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Geochemistry of springwaters in Molasse aquifers: Typical mineral trace elements

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Key words: Molasse, groundwater geochemistry, hydrogeology, trace elements, spatial variation, aquifer sub-type definition

ABSTRACT

Water investigations have been conducted throughout the Molasse basin between Chambéry (France) and Linz (Austria), but mainly in the Swiss Molasse basin, in order to provide an overview of the spatial distribution of inorganic water compounds in different Tertiary aquifer lithologies.

The data set comprises more than a hundred water analyses from different springs with catchments that completely drain a single, lithologically mostly homogenous Molasse terrain unit. Recharge areas of selected springs were generally not affected by runoff from urban waters, waste deposits, agricultural activities or roads. The chemical marking due to various sorts of metallic water pipe materials was taken into account. Such spring water should be free of major human influences and represent the most natural conditions possible. Leachate tests of crushed rocks and comparison with precipitation and soil water compositions allowed to identify the geogene origin of the dissolved ions in natural groundwaters.

The water analyses have been evaluated by integrating sedimentological, stratigraphical and structural data. With this procedure, about 30 different aquifer sub-types could be defined within the Molasse deposits according to their sedimentary petrography (sediment feeder system, "Schüttung"), to their tectonical structure (hydraulic conductivity) and to their grain size distribution (depositional environment).

Complete analyses comprising 33 inorganic compounds have been executed and contribute to a definition of natural groundwater quality. Due to the very low detection limits of the HR-ICP-MS in the order of magnitude of µg/l, multielement trace analyses, such as those of chromium, uranium, lithium, molybdenum and barium, have proven to be of interest for the determination of the geological water origin in Molasse deposits. Moreover, the presented results show, that the great variety of the Molasse basin sediments forming aquifer hostrocks is reflected by the chemical groundwater composition. Thus, a great number of springwater, usually classified as calcium-magnesium-bicarbonate type, can chemically be clearly distinct with respect to the geological nature of the aquifer as well as the flow system to which the studied waters belong.

ZUSAMMENFASSUNG

Wasseruntersuchungen wurden im gesamten Molassebecken zwischen Chambéry (Frankreich) und Linz (Österreich), aber hauptsächlich im Schweizer Molassebecken, durchgeführt. Sie geben einen Überblick über die natürliche räumliche Variabilität von anorganischen Wasserinhaltsstoffen aus verschiedenen tertiären Aquiferlithologien.

Die Datenbank umfasst über hundert Wasseranalysen von Quellen mit Einzugsgebieten, die jeweils einen einzigen, lithologisch weitgehend homogenen Molassesedimentkörper entwässern. Die Einzugsgebiete der ausgewählten Quellen sind im allgemeinen unbeeinflusst von Abwässern, Deponien, Landwirtschaft oder Strassen. Korrosionsbedingte chemische Einflüsse von metallischen Leitungsröhren wurden berücksichtigt. Derart unbelastete Quellwässer repräsentieren deshalb weitgehend natürliche Verhältnisse. Auslaugversuche von Gesteinsproben und der Vergleich mit Niederschlags- und Bodenwasserzusammensetzungen ermöglichten die qualitative Identifikation des geogenen Anteils an den gelösten Ionen in natürlichen Grundwässern.

Zur Auswertung der Wasseranalysen wurden sedimentologische, stratigraphische und Strukturdaten hinzugezogen. Innerhalb des Aquifertyps der klastischen Ablagerungen mit Poren- und Kluftdurchlässigkeit konnten, ausgehend von der Sedimentpetrographie (Schüttungszugehörigkeit), der tektonischen Struktur (hydraulische Durchlässigkeit) und der Korngrösse (Ablagerungsfazies), rund 30 verschiedene Aquifer-Subtypen unterschieden werden. Vollständige Wasseranalysen, die 33 anorganische Inhaltsstoffe einschliessen, wurden ausgeführt und tragen zur Definition einer natürlichen Grundwasserqualität bei. Analysen mineralischer Spurenelemente erfolgten mittels Massenspektrometrie mit induzierter Plasmakopplung (HR-ICP-MS), die dank hoher Auflösungstechnik eine Nachweisgrenze im ppb-Bereich erlaubte.

