration system with a cut-off of 0.8 μm could be used for the treatment of spring water or natural mineral water with the goal of trapping particles naturally found in water at the catchment or those resulting from a dissolved manganese or iron oxidation treatment, but that it should not be used to bring a water's microbiological characteristics into compliance with the regulatory provisions.

In the event that such a system is installed in a packaging plant for natural mineral water, AFSSA therefore requested that the microbiological quality of water be monitored not only at the catchment but also before and after filtration to make sure the water is not disinfected (Opinion of 29 November 2001).

II.7 - LIMITS OF TREATMENTS AUTHORISED FOR NATURAL MINERAL WATERS

If, in light of the regulatory requirements mentioned in Part I of this section (AFSSA Report and Opinion of 17 March 2005), we evaluate the efficacy of traditional treatments used to remove some parameters from water intended for human consumption, we see that for the removal of:

- **barium** and **nitrates**, there is no treatment that satisfies the requisite conditions for natural mineral waters. It should be noted that the *Codex Alimentarius* is to address the limit applicable to barium in 2008.
- **boron**, there is no method that allows it to precipitate at the pH of natural mineral waters. To do so, it would be necessary to use synthetic materials specifically designed to that end but the criteria that could be used to determine the reduction of its content in consideration of the constraints applicable to natural mineral waters have not been assessed.
- **arsenic** by co-precipitation with iron after prior oxidation, treatment is efficacious only for waters with a very high iron content (> 0.5 mg/L) and there is no assurance that an arsenic content lower than 10 μg/L will be obtained at any time. To do so, it would be necessary to implement filtration on a manganese dioxide or iron oxyhydroxide medium, or on sand coated with manganese oxide or iron oxyhydroxide.

Parameter from Directive 2003/40/EC	Nature of treatments	Origin	By-products likely to form
Antimony	Selective adsorption on ferric oxyhydroxide, manganese dioxide or activated alumina	Natural origin	(1)
Arsenic	Selective adsorption on various media: ferric oxyhydroxide, manganese dioxide or activated alumina	Natural origin	(1)
	Co-precipitation possible if using iron and manganese treatment (with prior oxidation using oxygen or ozone)		Neoformed products, bromates, iodates
Barium	None	Natural origin	
Boron	None	Natural origin	
Cadmium	Selective adsorption on various media: ferric oxyhydroxide, manganese dioxide or activated alumina	Resource pollution and natural origin	(1)
Hexavalent chromium	Selective adsorption on various media: ferric oxyhydroxide, manganese dioxide	Resource pollution	(1)
Total cyanides	Activated carbon then biodegradation	Resource pollution	(1)
	Chemical oxidation (ozone)		bromates, iodates
Fluorides	Adsorption on activated alumina or apatite.	Natural origin	(1)
Manganese	Selective adsorption on various media: ferric oxyhydroxide, manganese dioxide	Natural origin	(1)
	Ozonation and co-precipitation in the presence of iron. Biological manganese removal		Neoformed products, bromates, iodates (1)
Total mercury	Adsorption on activated carbon	Resource pollution or natural origin	(1)
Nickel	Selective adsorption on various media: ferric oxyhydroxide, manganese dioxide	Natural origin	(1)
Nitrates	None	Resource pollution	
Lead	Selective adsorption on various media: ferric oxyhydroxide, manganese dioxide or apatite	Resource pollution	(1)
Selenium	Selective adsorption on various media: ferric oxyhydroxide, manganese dioxide or activated alumina	Natural origin	(1)

(1) At the time of filtration, and regardless of the medium used, if the pH is greater than 7, the ammonium ions can be oxidised into nitrites and/or nitrates.

Table 1: Treatments likely to be used for natural mineral waters

II.8 - CONCLUSION ON TREATMENTS

The treatment methods applied to natural mineral waters listed above are authorised in Europe. For an optimum implementation of these methods, the profession is advised to draw up technical guides.

<table>
<tr><td align="center">REFERENCE TEXTS</td></tr>
</table>

- Regulation (EC) no. 852/2004 of the European Parliament and Council of 29 April 2004 on the hygiene of foodstuffs.
- Regulation (EC) no. 882/2004 of the European Parliament and Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules.
- Regulation (EC) no. 1935/2004 of the European Parliament and Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC.
- Directive 80/777/EEC of 15 July 1980 (Annex II).
- Articles R. 1322-28 to R. 1322-38 of the Public Health Code.

The respective obligations of manufacturers and control bodies are clearly defined in Regulations EC no. 852/2004 and EC 882/2004 on food processing industries. That is why the natural mineral water regulations (Articles R. 1322-28 to R. 1322-38 of the Public Health Code) do not set forth obligations of means but obligations of results for everything that contributes to the exploitation of natural mineral waters independently of specific provisions in the directives on natural mineral waters and packaging materials (Regulation EC no. 1935/2004).

While manufacturer responsibility in technical choices remains a major prerogative, some phases of exploitation, specific to natural mineral waters, may warrant further explanation or special comments.

These include phases aiming to mix and transport water through pipes, in any form, to store it under satisfactory sanitary conditions and to package it in recipients.

The purpose of this section is not to supersede operator responsibility by running through the HACCP (Hazard Analysis Critical Control Points) approach in detail or identifying hazards and risks in detail, but rather to draw attention to general critical points in terms of public health.

These include the quality of materials and the growth of resulting biofilms.

I- MIXING

Natural mineral water "*originates in an underground water table or deposit and emerges from a spring tapped at one or more natural or bore exits*" (Article R. 1322-2 of the Public Health Code).

The notion of mixing therefore derives from the definition of a natural mineral water spring that can comprise one or more exits.

Waters from several exits may be mixed because of the various catchments' exploitation conditions and water requirements. If water requirements rise, the maximum flow authorised for an exit can become insufficient and the possibility of mixing water from several exits may therefore increase available resources. In the case of a spring comprising several exits and to prevent health risks related to the over-exploitation of an exit, it is recommended to distribute hydraulic head over a sufficient number of catchments. Preserving the resource's hydrogeological functions is necessary to maintain a stable water quality.

However, it should be noted that if waters are mixed, waters from the same deposit must separately satisfy all the criteria for a natural mineral water.

In all cases, all catchment waters that are mixed must:

- comply with the general provisions applicable to natural mineral waters and, in particular, those related to the stability of essential characteristics,
- have the same geological origin and belong to the same deposit,
- have the same physico-chemical profile.

The conditions under which waters from several catchments can be mixed are as follows:

- mixing in any proportion if the waters used have an identical and stable physico-chemical composition,
- mixing in defined proportions when the waters have identical physico-chemical profiles but at different concentration levels. Stability must in no case be artificially maintained by automatic regulation of flows at the conductivity level, which could conceal unstable water composition from one or more catchment(s).

A mixture is characterised by its composition and its essential characteristics must remain stable.

Regardless of the method used, the mixture must not include water from any spring that no longer satisfies the criteria applicable to natural mineral waters (instability at source, microbiological or physico-chemical contamination).

> To conclude, while mixing can prevent health risks related to the over-exploitation of a limited number of catchments, the quality of the water produced at each catchment must be controlled.

II - EXPLOITATION EQUIPMENT

II.1 - REGULATION

The transport and storage of water prior to packaging must not alter the water's quality with regard to major elements or trace minerals and organic substances.

Article R. 1322-31 of the Public Health Code states that "*Materials in contact with natural mineral water must be compatible with its composition so as to prevent any chemical, physico-chemical, microbiological or organoleptic alteration of the water after emergence*".

All materials used must comply with the regulations applicable to water intended for human consumption and show proof of this compliance.

However, the specific characteristics of some of these waters (hot water, CO_2-rich water, etc.) are not taken into account in the compliance assessment of materials in contact with water intended for human consumption and the operator must therefore ensure that the quality of the natural mineral water is not altered (AFSSA Opinion of 9 February 2006).

The main equipment concerned includes pipes and storage structures made of metal or concrete and cement, as well as pipes, storage structures and coatings made with organic compounds.

II.2 – MATERIALS USED

Pipes are generally made of stainless steel or an organic material (PVC or more rarely polyethylene or reinforced polyester). Designers usually make this choice due to alloy steel's excellent resistance to corrosion and the inertia of organic materials. However, there are still some steel or cast-iron structures which may be coated with organic resin or more rarely cement mortar.

Storage tanks are made of stainless steel, ordinary steel coated on the inside or a cement-based material (concrete or cement mortar). In these structures, the water is brought into contact with the atmosphere and can thus exchange gases, particularly oxygen, carbon dioxide or hydrogen sulphide with the outside air.

II.3 – ALTERATION OF MATERIALS

As far as **metal or concrete and cement materials** are concerned, they must not be corroded or dissolved by the acidity of water.

It should be noted that cement-based materials can alter water's characteristics when transported, particularly when it has a strong tendency to dissolve calcium carbonate (case of waters with high concentrations of CO_2 or very low-mineral waters).

Concerning materials made with organic compounds, two risks should be taken into consideration:

- firstly, the release of organic substances into the water, which concerns all materials (pipes, reservoirs made entirely of organic compounds, coatings that are often applied to metals or cement-based materials),
- secondly, for pipes or tanks made entirely of organic compounds, the migration of organic compounds from the outside to the inside of the structure (soil pollutants for example).

Concerning the permeation of some compounds from the outside to the inside of the pipes or tank, like for water intended for human consumption, rules of prevention should be defined to prevent compounds or vapours from contaminating the water: chlorinated solvents, aromatic hydrocarbons, fragrances or aromas that may be used to prepare beverages or clean premises, etc.

Uncoated black-iron pipes are not authorised.

The use of some materials for pipes, valves or accessories may present a risk as shown in the table below:

	Material used	Risks	Water's characteristics
Pipes	*Steel coated with zinc (galvanised steel)*	Corrosion and release of zinc, iron and zinc impurities (lead and cadmium)	According to the water's mineral content, acidity, oxygen reduction potential
	Copper	Release of copper	
	Stainless steel type 316 or 304	Release of nickel	For high-mineral waters and particularly chloride waters
Accessories	*Copper alloy (brass, bronze)*	Release of copper, zinc and lead	
Valves	*Chromium copper alloy*	Release of nickel (used as a chromium primer)	

Table 2: Risks related to the use of some materials according to the characteristics of natural mineral waters

Corrosion can be accelerated by a high water temperature, particularly for high-mineral waters or waters that have high concentrations of hydrogen sulphide.

It should also be noted that:

- large calcium deposits can form in pipes or tanks in the case of high-mineral deep waters (calcium bicarbonate) containing high concentrations of dissolved gas (nitrogen, methane, carbon dioxide, etc.),

- ferric deposits can appear when the transported water contains ferrous iron as a result of ferrous iron oxidation by atmospheric oxygen and be the seat of biological developments which may be pathogenic or may cause the production of hydrogen sulphide in the presence of sulphate-reducing bacteria,

- punctures may be observed for type-304 stainless steel systems that are disinfected with sodium hypochlorite before they are commissioned, after repair work, after long exploitation stoppages or after contamination.

A prior case-by-case study is therefore necessary to choose the materials used in pipes and storage structures and adapt them to the characteristics of the transported or stored natural mineral water, particularly in terms of:

- its physico-chemical properties (mineral content, aggressivity, etc.),

- its temperature, which is generally higher than that found in supply water. Note that bottling plants, which contain internal piping, have a relatively high temperature (20°C) which raises that of the catchment water.

II.4 – CLEANING AND DISINFECTION PRODUCTS

Products used to clean and disinfect structures must comply with the regulations in force for water intended for human consumption (Order of 8 September 1999[30] and Circular of 7 July 1997[31]). Moreover, these products must satisfy the requirements set forth in Directive 98/8/EC of 16 February 1998 concerning the placing on the market of biocidal products. Active substances must be notified and a dossier must have been submitted and be under review in the Rapporteur Member State in accordance with Regulation 1048/2005 of 13 June 2005[32].

III- PACKAGING MATERIALS AND BOTTLING PROCESSES

III.1- PACKAGING MATERIALS

Prior authorisations to use packaging materials for natural mineral waters were repealed on 1 January 2005 to align the French regulations with the European Community provisions on food packaging. Packaging quality is the responsibility of the manufacturer which, when requested by the Health authorities, must provide proof that the materials comply with the European Community provisions.

Whether they are for bottles or closures (caps, liners), the materials used to package natural mineral water "*must be so treated or manufactured and used as to avoid any alteration to the chemical, microbiological and organoleptic characteristics of the water*" as set forth in Article R. 1322-36 of the Public Health Code.

This means that plastic packaging materials must comply with the amended Order of 2 January 2003 regarding plastic materials and articles brought or intended to be brought into contact with foodstuffs, food products and food drinks.

These provisions concern:

- firstly, the original substances on the positive lists of food contact materials,
- secondly, the control of overall migration and specific migration.

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[30] **Order of 8 September 1999 issued for implementation of Article 11 of Decree no. 73-138 of 12 February 1973 as amended implementing the Act of 1 August 1905 on fraud and adulteration concerning processes and products used to clean materials and articles intended to be in contact with foodstuffs, products and beverages for human food and animal feed.**

[31] **Circular DGS/VS4/97 no. 482 of 7 July 1997 on the use of products to clean tanks of water intended for human consumption.**

[32] **Commission Regulation (EC) nà. 1048/2005 of 13 june 2005 amending Regulation (EC) no. 2032/2003 on the second phase of the 10-year work programme referred to in Article 16(2) of Directive 98/8/EC of the Parliament and Council concerning the placing on the market of biocidal products.**

In practice, manufacturers order materials from their supplier(s) that fulfil the aforementioned provisions. It is their responsibility to produce certificates of compliance and, when applicable, perform tests verifying overall and specific migration limits.

In most cases, packaging is made of poly(ethylene terephthalate) (PET) in accordance with a 2-phase method:

- high-temperature (around 265°C) injection of preforms from PET granules; above this temperature, the polyester starts to deteriorate to form acetaldehyde,
- blowing of preforms at a temperature of around 110°C to obtain a crystallised bottle.

The preform injection operation must be performed at a temperature above PET's melting point (265°C) but low enough to prevent or at least limit its conversion to acetaldehyde. This thermal degradation has two consequences: the appearance of acetaldehyde on the bottle's walls, then its migration into the water with the risk – above 20 µg/L – of altering the water's organoleptic properties by giving it an apple taste and weakening the bottle's mechanical properties (deformation, lower pressure resistance).

The injection of preforms with injection-moulding machines can take place in or outside of the packaging plant. The preforms are blown in machines placed as close as possible to the bottling lines and at a temperature that sterilises them. They are then stored in containers away from dust.

There is therefore no risk of empty-bottle contamination at this level with the exception of the conveying operation to the bottling lines which uses air conveyors. The replacement of Polyvinyl chloride (PVC) with PET entailed the removal of storage silos for empty bottles needed for their degassing.

Concerning caps that are used directly, the sole risk lies in the manual loading of bottling lines.

In some small bottling plants, bottles are sometimes purchased directly and delivered ready to use. There is no objection to this practice in principle, but manufacturers need to include it in their risk analysis.

III.2 - USE OF RECYCLED POLY(ETHYLENE TEREPHTHALATE) [PET]

In the past, food packaging and particularly water packaging had to be made of original materials. To respond to environmental issues, the recycling of packaging materials and particularly PET in water bottles has become an increasingly urgent matter and AFSSA has evaluated under what sanitary conditions the use of recycled PET could be considered, especially for packaging water.

Studies conducted on thousands of PET bottles collected from various countries have shown a maximum contamination level of 20 mg/kg PET, mostly caused by food flavourings. In its Opinion of 27 November 2006, AFSSA stated that recycling processes with a 99% decontamination rate lowered this level to 0.2 mg/kg, i.e. below the maximum tolerable concentrations, and affirmed that the use of materials made of recycled PET brought or intended to be brought into contact with drinking water does not present a health risk to consumers, when the recycling process:

- has been assessed from the collection of used PET to the production of recycled PET,
- provides proof of its ability to remove potential contaminants particularly by fulfilling decontamination criteria,
- complies with production monitoring recommendations.

III.3 - REUSE OF PACKAGING MADE OF ORGANIC MATERIALS

The methods used to treat reused glass packaging (hot washing in a soda solution followed by rinsing to remove trace impurities) cannot apply to the reuse of packaging made of organic materials.

Generally speaking, organic polymers can adsorb traces of organic compounds that have been added to the bottle. These are usually diesel, household pesticides, petrol or detergents. According to the polymer's constitution, these compounds can migrate to a greater or lesser extent into the polymer's cells to 'inflate' it. There is what is called a 'memory' effect.

Cleaning operations with a detergent then disinfection with ozonised water cannot always remove the last traces of these substances, which can then slowly migrate into the water when it is marketed.

Full-size tests performed in a few European Union countries have quickly shown that in spite of the use of 'sniffer' devices that are supposed to automatically analyse, through gas chromatography-mass spectrometry (GC-MS), the air in bottles before filling, there still remain bottles with an unacceptable taste or smell. This is why washed plastic bottles have been reserved for the packaging of flavoured drinks.

It is clear that water producers cannot control the use of empty water bottles in the home.

As for the 19-litre bottles that are almost entirely for institutional use, there is practically no risk that empty bottles will be filled with domestic products. The vast majority of these bottles are made of polycarbonate, a product that is much more resistant to chemical products than PET. Before reuse, they are washed with detergents and then disinfected with ozonised water before being filled.

No particular health risks have been highlighted in the reuse of these bottles.

III.4 - USE OF GLASS

Glass packaging materials must comply with the amended Council Directive 84/500/EEC concerning the declaration of compliance and the performance criteria of the analytical method for ceramic articles intended to come into contact with foodstuffs.

III.5 - TRACEABILITY OF MATERIALS

Regulation (EC) no. 1935/2004 of the European Parliament and Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC (Official Journal of the European Union, 13.11.2004, L 338/4-16) states:

1. *"The traceability of materials and articles shall be ensured at all stages in order to facilitate control, the recall of defective products, consumer information and the attribution of responsibility.*
2. *With due regard to technological feasibility, business operators shall have in place systems and procedures to allow identification of the business from which and to which materials or articles and, where appropriate, substances or products covered by this Regulation and its implementing measures used in their manufacture are supplied. That information shall be made available to the competent authorities on demand.*
3. *The materials and articles which are placed on the market in the Community shall be identifiable by an appropriate system which allows their traceability by means of labelling or relevant documentation or information".*

This is a new provision for manufacturers.

IV - MONITORING AND CONTROL

Article R. 1322-29 of the Public Health Code transposed the provisions laid down in Regulations (EC) no. 178/2002 on food law and (EC) no. 882/2004 particularly concerning compliance with good hygiene practices and procedures based on HACCP principles (Hazard Analysis Critical Control Points).

"Operators shall ensure that all stages of natural mineral water production and distribution under their responsibility comply with hygiene rules. They shall apply ongoing hazard analysis and critical control point procedures based on the following principles:
1. *Identify any hazards that need to be prevented, eliminated or brought to an acceptable level;*
2. *Identify critical points where surveillance is essential to prevent or eliminate a hazard or bring it to an acceptable level;*
3. *Establish, at critical control points, limits that distinguish between acceptability and unacceptability for the prevention, elimination or reduction of identified hazards;*
4. *Establish and implement procedures for the effective surveillance of critical points;*
5. *Establish corrective actions to be implemented when surveillance reveals that a critical point is not controlled;*
6. *Establish periodic procedures to verify the effectiveness of the measures mentioned in 1) to 5);*
7. *Establish documents and dossiers suited to the nature and size of the site to prove the actual implementation of the measures mentioned in 1) to 6).*
The operator shall adapt the procedure after any product, process or production stage is modified".

This report does not aim to examine the chapters of this article point by point but rather to highlight what is important and underlying in this risk analysis, which is the monitoring of plants.

One of the strengths of the manufacturer accountability approach lies in the development of a guide to good hygiene practice and its adaptation at each plant. It is a **tool written BY professionals FOR professionals** that is validated by the relevant authorities. It is a tool intended to help professionals implement appropriate control measures to reach the objectives established by the regulations.

It should be noted that no guide to good hygiene practice for packaged water has been validated to date.

As operators are responsible for the quality of the water they produce, they must have continuous knowledge of the water's quality at all production stages, from catchment (the resource) to the finished product (marketed bottled water). One of the tools at their disposal is monitoring, which is different from official inspections.

For clarification purposes this report will use:

- the term 'monitoring' for the analytical operations undertaken by the water producer,
- the term 'control' for official inspections undertaken on request of the authorities.

The goal of monitoring is to continuously guarantee the quality of water produced. It will therefore be combined with obligations of means and results concerning the choice of materials, reagents, treatment media and disinfection frequency.

At the analytical level, the frequency for parameters to be monitored will be determined by a solid risk identification approach: the HACCP approach from the ISO 22000 standard.

Insofar as possible, the ongoing monitoring of some parameters will allow for alerts to be rapidly triggered if a drift is detected. This could include:

- the measurement of residual chlorine in water, which is an easy way to verify the effectiveness of rinsing after disinfection,
- the continuous measurement of conductivity to verify the efficacy of rinsing after acid regeneration of a material used as a selective adsorbent.

This monitoring will verify whether bottled waters are compliant.

To implement a monitoring procedure, manufacturers have two options:

- either call upon an external laboratory recognised by the health authorities for testing analyses,
- or perform these analyses in an internal laboratory. The latter solution is preferable because response speed is a critical parameter in the event of a health risk. However, the results also need to be reliable and obtained with ISO 9001 or 22000 certification or ISO 9001/22000 combined certification.

Using an internal laboratory gives operators greater responsibility by allowing them to have better knowledge of their plants' critical points.

Given that monitoring must be defined on a case-by-case basis, no standard programme can be established.

However, the guide to good practice that was mentioned above would be a valuable tool for professionals to help them define monitoring points and the nature and frequency of analyses and implement the appropriate control measures.

To conclude, the choice of an internal monitoring laboratory with quality certification guarantees greater responsiveness in the event of health risks. A guide to good practice that takes professional constraints into consideration should also be written. It could also be part of a process of recognition by health authorities and help manufacturers control their plants.

CONCLUSION AND RECOMMENDATIONS

In France, the sixty-seven natural mineral waters recognised as such are products available for consumption by the entire French population and may even, for infants in particular, represent an essential part of the diet. They must:

- be exempt from all microbiological contamination,
- be subject to health controls,
- comply with the standards set by the regulations for a certain number of unstable, undesirable or toxic parameters of natural origin.

I - Recognition and authorisation procedures

Act no. 2004-806 of 9 August 2004 on public health policy, classified under Articles L. 1322-1 to L. 1322-13 of the Public Health Code, laid down statutory bases related to natural mineral waters and applicable procedures for their recognition, authorisation and exploitation, which have now been devolved to the prefectural level.

On that occasion, many procedures were simplified and harmonised with those governing water intended for human consumption.

Applications to exploit a natural mineral water must include the results of evaluations needed to obtain knowledge of their origin and vulnerability, which implies that at least the following must be produced:

- a detailed summary of the geological context,
- a study of the hydromineral system's hydrogeological functioning,
- an analysis of the relationship between the nature of the terrains and the water's mineral content,
- a solid assessment of the resource's intrinsic vulnerability and an inventory of pollution sources both in the intake area and in the emergence area,
- a detailed proposal of protection, monitoring and alert measures that will be implemented.

II - Catchment and exploitation of natural mineral waters

Whether it is a case of natural or bore exits, catchworks must strictly comply with accepted practices and hygiene rules. Furthermore, the materials used (drill strings, cements, equipment, etc.) must be checked to ensure they are suited to water's characteristics in order to prevent corrosion and the premature ageing of the structure.

The advantages of artesian flow are twofold: firstly, it keeps mineral water from mixing with cold surface water and secondly, it helps maintain a stable water quality, which is one of the main requirements for natural mineral water.