Bisher wurden oberflächennahe Grundwässer des Mittellandes aufgrund von Hauptkomponenten-Analysen generell als Kalzium-Magnesium-Hydrogenkarbonat-Wässer klassifiziert. Der Beizug von Spurenelementanalysen ermöglicht hingegen unter Berücksichtigung der Geologie des Aquifers und des Fließsystems eine genauere chemische Differenzierung der Molasse-Quellwässer. So erwiesen sich Spurenelemente wie Chrom, Uran, Lithium, Molybdän und Barium nebst Sulfat- und Kieselsäuregehalte als interessante Indikatoren für die geologische Herkunftsbestimmung von Wässern in der Molasse. Die präsentierten Resultate zeigen auch, dass die grosse Variabilität der aquiferbildenden Beckensedimente sich in der chemischen Grundwasserzusammensetzung widerspiegelt.

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1. Introduction

1.1 Generalities

The Molasse basin underlies a densely populated region which hosts industrial centres and agricultural land. In view of the important role the basin plays as groundwater storage and waste disposal, underground works and water exploitation are increasing risks for a sustainable availability of this renewable but limited resource for the ever increasing demand for usable water.

Concerning water quality, policy makers have to distinguish between polluted and unpolluted waters. Nevertheless, the presence of metals and metalloids in groundwater, such as e.g. chromium, zinc and arsenic, is not always man made, but can also be naturally released by the aquifer host rock during weathering. Thus, detailed knowledge of naturally occurring element contents ("background concentrations") is needed to form a scientific basis for water quality criteria as listed in the Swiss ordinance for wastewater discharge (Behra et al. 1994).

A number of contributions to the knowledge of chemical composition of shallow Molasse groundwaters have been published by e.g. Högl 1980, Schmassmann et al. 1984 and Schmassmann 1990, whereas numerous hydrogeological studies may be found e.g. in Petch 1970, Parriaux 1981, Balderer 1982 and 1989, Baumann 1987, Egger 1978, Goldbrunner 1988, Schmassmann et al. 1984 and 1990, Thierrin 1990 and Wimmer 1990. This previous research works are usually local studies and focussed on the general assessment of global water resources of single catchment areas, composed of several aquifer types. Although, aquifer forming rocks are major sources of inorganic constituents naturally contained in groundwater (Garrels & Mackenzie 1971, Berner & Berner 1987), rock geochemistry was not especially considered. Moreover, hydrochemical emphasis has been on routine analysis for water quality, measuring the concentrations of major and minor constituents, such as calcium, magnesium, hydrogencarbonates, sulfates, etc., with scant attention given to trace quantities of the same waters. Therefore, despite the considerable heterogeneity of Molasse deposits, only two water types are usually distinguished within the shallow part of the subsurface Molasse deposits: Ca-HCO₃ and Ca-Mg-HCO₃-type waters (Balderer 1985, 1989, 1990a, b, c; Schmassmann 1984 and 1990). This is of importance, as the hydrogeological significance of the multi-element analysis in terms of a water characterization is a subject of considerable recent activity (Parriaux et al. 1990, Lahl & Lavanchy 1991).

The aim of the research is therefore double: First, to establish a consistent and comparable water data set in order to know the chemical composition and the spatial variation of natural inorganic contents in Molasse groundwaters. In fact, the few existing data in literature must be used with care as they might originate from different sampling techniques, sample treatments and analysing methods used for them. Secondly, the investigations are aimed to check a link between aquifer

lithology and groundwater composition and if so, to identify typical mineral tracer elements originating from different clastic sedimentary deposits. Bensimon et al. (1991) already pointed out, that the analysis of the complete chemical composition might be a technique which allows to distinguish Ca-Mg-HCO₃-type waters from different lithological origins.

The present study is part of a long term water monitoring project, called AQUITYP observation network, which aims the hydrogeological and geochemical characterization of the principal aquifer rock types found in the Alpine orogen of Switzerland (Parriaux et al. 1990, Mandia 1991, Basabe 1992, Dubois 1992, Dematteis 1995 and Hesske 1995). The hydrochemical study reported here is an interdisciplinary approach to the geochemistry of natural waters based on sedimentology, as well as on hydrogeology, geochemistry and applied geology. In addition, it considers not a single catchment area, but a hundred local aquifers carefully selected all over the Molasse basin between France and Austria. This spatial observation at a basin scale is designed to answer questions about water chemistry variation and takes at the same time into account the great lithological variety of Alpine clastic sediments.