Conversely, pumping creates conditions that foster mixing with cold surface water or hot high-mineral deep water, hence the need to define and respect a pumping flow favourable to the maintenance of the extracted water's composition stability.

III - Protection of catchments

Unlike publicly distributed water, mineral waters can only be protected by the regulations at their exit point through a 'sanitary perimeter of emergence'. Usually having a small surface area, its sole objective is to prevent intrusions and eliminate the risk that pollutants will be spilled immediately next to the catchment which could contaminate the water and consequently present a health risk.

However, the owner of a mineral spring has the option of requesting that a declaration of public interest be issued by Decree from the Council of State. This delimits a perimeter of protection within which activities, deposits, facilities, etc. likely to jeopardise the mineral water's quality can be prohibited or regulated.

IV - Characteristics of natural mineral waters

These characteristics are acquired when the water comes in contact with the geological formations it flows through and are essentially related to the temperature, pressure and residence time of the water in the aquifer.

Two characteristics are particularly important:

1- the water's composition and temperature stability at the source:

In the past, for water composition stability, an arbitrary tolerance of 10% was mentioned in some ministerial Orders but this tolerance was not based on any reliable scientific source. Stability should depend only on the parameter in question and its concentration over time.

This is why the working group undertook a study to assess the stability of the selected parameters. To attempt to highlight fluctuations in water quality as well as longer- or shorter-term drifts requiring an evaluation of the site's hydrodynamic context, AFSSA is proposing:

- a stability characterisation methodology,
- validation of the stability criterion.

Any significant drift over time observed for a parameter should be considered a sign of water quality degradation with potential health consequences and should give rise to an in-depth assessment to implement essential resource management measures (e.g. limiting the pumping flow).

In the current state of knowledge:
- *this proposal should be considered a decision-support tool and not a decisive criterion as stability criteria are mainly used to check that there are no anomalies that may have health consequences,*
- *for carbogaseous waters, this model is not applicable as is.*

2- the natural mineral water's original purity:

Natural mineral water's original purity should be assessed from a microbiological perspective: a natural mineral water must never contain a number or a concentration of microorganisms or parasites that constitutes a hazard to public health.

From a physico-chemical perspective, the texts in force establish concentration limits and labelling requirements for water's constituents for which a guideline value has been set by the World Health Organization. Here it is relevant to highlight the lack of regulatory standards for organic substances despite these parameters logically coming into play in the notion of purity.

According to the approach presented in the report, the following purity objectives may be recommended:

a- **For the organic substances listed in table B2 of Annex 1 of the 17 March 2007 Order** (apart from tetrachloroethylene and trichloroethylene), **values must be 30% lower than the quality limit established for water intended for human consumption**,

b- **for trichloroethylene and tetrachloroethylene, concentrations must be lower than 1 µg/L.**

> c- for emerging organic products and compounds not listed in the European regulations, concentrations must be smaller than 0.03 µg/L per individual substance,

V- Treatments and additions

For natural mineral waters, the Order of 14 March 2007 limits treatment and addition possibilities to the removal of unstable elements and carbon dioxide, the introduction or reintroduction of carbon dioxide and the separation of unstable compounds and undesirable constituents of natural origin. *These treatments must not modify the natural mineral water's composition with regard to its essential constituents or its microbiological characteristics.*

These provisions show that not all treatments applicable to water intended for human consumption can be implemented for natural mineral waters.

Treatment methods have been established by the European Union for some parameters.

On this topic, it should be noted that:

- for ozone treatment, concentration limits have been set for some by-products,

- some mineral or organic compounds expressing contamination further to treatments or human activity are not regulated. This led the working group to examine the purity of natural mineral waters in order to establish threshold values independent of laboratories' analytical performance and propose the following conclusions and recommendations for a mineral water to be considered pure:

> a- compliance with the criteria set in the regulations for microbiology, toxic mineral elements and by-products of ozonation;
> b- concentrations lower than 1 µg/L for each of the molecules that are by-products of chlorine.

Given that these treatments are often complex, manufacturers should adapt their implementation to each water type because a lack of control at this level can cause health risks for consumers.

VI - Exploitation conditions

1- Mixing:

The notion of mixing derives from the definition of a natural mineral water spring that can comprise one or more natural or drilled exits. However, <u>such mixing is possible only if the waters come from the same deposit</u>.

Precise mixing rules must be followed. These are:

- mixing in any proportion when waters from different catchments have an identical and stable physico-chemical composition,
- mixing in defined proportions when the waters have identical physico-chemical profiles but at different concentration levels.

These conditions prohibit stability from being maintained artificially by a measurement of conductivity after automatic regulation of flows at various exits, since such an operation could conceal unstable water composition at the exits in question.

2- Exploitation equipment:

All of the equipment used must comply with the regulations applicable to water intended for human consumption but since some natural mineral waters have specific characteristics (temperature, CO_2, etc.), the operator must ensure that the water's quality is not altered.

3- *Cleaning and disinfection of catchworks:*

All of the products used to clean and disinfect catchworks must comply with the regulations laid down for water intended for human consumption.

VII - Bottling of natural mineral waters

No original or recycled materials likely to alter water quality may be used for the packaging of natural mineral waters.

VIII - Monitoring and control of packaged natural mineral waters

Monitoring is the responsibility of operators who must ensure that the natural mineral water they package complies with hygiene rules at all stages of production and distribution. This requires the ongoing monitoring of production facilities. Moreover, and for greater responsiveness in the event of a health risk, the creation of an internal laboratory with quality certification is highly recommended.

Controls are performed on the request of the authorities.

As for the optimal implementation of authorised treatment methods and exploitation conditions, it is unfortunate that guides to good practice have not been developed by the profession and validated.

ANNEX 1
CONCEPTS AND METHODS USED IN HYDROGEOLOGY

I – Concepts and definitions

I.1 - Phases and media

When investigating groundwater, whether or not "mineral" water, there are usually two or three "phases" to be considered as defined by the laws of physics: a solid phase and one or more liquid phases.

- The solid phase, almost solely mineral, comprises consolidated or loose rock whose pores, interstices, fissures or fractures are occupied by one or more liquids trapped there or able to flow to a greater or lesser degree;

- The liquid phase: if only gaseous, the medium is considered to be dry. If gaseous and liquid phases coexist, then the medium is unsaturated (moist, in the case of water) but if all the voids are filled with liquid, the medium is obviously saturated.

▪ The solid phase has a twofold role to play:

- *physical* role:
  . linked to capacity and geometry. The number and distribution of voids in the rock determines the type and proportion of porosity;
  . linked to the mechanics of transport. Friction is created when liquids move, revealed by the concept of permeability;

- *geochemical* role: it contributes to a large extent by fluid/mineral exchanges to the physico-chemical quality of the liquid phase, and especially the water residing in or passing through its voids.

▪ The gaseous phase (mainly air and carbon dioxide but sometimes H_2S and hydrocarbons) can also play a twofold role:

- *physical* or *mechanical* role: fragmentation of the liquid phase in an unsaturated medium with trapped bubbles obstructing water flow, and creation of liquid/gas interfaces where surface tension leads to capillary retention, without forgetting the role of dissolved gases released when pressure drops, which can lead to an eruption of a mixture of water and gas widely known as a *gas lift* and particularly common in carbogaseous water;

- *chemical* role: exchanges between the gas and rock, with or without the participation of water, dissolved gases that play a role in water quality, whether directly or by action on the minerals of surrounding rocks (e.g. carbonate removal).

▪ The liquid phase is divided into categories whose properties differ according to their energy state (intensity of total potential: gravitational potential + pressure potential): some of the water is immobilised to a greater or lesser degree, while the rest is mobile. Distribution is unequal within the same solid environment, depending on whether the medium is saturated or unsaturated:

In a saturated medium,

The *immobile* liquid phase includes:

- *adsorbed* water (adsorbed by electrostatic or molecular attraction) in layers that are more closely linked the nearer the surface of the solid they are: this water is at a much lower pressure than atmospheric pressure,

- water *trapped* in the pores or dead-end fissures of the solid rock matrix;

- The *mobile* liquid phase fills all the remaining voids: it is at a pressure equal to or greater than atmospheric pressure. This is the *gravitational water* that outflows at exits or is collected by gravity in draining or pumping works.

In <u>a partially unsaturated medium</u>,

- The *immobile* liquid phase includes:

  - *adsorbed* water and *trapped* water,

  - and**,** in the unsaturated part only, *suspended capillary* water: isolated drops that are trapped where pressure is below atmospheric pressure. This water cannot flow by gravity. It is what makes soil moist and is drawn out of the ground by plant roots;

- the *mobile* liquid phase includes:

  - in the saturated part, the same type of gravitational water as above,

  - together with, in the unsaturated part**,** above the level where pressure is equal to atmospheric pressure (piezometric level of unconfined groundwater: see §1.3.3): a *capillary fringe* whose height is inversely proportional to the mean radius of interstices (Jurin's law), this water is known as *sustained capillary* water because the capillary fringe fluctuates with the level of the subjacent groundwater.

I.2 - Porosity, storage coefficient, permeability and transmissivity

I.2.1 - Porosity

Porosity expresses the ratio of voids to the total volume of a polyphase medium. <u>Total porosity</u> takes into consideration the volume of all the voids.

The term *matrix porosity* is conventionally used to describe the total porosity of a rock: pores or narrow fissures in a compact rock such as chalk or dolomite, or a vesicular rock such as foamy basalt. In unconsolidated rock such as sand or gravel, or cemented granular rock such as sandstone, we talk of *interstitial porosity*, whereas in granite or limestone rock it is more likely to be *fissure porosity* or *fracture porosity.* Some rocks can manifest two or even all three types of porosity.

As not all voids allow water to flow by gravitation, this concept should be detailed for water in:

- a constantly saturated medium: the term <u>kinematic porosity</u> expresses the ratio between the volume occupied by gravitational water and the total volume; this is a key parameter for calculating mass transfer (or transit) in a saturated medium (e.g. transfer of a pollutant);

- a saturated medium during drainage (i.e. becoming unsaturated). The quantity of gravitational water freed by a drop in the level of saturation is less than in the previous case because part of the water remains trapped by capillarity: the volume of water collected gravitationally with respect to the total volume is then known as the *effective porosity*, which is below that of kinematic porosity in the same medium.

I.2.2 – Storage coefficient

It is important to estimate a terrain's capacity to store gravitational water (terrain being a geological formation, whether sedimentary or not).

The storage coefficient (S) is expressed by the volume of water freed (dV) by a head loss (dh) in a vertical prism of unit cross-section (dA): $S = - dV/(dh \cdot dA)$.

- in unconfined groundwater (see definition in § 1.3.3), it is part of the saturated medium which, when becoming less saturated through drainage frees gravitational water: the storage coefficient is then identical to *effective porosity* (generally $10^{-2} < S < 10^{-1}$);

- in confined groundwater (see definition in § 1.3.3), the saturated medium remains saturated but the drop in pressure leads to a slight increase in volume of the water (as it is not totally incompressible) and especially compression of the terrain (due to the increase in effective stress) which leads to a decrease in the volume of voids and thus the expulsion of a corresponding volume of gravitational water. The storage coefficient is thus much lower than the effective porosity of the same medium ($S << 10^{-2}$).

I.2.3 - Permeability

According to Castany and Margat, 1977, permeability is the aptitude of a medium to allow itself to be traversed by a fluid under the effect of a hydraulic gradient. For water, this is the specific discharge (q *or* v = Q/S) through a filtering medium subject to a unit hydraulic gradient (i = - dh/dl) i.e. through a prism of the filtering medium considered as continuous of cross-section (S) and of length (dl) units, subject to a head loss (- dh) per unit between inlet and outlet, under the conditions where Darcy's law applies. We should then talk of *Darcy's permeability coefficient* or, by analogy with similar laws proposed by Ohm, Fourier or Fick in continuous media, of *hydraulic conductivity*. In hydrogeology, this is often the parameter understood when the generic term "*permeability*" is used. It is therefore expressed in terms of velocity ($L \cdot T^{-1}$), normally in m/s, and represented by "K":

$$Q = - S K (dh/dl) = S K i \qquad \text{(Darcy's law)}$$
$$q \ or \ v = Q/S = - K (dh/dl) = K i$$

As most sedimentary layers are stratified and as in rock formations there is often a main direction of fracturing, permeability is generally higher along these fracture planes than perpendicular to them. It is always easier to flow along layers or most fracture planes than perpendicular to them. In an anisotropic medium, permeability must therefore be represented by a tensor.

As this coefficient depends both on the nature and state of the fluid (dynamic viscosity and per volume ratio depend on the nature of the fluid and vary according to temperature and pressure) and on the geometry of the solid phase (possibility of entering pores, interstices or fissures to a greater or lesser extent), it is sometimes necessary—and particularly for very hot water—to use the values conventionally used in oil exploration of *intrinsic permeability,* which only depends on the reservoir and is therefore equal to a surface area (the AFNOR standard unit to measure this permeability is the darce, equal to 10^{-12} m². The darcy, which is 0.987 of a darce, is no longer a legal unit as it was defined according to the CGS system).

I.2.4 - Transmissivity

The transmissivity parameter (T) expresses flow by one unit of width (measured orthogonally to the direction of flow) of a saturated terrain with unit hydraulic gradient. It is therefore the product of the Darcy permeability coefficient (K) per saturated thickness (e), which is easy to use because it is T and not K that is determined by a pumping test. If the cross-section orthogonal to the flow is $S = e \cdot L$ (where L is the horizontal width of the flow front), Darcy's law may be written:

$$Q = S K i = L e K i = T i L \qquad \text{where } T = K e$$

Transmissivity is therefore $L^2 \cdot T^{-1}$ and is usually expressed in m²/s. Like permeability, it must be represented by a tensor if the medium is anisotropic.

Transmissivity and the storage coefficient are the main two *hydrodynamic characteristics* of an aquifer (see definition in § 1.3). It should be noted, however, that these hydrodynamic characteristics, used mostly when studying groundwater, are not very well suited to karstic aquifer networks.

I.3 - Aquifers and groundwater

These two terms must never be mixed up. An *aquifer* refers to the water <u>bearer</u>, whereas *a groundwater* refers to the water being <u>borne</u>.

I.3.1 – Behaviour of different kinds of terrain with respect to water

Soil, loose rocks and consolidated rock in geological formations may be:

- <u>aquifers</u> if the pores or fissures communicate and are sufficiently wide for water to circulate freely as dictated by a difference in hydraulic potential (hydraulic head). This kind of water-bearing layer is said to be permeable ($K > \sim 10^{-5}$ m/s);

- <u>aquicludes</u> if the pores or fissures do not communicate or are too narrow for water to circulate freely as dictated by a difference in hydraulic potential. This kind of layer is considered to be impermeable ($K < \sim 10^{-9}$ m/s), although aquicludes such as clay and mud can sometimes bear much more water than aquiferous rocks because of a more developed total porosity, and allow significant quantities of water to flow over the time associated with geological features (in other words no ground is completely impermeable);

- <u>aquitards</u> or semi-permeable layers, which lie between the two extremes described above ($\sim 10^{-5} > K > \sim 10^{9}$ m/s). They are not permeable enough to allow water to flow horizontally but are sufficiently permeable to allow a slow vertical transfer from or to an aquifer (a movement known as leakage). They play a major role in replenishing semi-confined groundwater (see the section on groundwater § 1.3.3.).

I.3.2 - Aquifers

When studying strata, an aquifer is considered to be a geometrically defined body (strata or block) made up of aquiferous (permeable) rocks. It may:

- be fully saturated under a nearly impermeable or aquiclude stratum (confined aquifer) or under a semi-permeable or aquitard formation (semi-confined aquifer),

- include a saturated area above which lies an unsaturated area allowing direct exchange with the atmosphere. In this case, the aquifer is said to be unconfined.

The position and nature of its boundaries dictate not only the volume of the aquifer reservoir but more especially the hydrodynamic phenomena (flow and pressure transfers) affecting it.

An aquifer has two very different yet complementary functions materialised through its *hydrodynamic characteristics* (T & S: see § 1.2.2 & 1.2.4):

- a <u>capacitive function</u> relating to water storage and measured by its "storage coefficient" (equivalent to "effective porosity" in the case of unconfined groundwater). The total volume of water contained in an aquifer at a given moment and able to be freed under gravitational forces is its total *groundwater storage*, part of which may or may not be permanent, because some aquifers do not have any permanent storage and others may no longer be recharged at present and only contain permanent storage. It is only in the latter case ("fossil water") that we can talk of a water deposit in the same way as we talk of oil deposits in oil exploration;

- A <u>transmissive function</u>, expressed by the "transmissivity" parameter (see § 1.2.4), which demonstrates the aquifer's ability to let water flow under gravity to exits, catchworks or drains. This transmissive function emphasises the fact that an aquifer is not just a reservoir but that water flows through it. It is a place of transfer (*pressure transfer* in water) and transit (water movement or *mass transfer*).

This dynamic aspect, linked to <u>water flow</u> through an aquifer, means that **all quality and quantity issues should be addressed in terms of flow rather than volume**: recharge, turnover, volume

balance, resources, acquiring or modifying quality, pollution hazards and sustainable exploitation. None of these aspects should be left out when considering an aquifer, let alone when considering an aquifer system, which is the best groundwater management unit (see § 1.5.3).

I.3.3 – Groundwater

Groundwater is defined as *gravitational water* (see § 1.1) forming a continuous reservoir within the saturated zone of an aquifer.

Most of the major groundwater sites exploited in France are contained in porous sedimentary aquifers of a regional extension. Fissure groundwater —especially in crystalline rock formations—can also be of regional interest if only for its interaction with surface water (e.g. Armorican Massif groundwater). Some aquifers contain both interstitial groundwater and fissure groundwater or even fracture groundwater (one example being the chalk aquifer in the Paris basin).

When the aquifer is heterogeneous at terrain level (rocks with open fissures that are dispersed and discontinuous or criss-crossed by troughs and solution cavities) and there is no continuity for water between the various pathways, we talk of an "aquifer network" or "karstic network" rather than groundwater.

Groundwater, part thereof or even an aquifer network may be unconfined, confined or semi-confined.

- Unconfined groundwater consists of gravitational water saturating the lower part of an aquifer whose upper limit of saturation lies at atmospheric pressure and constitutes the real groundwater level (level of the water found in a well or borehole). Unconfined groundwater is always found underneath an unsaturated zone (capillary fringe and suspended capillarity zone) through which atmospheric exchanges take place (infiltration, evapotranspiration);

- Confined groundwater consists of gravitational water at pressure within a saturated aquifer confined between two impermeable strata (i.e. aquicludes). The groundwater level (altitude at which the water would be at atmospheric pressure and would therefore rise into a well or borehole) is virtual. When the altitude of this virtual level is above ground level, the groundwater is known as artesian water and artesian wells flow like natural springs;

- Semi-confined groundwater consists of gravitational water which, under pressure, saturates a semi-confined aquifer. It is "semi-confined" because its upper limit is a semi-permeable stratum (i.e. an aquitard). Again, the groundwater level is virtual. Underestimated for many years, semi-confined groundwater are much more common than truly confined groundwater .

I.4 - Resources

Although certain countries have to exploit fossil water in the same way as a mineral or oil deposit, in most countries with sufficient rainfall, it is only reasonable in the long-term to use as much water as the turnover amount. The mean and peak exploitation of fresh water (whether groundwater or surface water) must take turnover conditions into account (or the deposit's planned lifetime). Whatever the case, the parameters are water volume versus time. Water *resources* are discussed in terms of *flow rate* rather than volume. It is thus possible to make a distinction between (see Margat, 1996 and Crampon, 2003):

        ▪ renewable groundwater resources that are:
            - irregular (episodically, and even exceptionally, during high water)
            - regular (base flow):   - unavailable
                                     - available: - not exploitable
                                                       - exploitable
        ▪ non-renewable groundwater resources:
            - storage unable to be depleted
            - storage able to be depleted x P % / yr

Consequently, there are much fewer exploitable water resources than total resources even when there is a good turnover. However, as exploitability is often more of an economic concept than a

technical one, water resources can only be estimated within a geographical entity suited to its management methods (state, region, large aquifer, part of an aquifer, etc.).

Note: French standard NF X 50-911 on control of natural mineral water resources does not define the word "resource", but seems to refer to the Larousse dictionary's definition of *natural resources*: "all the potential offered by a physical environment, particularly in the areas of energy, mines, forestry etc.". Although the expressions "global management of the resource" and regular assessment of the "evolution of water resources" used in this standard lead to confusion because they are associated with the dubious notion of "deposits" (see § 1.5.4), they are nonetheless comparable to the abovementioned notion of "exploitable water resource".

I.5 – Management entities

The evaluation of resources therefore depends on the scale involved in their management. When dealing with a state, for example, it is important to distinguish internal resources from external ones, because some states are extremely dependent upon the cumulative natural flow from surrounding countries (and therefore upon any reduction, whether effected on purpose or not).

In a country like France, the natural management entity for groundwater would be that of each aquifer, defined geologically and hydrogeologically. Yet the issue is often more complicated than it first appears. On the one hand, some major aquifers are spread over several administrative areas such as regions, *départements* or even major basins. On the other, several overlying aquifers that communicate through leakage to a smaller or greater extent may coexist in certain regions (especially the Aquitaine region in South West France). Furthermore, in the same aquifer the groundwater may be compartmentalised by watersheds (piezometric divides) that may change according to the season and exploitation or by the drainage that streams and rivers represent.

I.5.1 – Hydrogeological basin

Simple or complex aquiferous zone in which groundwater flows towards the same outlet or group of outlets and delimited by a groundwater divide (watershed). It is the underground equivalent of a catchment area for surface water (Castany & Margat, 1977).

I.5.2 – "Body of groundwater"

A "body of groundwater" is a recent concept defined by European Water Framework Directive 2000/60/EC of 23 October 2000 (Article 2-12) as "a distinct volume of groundwater within an aquifer or aquifers".

Surface water and groundwater are the new "basic units of the reference system used to assess, per district, the status of resources and the efficacy of the measures implemented to comply with directive requirements". Again, the concepts behind these management units do not fully cover the "objects" known in hydrographic or hydrogeological terms, such as catchment areas or aquifer systems (Chadourne, 2002).

I.5.3 – Aquifer system

Assessing the groundwater resources of an aquifer available for various uses (or the sum of foreseeable uses) requires devising relatively independent units or parts of aquifers for which a water balance will be drawn up to compare inflowing and outflowing water (Caous, 1994). The concept of an aquifer system corresponds to both (Castany & Margat, 1977):

- a <u>sequential geometric unit</u>: one inlet (the infiltration or recharge zone), an underground system (within one or more aquifers or arising from one or more fractures) and an outlet (or group of outlets), corresponding to a particular geological structure,

- a <u>dynamic process</u>: water flow, whether permanent or transient, its boundary conditions (linked to the geological structure), and finally its initial and final conditions (more or less dependent on the weather conditions that govern recharge and on exploitation conditions).

The concept of an aquifer system is based on a hydrogeological approach to a specific underground system that forms part of the general water cycle. It can apply to one part of a vast aquifer (delimited with respect to lithological and geographical aspects) which functions autonomously (such as a hydrogeological basin), but it applies even better to a fissured or karstic network or part of a network which also functions independently and very differently from groundwater.

Standard NF X 50-910 on terminology related to spas has chosen the following definition: "Aquifer system: set of aquiferous terrains constituting a hydrogeological unit. Its hydrodynamic characteristics make it nearly independent with respect to the groundwater it contains (no effects outside its boundaries). It is therefore a management entity for this groundwater". This definition is similar to the hydrogeological definition but omits the essential concept of a dynamic system, i.e. a global flow system.

I.5.4 – "Deposit"

- Administrative definition and concept for natural mineral waters:

  - Standard NF X 50-910 on spa terminology has defined a deposit as the entire underground geological structure located under a delimited geographical area, from which it is possible to extract natural mineral water using appropriate techniques.