1.2 Geological setting

Our study area comprises nearly the whole Molasse basin, a classical peripheral foreland sedimentary basin (Homewood et al. 1989). Geographically, it extends from Haute Savoie (France) in the west through Switzerland and Bavaria to the Linz-Vienna area of Austria in the east, over a distance of approximately 700 km (Fig. 1). Geologically, the southern limit of the basin is marked by the Alpine belt while the northern margin of the basin is delimited by the Jura mountains and by blocks of crystalline basement such as the Bohemian Massif in the northeast.

The clastic sediments are mainly derived from the rising Alps and deposited in Oligocene/Miocene time. According to the sediment deposition in a continental or marine to brackish environment, four lithostratigraphic groups are generally distinguished (Matter et al. 1980), in ascending stratigraphic order (Fig. 2): (1) the Lower Marine Molasse (UMM and North Helvetic "flysch" p.p.), (2) the Lower Freshwater Molasse (USM), (3) the Upper Marine Molasse (OMM) and (4) the Upper Freshwater Molasse (OSM). In lack of aquifer homogeneity, UMM sediments as well as the Molasse deposits in the Jura synclines are not considered here.

As a consequence, the basin fill represents a considerably complex and heterogeneous sedimentology. Its heterogeneous nature, expressed for our purposes by three major features, namely sedimentary petrography, tectonic structure and grain size distribution, is explained below:

- Sedimentary petrography: In late Oligocene and Miocene times different sediment feeder systems ("Schüttungen") deposited various fans. They are built up from eroded material originating from various tectonic source terranes of

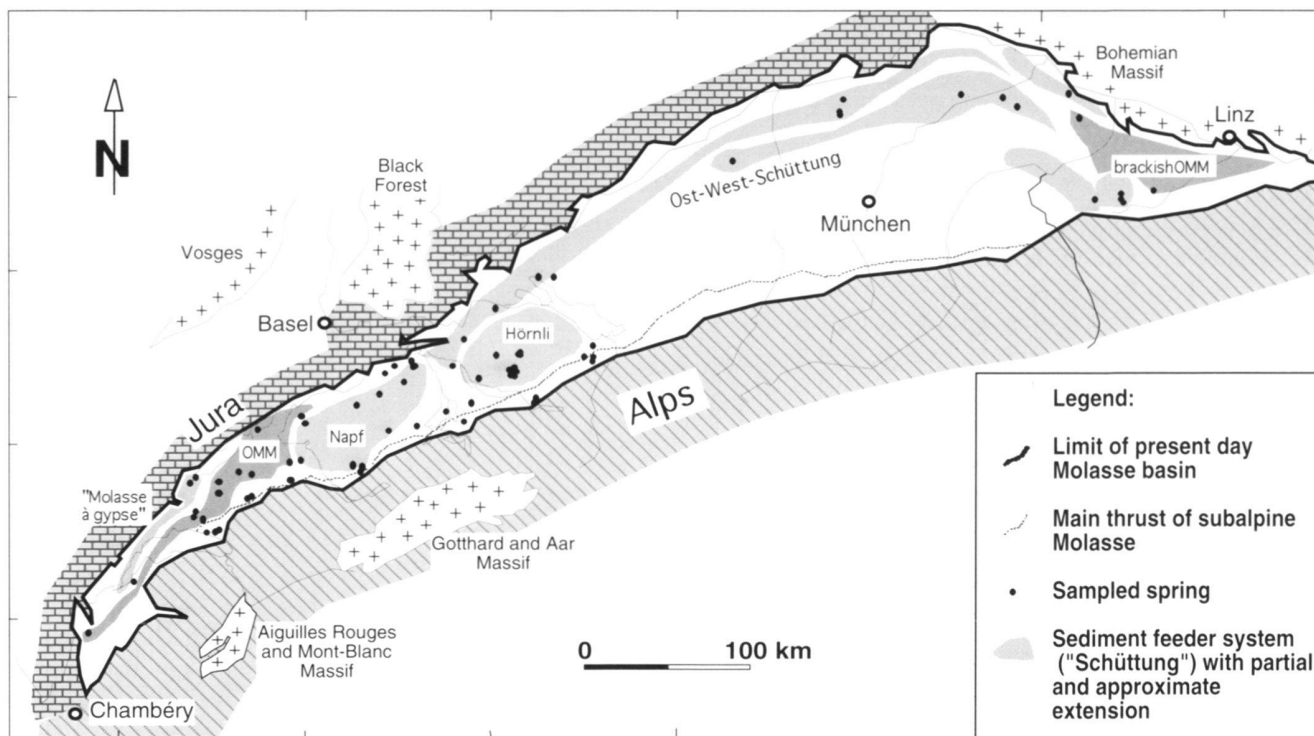


Fig. 1. Overview map of the Molasse basin with location of the individual sampling points (springs). Some major sediment feeder systems ("Schüttungen") are schematically indicated without respect to their exact extension and to their sedimentation epoch.