  - Standard NF X 50-911 on control of natural mineral water resources, when recommending self-monitoring of the whole aquifer system, is nonetheless more accurate, appearing to assimilate "deposit" and "aquifer system".

- Dictionary definition:

  - Deposit: a natural, local accumulation of mineral matter (solid, liquid or gas) that can be exploited.

  - Deposit comes from the Latin *depositus*, meaning "laid down".

- From a hydrogeological viewpoint

The word "deposit" is hardly ever used because it could only apply to a large volume of immobile water (large, permanent groundwater storage) or fossil water, both of which could be exploited in the same way as the mining or oil industries extract ore or oil.

To conclude, it would be preferable to exclude (or strictly limit) the use of the word "deposit" for groundwater and replace it by the term "aquifer system".

I.6 – Inlets and outlets of an aquifer system

I.6.1 – Recharge

- The recharge area is the "area where water arrives either continuously or temporarily to flow into groundwater or a defined aquifer, especially a semi-confined aquifer that is not replenished over the whole area. It is the place where the current lines of a water table originate" (Castany & Margat, 1977). We can also talk of a recharge area for a defined outlet (spring or catchwork). A distinction must be made between:

  - The intake area is the "recharge area of an unconfined aquifer: part of the surface receiving water by the *effective infiltration* of precipitation or surface water contained in streams or rivers" (the term *impluvium* is sometimes used);

  - The inflow area is a "recharge area for a semi-confined aquifer through one or more underlying or overlying semi-permeable strata by *leakage* from aquifers with a higher hydraulic head."

I.6.2 - Outlets

Of all the outlets into open air that an aquifer system may have, there are several kinds of natural discharges (effluent or other seepage, springs, exsurgences, resurgences, etc.) that may or may not be collected, but often the aquifer system has been modified by drilling which has created new discharges (artificial boreholes) or allowed exploitation by pumping. Much could be said on the exact meaning of each of these terms. Only the concepts covered by the words "discharge", "discharge point" and "spring" are defined hereafter:

- **discharge**: "Any appearance of groundwater at the surface, whether local (spring) or diffuse (effluent or other seepage, exfiltration)" (Castany & Margat, 1977). It expresses the fact (and place) that the water appears one day. By extension, we may consider an outlet of natural water from an Artesian well as a discharge, but not water that has been pumped out. Yet Artesian wells modify the balance of pressure within an aquifer system.

  The definition of <u>standard</u> NF X 50-910 on spa terminology is no longer scientific because it applies to boreholes. It defines a discharge as the point at which the emerging natural mineral water can be exploited.

- **spring:** "Place where water begins to well out, where it appears above ground and starts a constant flow" (*Dictionnaire de l'Académie*, 1964 in Castany & Margat, 1977) or, more accurately, "place and quite easily located phenomenon of natural groundwater flowing out onto the surface, usually at the origin of a stream" (Castany & Margat,1977).

- **discharge point:** "Any easily identified and located (on a large scale) individual point of discharge" (Castany & Margat, 1977). The term "discharge point" is usually only used for natural mineral waters and the *Petit Larousse illustré*, 1992, describes it more explicitly as a "discharge point of mineral or thermal water."

  The definition used in <u>Standard</u> NF X 50-910 on spa terminology is a "complex consisting of one or more natural discharges or boreholes from the same groundwater or underground deposit." This <u>definition</u>, which neither complies with the dictionary nor the scientific definition, and furthermore refers to the inappropriate notion of a deposit, is consequently itself <u>inappropriate</u>.

I.7 – Vulnerability, hazards and risks

Vulnerability is a relative property of a medium that cannot be measured, has no dimension (Vrba & Zaporozec, 1994, Goldscheider & Popescu, 2004) and facilitates communication between the surface and point of catchment. It is based on the concept of source-pathway-target.

- *Intrinsic vulnerability* is defined as the ease with which water follows a path from the surface to the point of catchment inherent to that medium. This implies determining transit by a conservative tracer flowing at the same speed as the groundwater. Intrinsic vulnerability is therefore assessed "by excess" and does not take into account delays or attenuation. It mainly depends on the rainfall and three factors peculiar to the geological medium:

  - Infiltration, which can be diffuse, occur around a particular site (such as local run-off towards a fault) or concentrated (occasional loss);
  - Protective cover: the aquifer may lie under a thick stratum which does not allow water to pass easily;
  - Drainage, assessed using tracing techniques (see § II 10.1) and a residence time distribution (RTD) curve. These methods reveal several fracture networks and determine the medium's dispersivity. Natural tracing (see § II 10.2) using non-conservative markers is used to date outflowing water.

- *Specific vulnerability* (Sinreich *et al.*, 2004), on the other hand, takes into account the physico-chemical behaviour of contaminants (adsorption, precipitation, complexation, oxidation-reduction etc.) in the ground through which they pass due to their physico-chemical properties (% clay, carbonates, organic matter, iron oxides etc.). The specific vulnerability coefficient is used to

weight intrinsic vulnerability. It always reduces it but the reduction depends on the nature of the contaminant.

▪ A *hazard* is a human activity likely to permanently or accidentally contaminate the resource. There are diffuse hazards such as agricultural fertilizers, herbicides and by-products, linear hazards such as road, rail or canal networks and local hazards such as industrial sites, discharge from sewage works or tips.

▪ A *risk* is defined as the conjunction of a high hazard rating and high vulnerability. A medium may be vulnerable but, if there are no or only well-controlled hazards, there is little risk of contamination. If the hazard rating is high but vulnerability low (for example if there is a thick, nearly impermeable stratum above the aquifer), again the risk is low.

It is therefore necessary to assess and map vulnerability and hazards separately. The resulting map can then be used for land development purposes, to determine land use. It is not easy to manage land in this way when dealing with natural mineral waters because a private company cannot establish access on other private land unless it can buy the land making up the sensitive recharge (or circulation) area or if the water is bought from a body authorized to establish a protective perimeter.

II – Means and methods

The investigations needed to pinpoint the origin and vulnerability of natural mineral water (see the second part of the report, "*Hydrogeological context, vulnerability of the aquifer system and catchment*", § IV) involve not only acquiring the concepts and definitions laid out in the previous section, but also implementing suitable means and methods, especially those described below.

II.1 – Geological mapping

- Documentation: find general and specific documents relating to the area: published geological maps, regional and local geological cross-sections, University papers or other, mining surveys or surveys relating to major work in the area, any surveys (even if old) on tapping mineral water;

- Detailed mapping of the site: if no map is available, one must be drawn up to detail lithology and structure, fracturation, weathering and surface strata.

II.2 - Geophysics

Collection of all the results of geophysical surveys carried out in the area: cross-sections, synoptic profiles and maps identifying marker horizons and major fractures.
Comparison with the geological data and synopsis.

II.3 – Piezometric level

To define an aquifer system's hydrodynamic type, it is necessary to try to establish its piezometric level in natural conditions (no pumping):
- measure the water level (with respect to the French NGF sea level reference system) at the catchment point at rest as drilling continues in order to reveal connections between the catchwork and any other parts of the aquifer system, and to compare the arriving water with surrounding water (surface water or groundwater). The goal is to reveal the existence of a multilayer, any independent arrivals via fissures or even extraneous water. Once the catchwork has been finished, it is necessary to compare the static water level with the borehole's geological cross-section to determine whether the aquifer is confined or not. When measuring artesian pressure, the outlet pressure will be assessed as zero. Comparing the piezometric data with the altitude of the assumed intake area may resolve certain ambiguities;
- measure the water level in other wells, boreholes or piezometers in the area, whatever the related aquifer system. In certain cases, this can allow us to differentiate the aquifer systems being

tapped at each catchment point, to estimate the possibilities of exchange between the systems and, when it is the same aquifer system, to determine the hydraulic gradients and direction of flow;

- record water levels at the catchment point during rest and in the piezometers measuring the same aquifer system. The analysis of fluctuations with respect to rainfall (amplitude, delay) will provide important information on effective porosity, the degree of fracturation and the response time to infiltration (pressure and not mass transfer), which can be particularly useful for quantifying the resource and determining its vulnerability.

II.4 – Water balance

The quantitative comparison of inlets and outlets for any one aquifer system is a useful method to assess its general operation. With enough sufficiently accurate data on the flow rate of receiving streams, the flow rates of natural discharges and production boreholes, the amount that returns to the natural environment and on total precipitation, we can deduce the aquifer's renewable natural resources. This method can also be used to estimate actual evapotranspiration and, consequently, validate the balance by comparing the actual evapotranspiration value thus deduced with other values obtained by the usual empirical calculation methods (Crampon & Caous, 2006). If we know the total average groundwater storage (volume of the saturated aquifer multiplied by effective porosity or the storage coefficient, depending on the case), we can deduce the rate and time taken for its replenishment (Detay, 1997). This method is more easily applied to a system containing a groundwater than a karstic or fractured system. Nonetheless, it is still essential to assess the water balance even for the latter systems, because we can check whether the flow rates of known or assumed inlets are in accordance with outlet flow rates and, in the event of a systematic lack of correspondence, we may seek previously unidentified inlets or outlets. In the case of pumping, a relevant water balance means that it is possible to check that the aquifer system is not being overexploited and, if necessary, to set a ceiling production flow rate.

II.5 - Hydrometry - hydrology

Data on the regimen of surrounding surface water and especially the regimen of water coming directly from the aquifer system can afford precious information. We therefore need to study the catchment area(s) likely to provide the underground aquifer system with inflowing water (more or less diffuse losses) or, even more relevant, outflowing water.

Useful information on how the aquifer system functions (dynamic volume, inertia, overflow or complementary inflows etc.) and its type may be gained from analysing hydrographs (logs of flow rates or levels) at the outlet (classified flow rates, recession curve). Correlatory and spectral analyses using all the rainfall/flow rate records may show how inlet information is echoed at the outlets and could be used to compare, through correlation techniques, one or more systems of the same type (Mangin, 1984; Maqsoud, 1996; Maqsoud *et al.*, 2003-a).

II.6 – Cross-section of the catchwork and logs

A detailed geological cross-section of the catchwork producing mineral water, showing boreholes, infiltration galleries or any other system tapping the groundwater is necessary to determine whether the aquifer reservoir is in a porous medium or has a fine network of fissures and will give a preliminary idea of its lithological nature. The section will also show whether the aquifer system is a karstic system and will reveal networks of fissures or veins. Point data must be indicated and quantified. A technical cross-section will specify certain points such as the levels tapped (presence of a liner and/or additional infiltration galleries).

Of the different methods of investigating a borehole, velocity measurements using a pygmy current meter are among the most useful to sound out an aquifer and determine its possibilities. The distribution of vertical velocity in a borehole, whether natural or the result of pumping or the injection of water, may be used to determine productive and unproductive areas, and the actual thickness of a productive aquifer. If the borehole was correctly drilled and there are not many anomalies (particularly

cavities), it is possible to compare flow rates by increments of level and total flow rate to give an idea of individual transmissivities once global transmissivity has been determined by a pumping test. Such a log will allow the liners to be placed at the most productive levels and thus make substantial savings. This low-budget but very useful method should be systematically applied to each exploratory borehole, particularly for mineral water.

II.7 – Pumping tests

- A <u>long-duration</u>, <u>constant flow</u> pumping test (aquifer test) with a log of levels (or pressures) in the catchwork may be used to determine the total transmissivity throughout the height of the aquifer traversed. An additional piezometer will specify the value of transmissivity and determine the storage coefficient. The test should be complemented by a measurement of the new water level once pumping has stopped.

- A well production test is often a useful complement to set the maximum production flow rate. Such tests, conventionally performed when tapping groundwater, are more difficult to interpret when dealing with a karstic or fissured aquifer system.

- Very useful information on the hydrodynamic role of fractures and the functioning of the aquifer system can be obtained whether the aquifer is in bedrock or a fractured limestone medium by methods specific to each medium (Gringarten, 1982; Bangoy, 1992; Louche *et al.*, 1994).