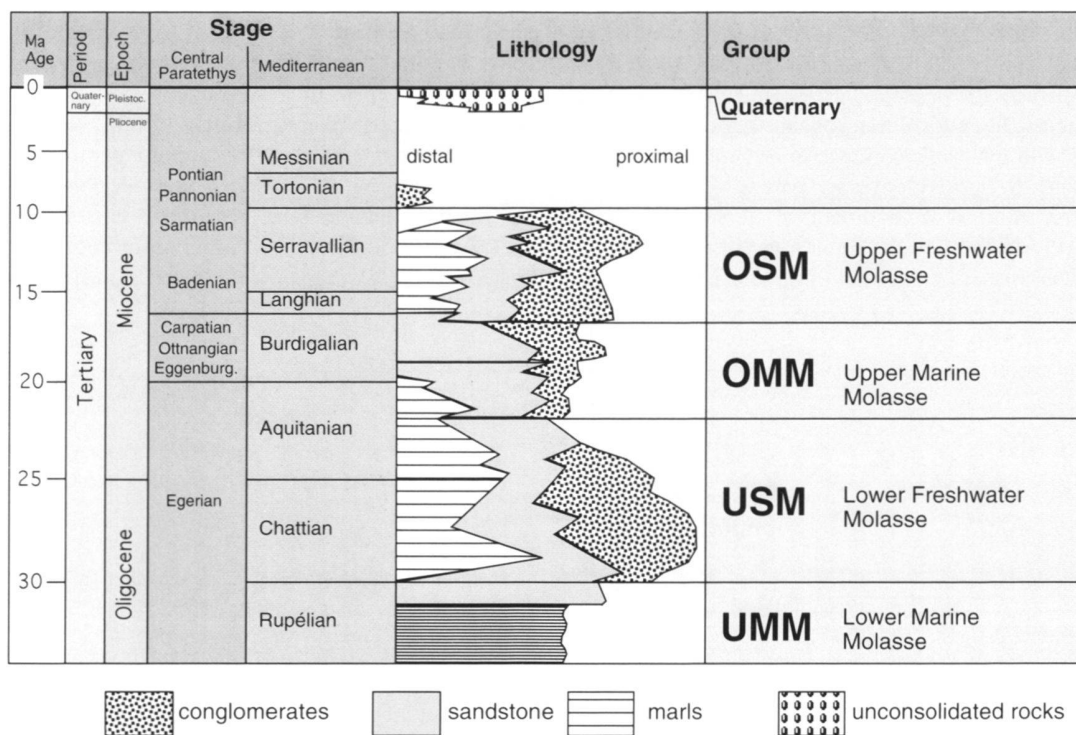


Fig. 2. Schematic stratigraphic Molasse sequence (modified after Keller 1992 and Pearson et al. 1991).

the Alps. Therefore, each of these feeder systems shows its own petrographic composition at a certain depositional stage.

- Tectonic structures: The deposits have been affected by tectonic events and are consequently deformed, fractured and even folded and thrust in the subalpine region at the southern basin margin.
- Grain size distribution: The major sediment feeder systems of variable age such as the Mont-Pélerin fan in western Switzerland, the Napf fan and the Hörnli fan in central and eastern Switzerland built up boulder and pebble rich proximal areas, whereas this fluvial systems deposited fine grained sediments forming floodplains, lakes and swamps in the distal areas. In addition, the geological pattern is affected by numerous lateral and vertical changes in the stratigraphic sequence due to changes in the depositional environment and due to tectonic events.

Nevertheless, the heterogeneous nature of the Molasse basin fill offers the possibility to check whether chemistry variation in groundwater correlates with lithological and structural changes in the sedimentary deposits.

1.3 Hydrogeological setting

The present relief of the Molasse basin was largely fashioned by post-Molassic uplift and by the Pleistocene glaciers providing the morphology of the study region. As a consequence, the Tertiary sediments appear mostly as hills, presenting local flow systems (Balderer 1979, 1982, 1983) and are often covered by Quaternary deposits. The molassic sandstones and conglomerates on the surface show secondary permeabilities due to weathering effects. They form heterogeneous porous and fissured aquifers with hydraulic conductivities generally varying between 10^{-4} and 10^{-9} m/s with average values of about 10^{-6} to 10^{-7} m/s. Fissured aquifers are dominant in the Subalpine zone (Keller 1992). Productivity of the numerous springs from outcropping Molasse is small compared to Quaternary gravel de-

posits, but they are non neglectable water resources which provide generally good water quality, frequently used for human consumption. The shallow groundwaters reach maximum depths of 25 to 100 meters, and springwaters have commonly tritium contents indicating residence times of less than 35 years (Schmassmann et al. 1984, Geol. Landesamt Baden-Württemberg 1990, 1992, Thierrin 1990). They are generally of the calcium-magnesium-bicarbonate type (Pearson et al. 1991, Hesske 1995), with a mean total mineralization of about 470 mg TDS/l, what evidences water-rock interaction with fast dissolving minerals of the clastic sediments such as carbonates and occasionally sulfate-bearing components. The chemistry of waters is influenced effectively in an alkaline, oxygenated and low-temperature environment ($<12^{\circ}\text{C}$) providing cold spring waters.

2. Methods

2.1 Selection of springs

The selection of springs takes a key position in the study of lithogenic tracers. In order to be able to check geochemical links between aquifer hostrock and groundwater, the sampling sites were chosen by carefully taking into account three essential selection criteria: geology and hydrogeology, as well as anthropogenic influences. They are discussed below:

Geological conditions:

Only springwaters having small recharge areas, as hills are, have been sampled (Fig. 3). They have the advantage of draining a single, lithologically mostly homogeneous Molasse terrain unit and allow to reduce unknown external influences of chemical bias to the groundwater.

Deep waters, referring to sampling depth, instead, are least likely to represent typical Molasse water composition. They do not allow to individualize recharge areas of different aquifer rock types and often represent mixtures between recently infiltrated meteoric waters and deep groundwaters. Moreover, the

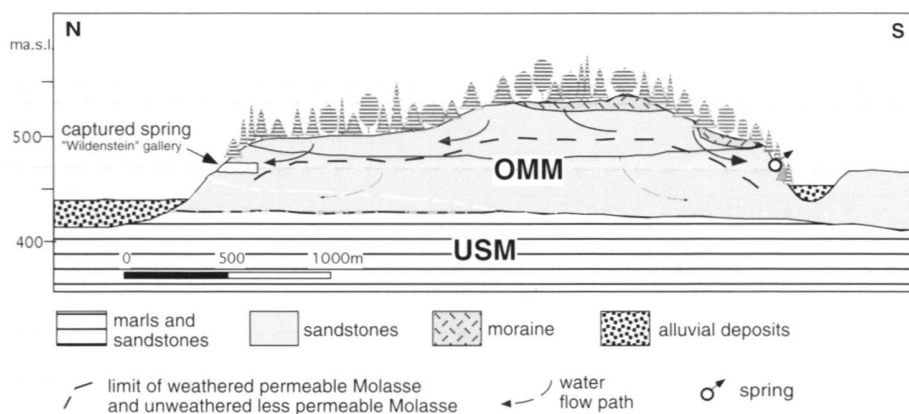


Fig. 3. Ideal aquifer site in the flat-lying Molasse. The aquifer is characterized by a simple geology, a small and natural recharge area, a neglectable quaternary cover (moraine) and a relatively deeply captured spring in a gallery (Wildenstein gallery in Lenzburg AG). (USM: Lower Freshwater Molasse; OMM: Upper Marine Molasse; modified after Jäckli 1966)

latter often contain old saline formation water (Balderer 1990c, Schmassmann et al. 1984).

Additionally, the number of suitable sites were considerably restrained by the presence of the Quaternary deposits over much of the Molasse basin. Thus, aquifers having no or only a thin Quaternary cover were selected in order to minimize the influence of allochthonous sediments.

Hydrogeological conditions:

Long residence times of groundwater in the aquifer increase generally water-rock interactions and therefore chemical imprints. Hence, we preferred deeply captured springs, such as galleries, in order to avoid sampling of surficial water. In addition, water samples were collected during low water periods in summer and autumn 1993 and 1994. Such periods have been selected in order to analyse representative aquifer waters with relatively long water-rock interaction time and to minimize external influences of very freshly infiltrated water.