II.8 - Modelling

Different methods have burgeoned in keeping with the increased capacity available for numerical calculations:
- <u>Global models</u> known as "<u>black box</u>" models, where the objective is to find the transfer function that transforms an input signal into an output signal. Such models work quite well for fissured or karstic aquifer systems when there is a record of both precipitation (input function) and outlet flow rates (hydrographs);
- <u>Global deterministic models</u>, based on the outlet of multiple reservoirs representing hydrogeological units making up the aquifer system, particularly the MMO8 model (Mero, 1978);
- <u>Discrete or Matrix deterministic models</u>, which resolve the differential transfer equations from one grid or node to another using the method of finite differences or finite elements, ensuring suitable potential or flow boundary conditions in addition to initial conditions in the case of the transient model. These 2- or 3D models are mostly used when groundwater is contained in a large aquifer system (summary of methods and bibliography in de Marsily, 1986);
- <u>Stochastic models</u> using probabilistic methods, often applied to reconstitute data or estimate parameters (including hydrodynamic characteristics) from a known spatial distribution (kriging), but also to simulate certain flows, particularly from random recharges, using partial differential stochastic equations (explanations and bibliography in de Marsily, 1986);
- <u>Neuronal models</u> based on a network of artificial neurones that simulate the way the nervous system processes information (summary of methods and bibliography in Lallahem, 2002).

II.9 – Chemical composition and hydrochemical data analysis methods

<u>Chemical composition of water</u>: as it flows through geological structures, water takes minerals and gases from the surrounding rocks. The gases may be in the rock due to genesis, they may be trapped there or be simply passing through. The water usually acquires its chemism gradually. It is not therefore unusual for the water to have different mineral compositions at the start and at the end of its journey through the aquifer system, nor for it to differ at the outlet from one season to the next. The chemical exchanges between the water and rock depend on numerous parameters such as the acidity of infiltration water, the nature of surface formations (particularly the soil), possible reactions due to dissolution, precipitation or oxidation-reduction, temperature, duration of contact (flow conditions influence mineralization), etc. Studying the water's chemical composition offers clues as to its pathway through the geological structure.

Logs of physico-chemical parameters (Bakalowicz, 1979, Mudry, 1987). If a log is kept, the data will show how mineralization changes. This is relevant not only when considering vulnerability but also when the goal is to determine the structure and operation of aquifer systems, by:
- Identifying recharging with young water (often surface water),
- Revealing the presence of deep water with a long residence time,
- Differentiating the different groups of water collected,
- Identifying the main aquifer (which would ensure waterhole recession) and characterising its mineral content so as to target it for recapture,
- Demonstrating that a borehole belongs to the same hydromineral source as neighbouring springs.
It is often beneficial to correlate physico-chemical parameter logs with rainfall and flow rate logs.

Hydrochemical data analysis methods The most common are as follows:

- Chemiographs (concentration versus time) of elements characteristic of mineral content which can be studied in a natural regimen or while pumping. Drops in concentration reveal recharging by young water which is often surface water and therefore exposed to chronic and/or accidental pollution (Mudry, 1987). Increases reveal the inflow of deep water with a long residence time, which can also contaminate the natural mineral water resource through excessive mineralisation by elements such as iron, fluorine, barium or arsenic.

- The distribution of content frequencies (Bakalowicz, 1979) through which it is possible to differentiate between types of water collected. A unimodal distribution curve reveals an aquifer that mixes the water well, does not vary much with the inflow of surface water or deep water and which therefore offers stability. A plurimodal curve reveals a sequential collection of different water groups at the outlet and does not guarantee a stable chemical composition.

- Chemical flow/flow rate curves (Blavoux & Mudry, 1983, Mudry, 1991) are used to identify the main aquifer (that will ensure waterhole recession) and characterise its mineral content so it can be targeted for recapture.

- Multivariable analyses based on physico-chemical analysis tables which summarise information: inter-variable correlation, similarities between different sampling points and/or sampling periods at the same site.
  - Principal component analysis (PCA) is a descriptive statistical method on continuous numerical data using the Euclidian metric (Blavoux & Mudry, 1986). The disparity between ranges of chemical contents requires an analysis using standard variables so that each variable has the same variance (same weight). The interpretation of the main axes of the space for variables (chemical contents) allows the interpretation of the space for individuals (sampling).
  - Correspondence analysis is also a descriptive analysis on discrete data (qualitative variables). It uses a probabilistic Chi^2 [33] metric and allows the simultaneous display, on the same graph, of quantitative variables (chemical contents previously discretised into classes) and qualitative variables, but also variables and individuals, thus simplifying the characterisation of samples using descriptors (Mudry, 1987). Qualitative variables may be geological (lithology, proximity to a fault, etc.), geomorphological (crest, slope, valley, etc.), to do with land use (grassland, maize, vines, greenhouses etc.), nature of the groundwater (unconfined or confined), climatological etc. (Lacroix, 1991)
  - Automatic classifications are other modes of representation in multidimensional space. While PCA and correspondence analysis represent points projected in two-dimensional space, bottom-up hierarchical classification represents the multidimensional distance between points. The algorithm clusters the closest points. The tree structure thus obtained materialises the similarity between the chemical composition of different samples.
  - Discriminant factor analysis is an inferential (or decisional) statistical analysis method designed to validate a hypothesis (Mudry, 1991, Abdelgader & Mudry, 1995, Abdelgader et al., 1996 a & b). Items (samples) are divided up into membership groups (qualitative variable to be tested). The algorithm calculates the distance of a point from the barycentre of different predefined groups. If the item is nearer the barycentre of its own membership group than that of the other groups, it is considered well categorised. If it is further from its own group's barycentre then it is reallocated to the group to which it is statistically closest and is considered poorly categorised.

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[33] **Chi^2 is a dispersion measurement of a statistical population with discrete data.**

This powerful method can show, for example, that a borehole belongs to the same hydromineral deposit as neighbouring springs.

II.10 - Tracing

II.10.1 – Artificial tracers

Artificial tracing is used to check the hypothetical relationships between an aquifer system's inlets and outlets and, consequently, identify intake points (recharging). Artificial tracers are usually pulse injected directly into the groundwater or at an aquifer intake point. The tracer must comply with numerous conditions: it must be highly soluble, not very absorbable by clay particles, non degradable, practically inexistent in the water to be traced, easy to dose even at very low concentrations, and must not be toxic. The most common are sodium or potassium iodide (colourless) and xanthene-based dyes such as uranine or rhodamine. Restitution is followed by sampling at a spring or in a borehole used for pumping. Enough samples must be taken over a long enough period to be able to establish the most complete restitution curve possible (Gaspar, 1987; Crampon *et al.*, 1994)

- For groundwater, tracing tests reveal the transfer times by pure convection and consequently the flow-through velocity (mass transfer), effective (kinematic) porosity and dispersivity, parameters needed to assess the vulnerability of a catchment point with respect to potential pollution sites. They are sometimes, but not often enough, carried out in order to determine the protective perimeter required for a catchwork used to supply institutions.

- When dealing with fractured aquifers (fracture network) or karstic media, they are primarily used to show the existence of a relationship between a localized inlet (loss) and a natural discharge or catchment point. Unlike the case of groundwater, the resulting curve is not used to determine hydrodispersive parameters (dispersivity and kinematic porosity) but to analyse residence time distribution and determine the aquifer system's characteristic pulse response (Duffy & Gelhar, 1985), to reveal the different pathways through the structure and, under certain conditions, to estimate restitution under different regimen conditions (Dzikowski, 1992; Crampon *et al.*, 1994).

II.10.2 – Natural tracers

Natural tracers are simply the physico-chemical parameters specific to conditions characteristic of a recharge area (mineralogical nature, temperature, rainfall intensity etc.) or of terrain through which the water in an aquifer system passes. For example, leaching from gypsum-rich ground influences the water's composition, just as dolomitic terrain adds magnesium. Analysing the water's chemical composition at a discharge point can help determine the aquifer system's structure (see § II.9).

This analysis can be usefully complemented by quantifying the <u>stable isotopes</u> of elements present in the water, which can also provide precious information on its source:

- The isotope fractionation of <u>oxygen</u> from precipitation ($^{18}O/^{16}O$) varies with <u>altitude</u>, making it possible to determine that of the recharge area so long as the altitudinal gradient of this fractionation has already been established in the region under study and assuming that the altitudes to determine are sufficiently wide apart.

- The isotope fractionation of <u>carbon</u> ($^{13}C/^{12}C$) can be used to retrace the origin of carbon in its dissolved gas phase (CO_2), mostly from deep sources, and/or the dissolved phase (carbonates or hydrogen carbonates).

- Determining the relative quantity of <u>sulphur</u> isotopes ($^{34}S/^{32}S$) is also very useful for specifying the origin of sulphates (evaporitic or through oxidation of pyrite etc.), a technique employed to analyse the region of Saint Amand les Eaux (Droz, 1985).

- The ratio of <u>nitrogen</u> isotopes ($^{15}N/^{14}N$), which can help determine the source of nitrogen compounds in groundwater subject to the influence of human activities (wastewater, mineral or organic fertilizers), is not supposed to be used for mineral water, which should be nitrate-free (or at least free of nitrates caused by human pollution).

II.11 - Dating

Dating is a method of natural tracing using non conservative markers whose physico-chemical or radioactive deterioration time is suited to the water's residence time in the reservoir and which can therefore be used to date the outflowing water. Residence time is a real time in the extreme case where the aquifer functions by successive recharges pushing out the previous ones (pure piston flow model). It is a probabilistic time when the inflowing water becomes mixed up with that of the reservoir (perfect mixing model). In nature, both phenomena occur at the same time (pierced piston flow model). The method applies equally well to a fissured aquifer system or a groundwater.

Times from a few days to a few weeks can be measured using dissolved organic carbon or ^{222}Rn, a few years using tritium (^{3}H) or chlorofluorocarbon, and a few centuries to several millennia using ^{14}C.

Prior to thermonuclear explosions in the atmosphere, the average activity of atmospheric tritium (then only due to cosmic radiation) was around 10 TU (Tritium Unit). One TU represents the activity of one atom of tritium (^{3}H) for 10^{18} atoms of stable hydrogen (^{2}H). At the height of atmospheric experiments, activity reached values of between 5000 and 6000 TU in mid-latitudes of the Northern hemisphere between 1963 and 1964. This peak has therefore been used as an input signal for meteoric water entering aquifer systems, but as this radioactive tracer's half-life is quite short (12.26 years), it is becoming increasingly difficult to detect in discharged water.

In the case of ^{14}C, which has a much longer half-life of 5730 years, dating can cover several centuries or even millennia. A doubt remains because the initial activity of ^{14}C is unknown and because of the possible presence of igneous carbon which contains no ^{14}C.

In any case, the age obtained can only be considered a global age: mean residence times vary according to the pathway chosen and, even if there is only one pathway, all the water molecules do not travel at the same speed. It could be, then, that short residence times with a low flow rate (likely to be contamination vectors) are masked by the global old age of a large body of groundwater moving much more slowly. A generally old age at an outlet does not therefore guarantee the complete absence of vulnerability.

II.12 - Geothermometers

Geochemical thermometers (or geothermometers) can provide an estimate of the temperature reached by infiltrating water and, consequently (taking into account the local geothermal gradient) can enable an estimate to be made of the maximum depth reached by the water. There are several types of geothermometer, such as the SiO_2, Na/K and Na/K/Ca (Michard, 1979) geothermometers used at Chaudes-Aigues. The best known is the silica thermometer. The solubility of silica depends mainly on temperature at a constant pH and the reaction is difficult to reverse in a saturated solution. Dissolved silica saturation curves from mineral phases can thus be used to determine the maximum water temperature reached (Pouchan, 1994).

ANNEX 2
PURITY CRITERION VALIDATION STUDY UNDERTAKEN BY THE AFSSA LABORATORY FOR STUDY AND RESEARCH IN HYDROLOGY (LERH)

As the most comprehensive data on the quality of bottled waters were collected during the 1995 inventory, this work needed to be updated particularly in relation to organic micropollutants on the basis of a representative sampling of natural mineral waters, which explains the LERH approach presented below.