Anthropogenic influences:

Great care has been taken to minimize external contaminations. Preferentially, catchments with a forest cover were selected which, generally, were not affected by runoff from urban waters, waste deposits or roads. Influences of agricultural activities have been discarded as well as possible. In order to check natural conditions, we compared water analyses which might show chemical bias due to external influences, with those not having them. Accordingly, 33 spring samples (30%) originating from catchments completely covered by forest served as a natural reference for those comprising agricultural land. In the same way, 20 springwaters (18%) sampled straight out from the aquifer rock without flow through any intermediate capturing tube on the spring allow to detect external chemical bias due to tube material. Furthermore, the laboratory findings of Parriaux & Bensimon (1990) allowed to take the chemical marking of various materials of tubes into account for both, the choice of the network points as well as the interpretation of the results. Equally, soil solutions were analysed, although soil on the Swiss Plateau generally plays an essential role in the immobilization of heavy metals, thus protecting groundwater from pollutions through atmospheric dust and fertilizers (Atteia 1992, Keller 1991, Dalla Piazza 1996).

To sum up, the sampled springwater should be free of major human influences. Only in a few cases they contain conspicuous components of fertilizer products (e.g. nitrates) and/or tube materials (e.g. zinc), which have been excluded from our evaluation of characteristic Molasse waters.

A location map of the individual sampling points is given in Figure 1.

2.2 Water analyses

Sampling and analysis had been carried out by the authors themselves providing the same techniques and sample treat-

ments for the whole data set. Field analyses were carried out for parameters like electrical conductivity (EC), discharge, temperature, oxygen, pH and redox potential. Water samples have been collected in polyethylene bottles after rinsing the bottles three times with spring water. Two bottles were filled for each spring, one for anion and one for cation determinations. The second ones were acidified with 2 ml of Merck Suprapur nitric acid (65%) per liter. Thus, the pH attained is around 2, we avoid adsorption of trace elements on the inner bottle surface. While anions have been analysed within 24 hours after sampling, samples for cation determination were stocked in a refrigerator by 4°C until analysed.

46 elements have been analysed. 17 of them have proven not to be measurable as their concentrations were in the order of magnitude of the general detection limit of 0.2 µg/l (As, Co) or below it (Be, Ga, Ge, Se, Zr, Nb, Ru, Cd, Sn, Hf, Ta, W, Hg, Tl, Bi). 29 elements, however, were present in concentrations significantly different from their lower detection limit.

Complete quantitative analyses of all samples, including 11 major and minor constituents, as well as 18 trace elements, have been executed in the chemical laboratory of the Laboratoire de géologie de l'Ecole Polytechnique de Lausanne (GEOLEP). Since we are studying naturally occurring element contents in clean running groundwaters, water samples with neglectable turbidity have not been filtrated. Thus, we report total concentrations, i.e. including the particle-bound fraction. Anions were determined by using standard methods such as ionic chromatography for chloride, sulfate, nitrate, specific electrode for fluorine, titration for alkalinity and silicon by using colorimetry. Multielement analyses have been performed with the High Resolution Inductively Coupled Plasma Source Mass Spectrometry (HR-ICP-MS) of VG/FISONS Instruments. Diluted and acidified standard solutions (Merck, Darmstadt, FRG) have been used for calibration and subsequent direct determination. The HR-ICP-MS technique proved to be very useful for the determination of trace elements in water as it offers the advantage of an unambiguous identification and quantification at ultratrace levels of elements going down to the detection limit of about 0.2 µg/l (Bensimon et al. 1994). Standard major-ion analyses were checked by ion balance methods accepting an error of up to 5%. Appendix 1 lists a selection of the chemical analyses of the sampled groundwaters. The complete data set can be found in Hesske (1995).

The usual description of the water type includes those ions which occur in concentrations higher than 10 milliequivalent (meq)-per cent. The ions are listed in order of decreasing concentrations. Those with concentrations higher than 50 meq-per cent are underlined and those below 20 meq-per cent are given in parenthesis (Jäckli 1970, Schmassmann et al. 1984). This proceeding allows a preliminary distinction of three main water types within the sampled Molasse springwaters. The most abundant type with 72% is the calcium-magnesium-bicarbonate type (Ca-Mg-HCO₃). 11% of the sampled waters are of the calcium-bicarbonate type (Ca-HCO₃) and 17% are

of the calcium-magnesium-bicarbonate-sulphate type, having increased sulfate contents ($\text{Ca-Mg-HCO}_3\text{-(SO}_4\text{)}$ and $\text{Ca-Mg-SO}_4\text{-HCO}_3$).