I Study methodology and parameters

- **Health control data**

For the years 2004 and 2005, the study data were extracted from the national register of natural mineral springs, which is kept up to date by the LERH and includes the results of health controls of all French natural mineral waters. 180,000 health control forms were issued, including 1,472 for finished products.

The extraction of the analysis results shows that the parameters monitored as part of the health controls vary by site (Table 1):

NMW site	No. of analyses 2004	No. of analyses 2005	No. of analyses of organic micro-pollutants	Parameters measured
A	41	55	0	alkalinity, chlorides, conductivity, pH, microbiology
B	43	49	35	alkalinity, chlorides, CO_2, conductivity, total iron, fluorides, manganese, microbiology
C	8	11	3	alkalinity, ammonium, chlorides, CO_2, conductivity, total iron, fluorides, manganese, nitrates, nitrites, pH, microbiology
D	74	73	4	alkalinity, calcium, conductivity, magnesium, nitrates, pH, microbiology
E	74	57	131	alkalinity, benzene, calcium, chlorides, CO_2, conductivity, magnesium, nitrates, potassium, dry residue at 180 °C, sodium, sulphates, microbiology
F	22	21	0	alkalinity, chlorides, conductivity, nitrates, pH, sulphates, microbiology
G	2	1	0	alkalinity, ammonium, phosphate anhydride, calcium, chlorides, conductivity, total iron, fluorides, magnesium, manganese, nitrates, nitrites, pH, SiO_2 silica, sodium, microbiology
H	10	15	0	alkalinity, chlorides, conductivity, sulphates, microbiology
I	4	2	2	alkalinity, conductivity, pH, microbiology
J	15	14	0	alkalinity, conductivity, lithium, pH, microbiology
K	37	36	1	alkalinity, chlorides, CO_2, conductivity, total iron, fluorides, manganese, nitrites, microbiology
L	30	60	12	alkalinity, chlorides, CO_2, conductivity, total iron, fluorides, manganese, microbiology
M	NC	NC	NC	Spring waters (no data in the base of natural mineral waters)
N	0	0	0	No analyses

Table 1: Parameters measured as part of the health controls at the various bottling sites in 2004 and 2005

Health controls therefore provide few data to evaluate the quality of natural mineral waters in terms of organic micropollutants. That is why specific analyses were undertaken by the LERH.

- **Natural mineral waters studied**

Fourteen bottling sites were used, for 49 outlets and 18 finished products, divided up by bottler, production level and geographic area. Analyses were undertaken in the specific framework of this study. Moreover, the analyses including organic micropollutants undertaken by the LERH in the framework of recent requests (since 2004) submitted to AFSSA for the recognition of natural mineral waters were also taken into account.

- **Information collected, samples taken and analyses performed**

The LERH took samples at source and from the finished product (bottled water), which allowed it to verify the effect of treatment operations on the bottling process.
For natural mineral waters taken from a mixture, only the highest contributing outlets were analysed. To identify potential old contamination of finished products with organic micropollutants, samples were taken in the plant's sample library.

Table 2 gives the list of organic micropollutants screened by the LERH in the framework of exploitation applications. This list was combined with regional lists for surface waters and groundwaters to take local molecules into account.

CHLORINE PESTICIDES (L/L-GC/ECD)	LOD ng/L	LOQ ng/L	AFNOR STANDARD
Trifluralin	10	30	NF EN ISO 6468 (02/1997)
α-Hexachlorohexane	3	10	NF EN ISO 6468 (02/1997)
Hexachlorobenzene	3	10	NF EN ISO 6468 (02/1997)
β-Hexachlorohexane	3	10	NF EN ISO 6468 (02/1997)
Lindane	3	10	NF EN ISO 6468 (02/1997)
Alachlor	17	50	NF EN ISO 6468 (02/1997)
Heptachlor	3	10	NF EN ISO 6468 (02/1997)
Aldrin	3	10	NF EN ISO 6468 (02/1997)
Isobenzane	3	10	NF EN ISO 6468 (02/1997)
Isodrin	3	10	NF EN ISO 6468 (02/1997)
Heptachlor epoxide B	3	10	NF EN ISO 6468 (02/1997)
24' DDE	3	10	NF EN ISO 6468 (02/1997)
α-Endosulfan	3	10	NF EN ISO 6468 (02/1997)
44' DDE	3	10	NF EN ISO 6468 (02/1997)
Dieldrin	3	10	NF EN ISO 6468 (02/1997)
24' DDD	3	10	NF EN ISO 6468 (02/1997)
Endrin	3	10	NF EN ISO 6468 (02/1997)
β-Endosulfan	3	10	NF EN ISO 6468 (02/1997)
44' DDD	3	10	NF EN ISO 6468 (02/1997)
24' DDT	3	10	NF EN ISO 6468 (02/1997)
44' DDT	3	10	NF EN ISO 6468 (02/1997)

NITROGEN PESTICIDES (S/L-HPLC-DAD)			
Deisopropylatrazine	4	12.5	ISO 11369 : 1997 (11/1997)
Desethylatrazine	4	12.5	ISO 11369 : 1997 (11/1997)
Ametryne	17	50	ISO 11369 : 1997 (11/1997)
Sebutylazine-desethyl	8	25	ISO 11369 : 1997 (11/1997)
Hexazinone	33	100	ISO 11369 : 1997 (11/1997)
Simazine	8	25	ISO 11369 : 1997 (11/1997)
Cyanazine	8	25	ISO 11369 : 1997 (11/1997)
Terbutryn	8	25	ISO 11369 : 1997 (11/1997)
Atrazine	17	50	ISO 11369 : 1997 (11/1997)
Metazachlor	17	50	ISO 11369 : 1997 (11/1997)
Sebutylazine	4	12.5	ISO 11369 : 1997 (11/1997)
Propazine	4	12.5	ISO 11369 : 1997 (11/1997)
Terbuthylazine	4	12.5	ISO 11369 : 1997 (11/1997)
Metolachlor	8	25	ISO 11369 : 1997 (11/1997)
Prometon	17	50	ISO 11369 : 1997 (11/1997)

PHENYLUREA PESTICIDES (S/L-HPLC-DAD)	LOD ng/L	LOQ ng/L	
Metoxuron	17	50	ISO 11369: 1997 (11/1997)

Methabenzthiazuron	8	25	ISO 11369: 1997 (11/1997)
Chlortoluron	33	100	ISO 11369: 1997 (11/1997)
Monolinuron	17	50	ISO 11369: 1997 (11/1997)
Isoproturon	17	50	ISO 11369: 1997 (11/1997)
Diuron	17	50	ISO 11369: 1997 (11/1997)
Metobromuron	17	50	ISO 11369: 1997 (11/1997)
Linuron	8	25	ISO 11369: 1997 (11/1997)

MISC. CHLORINE PESTICIDES (ELL/GC/ECD)	LOD ng/L	LOQ ng/L	
Folpet	17	50	NF EN ISO 6468

MISC. NITROGEN PESTICIDES (LC/MS/MS)			
Atrazine-2-hydroxy	7	20	IPL internal method
Secbumeton	7	20	IPL internal method
Desethyl-terbuthylazine	7	20	IPL internal method

MISC. CARBAMATE PESTICIDES (LC/MS/MS)	LOD ng/L	LOQ ng/L	
Carbofuran	17	50	IPL internal method

MISC. DIAZINE PESTICIDES (LC/MS/MS)	LOD ng/L	LOQ ng/L	
Bentazone	17	50	IPL internal method

MISC. PHENOXY-ACID PESTICIDES (LC/MS/MS))	LOD ng/L	LOQ ng/L	
2,4-D	17	50	IPL internal method
2,4-DP(Dichlorprop)	17	50	IPL internal method
2,4-MCPA	17	50	IPL internal method
MCPP (Mecoprop)	17	50	IPL internal method
Triclopyr	17	50	NF EN ISO 10695

MISC. PESTICIDES (LC/DAD/MS)	LOD ng/L	LOQ ng/L	
Oxadiazon	17	50	NF EN ISO 10695
Dinoterb	17	50	NF EN ISO 10695

MISC. PESTICIDES (HPLC)	LOD ng/L	LOQ ng/L	
Dinoseb	17	50	IPL internal method
Paraquat	170	500	IPL internal method
Diquat	17	50	IPL internal method

MISC. PESTICIDES (LC/MS/MS)	LOD ng/L	LOQ ng/L	
Aminotriazole	170	100	IPL internal method
Glyphosate	170	100	IPL internal method
AMPA	170	100	IPL internal method
Tebutam	7	20	IPL internal method
Diflufenican	7	20	IPL internal method
Carbendazim	17	50	IPL internal method
Imidacloprid	7	20	IPL internal method
Oxadixyl	17	50	IPL internal method
2,6-dichlorobenzamide	17	50	IPL internal method
Piperonyl-butoxide	17	50	NF EN ISO 10695
Tolylfluanid	17	50	NF EN ISO 10695
Sulcotrione	17	50	NF EN ISO 10695

Polynuclear Aromatic Hydrocarbons (PAH) (L/L- HPLC-Fluo)	LOD ng/L	LOQ ng/L	
Naphthalene	1.5	5	NF EN ISO 17993 (07/2004)
2-methyl-naphthalene	3	10	NF EN ISO 17993 (07/2004)
Acenaphthene	1.5	5	NF EN ISO 17993 (07/2004)
Fluorene	1.5	5	NF EN ISO 17993 (07/2004)
Phenanthrene	3	10	NF EN ISO 17993 (07/2004)
Anthracene	1.5	5	NF EN ISO 17993 (07/2004)
Fluoranthene	3	10	NF EN ISO 17993 (07/2004)
Pyrene	1.5	5	NF EN ISO 17993 (07/2004)
Benzo(a)anthracene	1.5	5	NF EN ISO 17993 (07/2004)
Chrysene	1.5	5	NF EN ISO 17993 (07/2004)
Benzo(b)fluoranthene	1.5	5	NF EN ISO 17993 (07/2004)
Benzo(k)fluoranthene	0.8	2.5	NF EN ISO 17993 (07/2004)
Benzo(a)pyrene	0.8	2.5	NF EN ISO 17993 (07/2004)
Dibenzo(ah)anthracène	1.5	5	NF EN ISO 17993 (07/2004)
Benzo(ghi)perylene	3	10	NF EN ISO 17993 (07/2004)
Indeno(1,2,3)cd-pyrene	3	10	NF EN ISO 17993 (07/2004)

TOTAL HYDROCARBONS (L/L- GC-FID)	LOD ng/L	LOQ ng/L	
Total hydrocarbons	0.03	0.08	NF EN ISO 9377-2 12/2000)