The validity of the lithogenic origin of the dissolved ions in the spring-water samples was checked through comparison with atmospheric precipitation and soil water compositions on the one hand and through rock leachate tests on the other hand. All of these solutions were analysed in the same way as the springwaters were. The leachate tests were carried out in an open system with crushed aquifer forming rocks where deionized water was added. Bubbling with carbonic gaz during four days, providing an initial pH of 4.9, accelerated the weathering processes (Hesske 1995).

2.3 Definition of an aquifer sub-type of the Molasse

Molasse deposits belong to the general aquifer type of sedimentary rocks with combined fissure and pore permeability which are also represented by the flysch sediments (Parriaux et al. 1990, Basabe 1992). Even so, the strongly heterogeneous nature of this Tertiary basin fill demands a more detailed distinction of this aquifer type. More precisely, a further subdivision should provide a lithological and hydrogeological unit containing a maximum of homogeneity which allows to check whether chemistry variation in groundwater correlates with respect to the geology of the aquifer. So, our water data set has been completed by integrating sedimentological data with stratigraphy compiled from literature.

In most cases, the formation defined as a lithostratigraphic base unit (Hedberg 1976) does not provide a sufficiently homogenous aquifer rock unit for a geochemical characterization of the Molasse aquifers. Architectural facies units as proposed by Keller (1992), on the other hand, are too small-scaled for our purpose. As a consequence, we created a subdivision of

the Molasse sediments on our own with respect to their sedimentary petrography, their tectonic structure and their grain size distribution. The general proceeding of reordering of the Molasse deposits is illustrated on Figure 4. In practice, we first grouped together the local aquifers belonging to the same sedimentary feeder system, called "Schüttung", having a similar sediment composition. Second, we distinguished the degree of tectonical deformation, i.e. Plateau Molasse and subalpine Molasse have been considered separately. And lastly, different depositional facies have been separated in order to consider grain size distribution influencing rock permeability of the aquifer. Long lasting fan depositions (e.g. "Napf-Schüttung") have been, additionally, divided into lithozones (Hedberg 1979) which allow to respect changes of sediment origin in the feeder system.

Proceeding like this, we created especially for this study an aquifer sub-type of the Molasse. An aquifer sub-type, therefore, is defined as a single depositional facies representing a homogeneous lithological unit of a feeder system. Hydrogeologically, it is, at the same time, characterized by about the same conductivity features (permeability). Hence, an aquifer sub-type comprises several local aquifers, mostly hills in our case. This definition is valid for morphologically outcropping aquifers as investigated in this study.

To summarize, our study comprises 73 local aquifers which could be lithologically grouped, as mentioned above, into 32 aquifer sub-types. Furtheron, these aquifer sub-types belong to 15 different feeder systems ("Schüttungen") of the Molasse basin (see Fig. 4).

On a pictorial way, each of the 112 water analyses has been arranged in a geological order with respect to the stratigraphical position of its aquifer rock. The result is shown in the semi-stratigraphical profiles of Figure 5. This procedure allows to compare spatial variations of water geochemistry straight forward with respect to the geology of the aquifer rock.