LD: limit of detection, LQ: limit of quantitation

VOLATILE ORGANOHALOGEN COMPOUNDS AND BTEX (dynamic HS-GC-FID/ECD)	LD ng/L	LQ ng/L	

	LOD	LOQ	
Dichlorodifluoromethane	0.01	0.04	NF EN ISO 15680 (01/2004)
Chloromethane	0.08	0.5	NF EN ISO 15680 (01/2004)
Vinyl chloride	0.08	0.5	NF EN ISO 15680 (01/2004)
Bromomethane	0.17	1	NF EN ISO 15680 (01/2004)
Chloroethane	0.08	0.5	NF EN ISO 15680 (01/2004)
Trichlorofluoromethane	0.002	0.01	NF EN ISO 15680 (01/2004)
1,1-dichloroethylene	0.03	0.2	NF EN ISO 15680 (01/2004)
Dichloromethane	0.17	1	NF EN ISO 15680 (01/2004)
trans-1,2-dichloroethylene	0.03	0.2	NF EN ISO 15680 (01/2004)
1,1-dichloroethane	0.03	0.2	NF EN ISO 15680 (01/2004)
2,2-dichloropropane	0.02	0.1	NF EN ISO 15680 (01/2004)
cis-1,2-dichloroethylene	0.02	0.1	NF EN ISO 15680 (01/2004)
Chloroform	0.003	0.02	NF EN ISO 15680 (01/2004)
Bromochloromethane	0.002	0.01	NF EN ISO 15680 (01/2004)
1,1,1-trichloroethane	0.002	0.01	NF EN ISO 15680 (01/2004)
1,1-dichloropropène	0.02	0.1	NF EN ISO 15680 (01/2004)
Carbon tetrachloride	0.002	0.01	NF EN ISO 15680 (01/2004)
1,2-dichloroethane	0.03	0.2	NF EN ISO 15680 (01/2004)
Benzene	0.02	0.1	NF EN ISO 15680 (01/2004)
Trichloroethylene	0.002	0.01	NF EN ISO 15680 (01/2004)
1,2-dichloropropane	0.02	0.1	NF EN ISO 15680 (01/2004)
Bromodichloromethane	0.002	0.01	NF EN ISO 15680 (01/2004)
Dibromomethane	0.002	0.01	NF EN ISO 15680 (01/2004)
cis-1,3-dichloropropene	0.01	0.04	NF EN ISO 15680 (01/2004)
Toluene	0.02	0.1	NF EN ISO 15680 (01/2004)
trans-1,3-dichloropropene	0.01	0.04	NF EN ISO 15680 (01/2004)
1,1,2-trichloroethane	0.01	0.04	NF EN ISO 15680 (01/2004)
1,3-dichloropropane	0.02	0.1	NF EN ISO 15680 (01/2004)
Tetrachloroethylene	0.002	0.01	NF EN ISO 15680 (01/2004)
Chlorodibromomethane	0.002	0.01	NF EN ISO 15680 (01/2004)
1,2-dibromoethane	0.002	0.01	NF EN ISO 15680 (01/2004)
Chlorobenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
1,1,1,2-tetrachloroethane	0.003	0.01	NF EN ISO 15680 (01/2004)
Ethylbenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
m–xylene	0.03	0.1	NF EN ISO 15680 (01/2004)
p–xylene	0.03	0.1	NF EN ISO 15680 (01/2004)
o-xylene	0.03	0.1	NF EN ISO 15680 (01/2004)
Styrene	0.03	0.1	NF EN ISO 15680 (01/2004)
Isopropylbenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
Bromoform	0.003	0.01	NF EN ISO 15680 (01/2004)
1,1,2,2-tetrachloroethane	0.01	0.04	NF EN ISO 15680 (01/2004)
1,2,3-trichloropropane	0.07	0.2	NF EN ISO 15680 (01/2004)
n-propylbenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
Bromobenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
1,3,5-trimethylbenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
2-chlorotoluene	0.03	0.1	NF EN ISO 15680 (01/2004)
4-chlorotoluene	0.03	0.1	NF EN ISO 15680 (01/2004)
tert-butylbenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
1,2,4-trimethylbenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
sec-butylbenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
4-isopropyltoluene	0.03	0.1	NF EN ISO 15680 (01/2004)
1,3-dichlorobenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
1,4-dichlorobenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
n-butylbenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
1,2-dichlorobenzene	0.03	0.1	NF EN ISO 15680 (01/2004)
1,2-dibromo-3-chloropropane	0.01	0.04	NF EN ISO 15680 (01/2004)
1,2,4-trichlorobenzene	0.01	0.04	NF EN ISO 15680 (01/2004)
Hexachlorobutadiene	0.003	0.01	NF EN ISO 15680 (01/2004)
Naphthalene	0.07	0.2	NF EN ISO 15680 (01/2004)
1,2,3-trichlorobenzene	0.01	0.04	NF EN ISO 15680 (01/2004)

Table 2: micropollutants screened for

As shown by the table, the various families that were analysed were pesticides (organic nitrogen, organic phosphorus, organic chloride, phenylurea, etc.), hydrocarbons (PAH, total PAH), volatile organohalogen compounds and BTEX (benzene, toluene, ethylbenzene and xylene). The analyses were conducted in accordance with current standardised methods, with confirmation of compound identification using mass spectrometry.

II - Results

II.1 - Uncorrected results

On the basis of the study's limited sampling at the 14 bottling sites:

- **Six sites** had **results lower than the limits of detection for all of the tested compounds** (sites C, D, E, F, G, H).

- **Eight sites**, or 12 outlets and eight finished products, contained **trace or quantifiable levels of micropollutants** (Table 3). Four of these eight finished products also had micropollutants in the sample library bottle, showing contamination dating back one to two years. The product families involved were pesticides, volatile organohalogen compounds, polycyclic aromatic hydrocarbons and oxidation by-products.

	Site A			Site L		Site K				Site B				Site M		Site N		Site I		Site J			
	E1	E2	Btl	E	Btl	E1	Btl1	E2	Btl2	E1	E2	E3	Btl	E	Btl	E	Btl	E	Btl	E1	E2	E3	Btl
Desethyl-atrazine	16	16	6[+]	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	57 / 58	<12.5	<12.5	21 / 43[+]	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5
Deisopropyl-atrazine	6	6	4[+]	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5
Atrazine	12	12	3[+]	<50	<50	<50	<50	<50	<50	34 / 35	34 / 35	34 / 35	34 / 35[+]	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Diuron	<50	<50	<50	62	75[+]	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Trichloroethylene	<10	<10	<10	12	3[+]	<10	<10	<10	<10	74 / 107	180 / 260	2 / 23	33 / 35[+]	<10	<10	<20 / <10	70 / <10	<10	<10	<10	<10	<10	<10
Tetrachloroethylene	<10	<10	<10	<10	<10	<10	<10	<10	<10	172 / 200	<20	10 / <20	50 / 140[+]	115	105	<10	<10	<10	<10	<10	<10	<10	<10
1,1,1-trichloroethane	<10	<10	<10	<10	<10	<10	<10	<10	<10	12 / 22	5 / 10	<20	6 / 9[+]	<20	<20	<20	<20	50	Gas: 60 Still: 40	<10	<10	<10	<10
Naphthalene	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	491	<20	<20
2-methyl-naphthalene	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	113	<40	<40
Acenaphthene	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	4	5	<5
Fluorene	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	24	22	<5
Phenanthrene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	52	44	<10
Anthracene	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	3	<5
Fluoranthene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	13	<10
Pyrene	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	8	<5
Chloroform	<20	<20	<20	<20	<20	<20	<20	<20	<20	110 / 150	10 / <20	36 / 50	48 / 67[+]	<20	<20	<20	<20	<20	<20	<20	<20	<20	19[+]
Bromodichloromethane	<10	<10	<10	<10	<10	<10	<10	<10	<10	<20	<20	10 / <20	<20	<10	<10	<10	<10	<10	<10	<10	<10	<10	18[+]
Chlorodibromomethane	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	27[+]
Trichlorofluoromethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	9-19	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Bromoform	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	1400[+]
Benzene	<100	<100	<100	<100	<100	24	49[-]	<100	24[-]	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	790	12600	550	<100
Toluene	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	2400	<100	<100
Ethylbenzene	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	140	110	<100
m,p-xylene	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	410	200	<100
o-xylene	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	65	700	600	<100
1,3,5-trimethylbenzene	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	40	40	<100
1,2,4-trimethylbenzene	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	200	180	<100

For each site, the sample's origin is indicated by 'E' for exits and 'Btl' for finished products. If the compound was also found in the bottle from the sample library, the result is accompanied by a '+' superscript; otherwise it is a '-' superscript.

Table 3: Results (in ng/L) of analyses performed at the 8 sites where trace or quantifiable levels of organic micropollutants were found

Organic micropollutants found in water at the source exit

When anthropogenic molecules are found in water at the source exit, they most likely result from contamination of the deep resource, which shows borehole vulnerability to infiltration water or pollution in the impluvium.

For plant protection products, atrazine and its degradation products as well as diuron and glyphosate are some of the most commonly found pesticides[34] in France's groundwater and surface water. This environmental polluting pressure affects both surface water and groundwater, as presented by the French Environmental Institute. For example, at 10,000 monitoring stations, 96% of measurement points in streams and 61% of measurement points in groundwater detect pesticides. The deep resources in natural mineral water deposits can therefore be affected as well.

The organic micropollutants found included several volatile halogens and hydrocarbons used in industrial or artisanal activities. At sites B and J, there were several of these compounds at the source and in bottles. At some of the sites under study, investigations are underway to understand the origin of these contaminations but, given the time that a surface pollutant needs to reach these deep resources, the history of industrial activities is very difficult to trace.

Organic micropollutants found solely in bottles

The mixing of water from several boreholes having different properties, combined with bottling methods, can lower volatile compound contamination in the finished product. But these same treatment methods can create oxidation by-products (chloroform, bromodichloromethane, chlorodibromomethane, bromoform) when they are inadequately managed, which was the case for site J.

II.2 - Results in relation to the proposed criteria for purity assessment

Eight out of 49 outlets and three out of 18 finished products did not fulfil the criteria proposed in the 3rd part of the report (§ IV.5) for purity assessment, or three out of 14 sites.

The results are shown in Tables 4 to 6 below, with the following notification: for each site, the sample's origin is indicated by 'E' for exits and 'Btl' for finished products. If the compound was also found in the bottle from the sample library, the result is accompanied by a '+' superscript; otherwise it is a '-' superscript.

	Quality limit for drinking water (ng/L)	Purity criterion limit (ng/L)	Samples	
			E (ng/L)	Btl (ng/L)
Diuron	100	**30**	**62**	**75** [+]

Table 4: Bottling site L: analysis results (in ng/L) exceeding the proposed purity criteria

	Quality limit for drinking water (ng/L)	Purity criterion limit (ng/L)	Samples			
			E1 (ng/L)	E2 (ng/L)	E3 (ng/L)	Btl (ng/L)
Desethylatrazine	100	**30**	**57-58**	**< 12.5**	**< 12.5**	**21-43** [+]
Atrazine	100	**30**	**34-35**	**34-35**	**34-35**	**34-35** [+]

Table 5: Bottling site B: analysis results (in ng/L) exceeding the proposed purity criteria

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[34] **IFEN 2006: Pesticides in water, 2003 and 2004 data**

	Quality limit for drinking water (ng/L)	Purity criterion limit (ng/L)	Samples			
			E1 (ng/L)	E2 (ng/L)	E3 (ng/L)	Btl (ng/L)
Naphthalene	/	**30**	< 20	**491**	< 20	< 20
2-methylnaphthalene	/	**30**	< 40	**113**	< 40	< 40
Phenanthrene	/	**30**	< 10	**52**	**44**	< 10
Bromoform	**1000**	/	< 10	< 10	< 10	**1400 +**
Benzene	**1000**	**300**	**790**	**12600**	**550**	< 100
Toluene	/	**30**	< 100	**2400**	< 100	< 100
Ethylbenzene	/	**30**	< 100	**140**	**110**	< 100
m,p-xylene	/	**30**	< 100	**410**	**200**	< 100
o-xylene	/	**30**	**65**	**700**	**600**	< 100
1,3,5-trimethylbenzene	/	**30**	< 100	**40**	**40**	< 100
1,2,4-trimethylbenzene	/	**30**	< 100	**200**	**180**	< 100

Table 6: Bottling site J: analysis results (in ng/L) exceeding the proposed purity criteria

The number of organic micropollutants involved was respectively:

- 1 for site L, with diuron at the source exit, in the sampled bottle on the bottling line and in the sample library bottle.

- 2 for site B, with atrazine and its degradation product at all of the sampling points.

- 11 for site J, with several compounds from the hydrocarbon family and a very large quantity of bromoform only in the sampled bottle on the bottling line and in the sample library bottle. Poor control of the oxidation process for iron removal caused the appearance of bromoforms as well as the removal of benzene from the finished product via stripping.

II.3 - Study conclusions

This study, which examined a limited sample selection from 14 bottled natural mineral water sites, assessed the purity of these waters at the source exit and in the finished product against the purity criteria proposed by the experts in the working group on 'Natural mineral waters'.

Various concentrations of organic micropollutants were detected at eight sites. When applying the purity assessment approach that takes into account the quality limits of compounds, three sites remained non-compliant (L, B and J). The identified compounds included various families: pesticides (often found in surface water and groundwater), hydrocarbons and oxidation by-products.

The results of this study show that more comprehensive and exhaustive data need to be obtained by organising a national inventory of numerous families of organic micropollutants and by incorporating into this inventory the main bottled waters on the European market distributed in France.

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