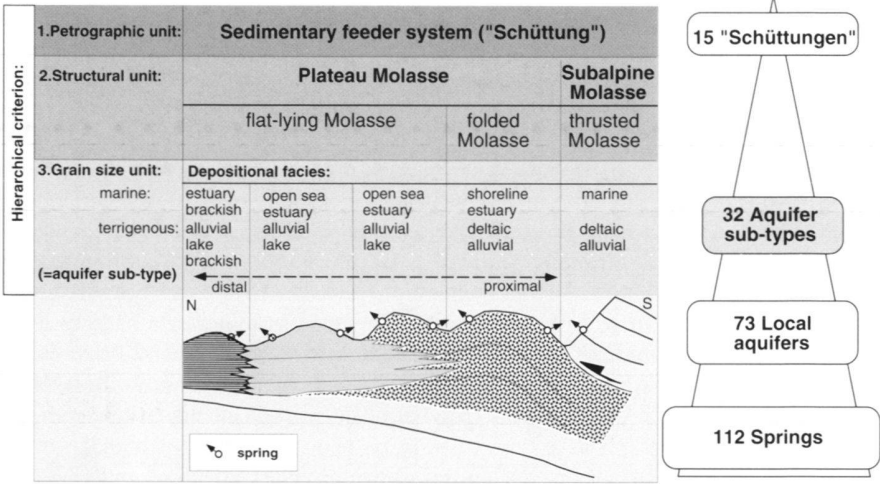


Fig. 4. Proceeding scheme of the reordering of the Molasse deposits into aquifer sub-types. 112 springs were sampled from 73 local aquifers which belong to 15 different "Schüttungen". The 32 different aquifer sub-types obtained are defined on the basis of the sedimentary petrography, hydraulic conductivity (rock structure) and grain size distribution (depositional facies) of the aquifer hostrocks.

3. Results

3.1 General findings

The geochemical marker distribution in the Molasse basin is illustrated by the schematic map on Figures 6a and 6b to give a pictorial overview of the typical geochemical tracers being detected in springwater. This picture shows the tendency, that spring waters in the Bavarian Molasse basin are generally characterized by elements such as lithium, silicon and uranium, usually linked to acid rocks, whereas those of the western Molasse basin show predominantly chromium-rich waters, an element which is preferentially associated with mafic or ultramafic rocks. Likewise, the sedimentary petrography of the deposits in the Bavarian basin, is characterized by silica-rich components (Unger 1989), whereas the influence of mafic and ultramafic clastic material is much stronger in the western part of the basin (Dietrich 1980). This general and certainly rough distinction of water samples within the Molasse basin can be consequently explained by the varying sedimentary petrography of the different feeder systems ("Schüttungen") transporting material from different source terranes in the Alps to the basin. To some extent, the presented results show, that the great variety of the Molasse basin sediments forming aquifer host rocks is reflected by the chemical groundwater composition.

3.2 Typical aquifer sub-types

Our findings are mainly established on the basis of geological aspects of groundwater geochemistry and require further statistical proof. As mentioned chemical bias due to anthropogenic influences can not be completely excluded in view of the densely populated study area. Nevertheless, some elements have proven to be of interest for characterizing groundwaters. In the following sections the individual aquifer sub-types with waters most typically marked by their hostrock will be discussed.

3.2.1 "Glimmersande" (OSM): $\text{Ca-Mg-HCO}_3\text{-(SO}_4\text{)-U-Mo-Li}$

The springwaters of the aquifer sub-type composed of OSM mica sands ("Glimmersande") in the area of the Lake of Constance have a very distinctive chemical footprint. Compared with the mean total of dissolved salts (TDS) of 450 mg/l ($n=104$) in the other sampled Molasse waters, these waters are higher mineralized with a mean value of 650 mg/l TDS ($n=8$). This is due to higher sulphate contents creating a $\text{Ca-Mg-HCO}_3\text{-(SO}_4\text{)-water}$ type.

In addition, the same waters are characterized by remarkably high concentrations of the association of molybdenum (Mo), uranium (U) and lithium (Li; Fig. 5, Tab. 1). With respect to average Molasse waters, median concentrations raise within this aquifer sub-type from 0.3 $\mu\text{g Mo/l}$ to 3.8 $\mu\text{g Mo/l}$, from 0.5 $\mu\text{g U/l}$ to 3.1 $\mu\text{g U/l}$, and from 2.0 $\mu\text{g Li/l}$ to 8.1 $\mu\text{g Li/l}$, respectively.

In order to explain this geochemical water markage, it is useful to remind here the particular sedimentological position of the "Glimmersande" within the Molasse deposits. They are believed to be accumulated by a large river system supposed to start in a silica-rich source terrane in the Salzburg (Austria) region in the east of the Molasse basin draining southwestward (Unger 1989, Hofmann 1959 and 1960). Consequently, they have undergone longer transport distances and mineral and grain size sorting processes as most of the Molasse deposited near the Alpine belt. In view of the sedimentary petrography, the sands are physically and mineralogically well sorted, i.e. quartz-rich (60–65%) and carbonate-poor (10–15%; Hofmann 1960).

Checking atmospheric and soil sources for these increased groundwater values, there is still a scarcity of trace element knowledge. Nevertheless, our few measured contents in snow samples are very low. In non industrial areas, the values vary around 0.1 $\mu\text{g Mo/l}$, 0.03 $\mu\text{g U/l}$ and less than 0.05 $\mu\text{g Li/l}$ (Hesske 1995).

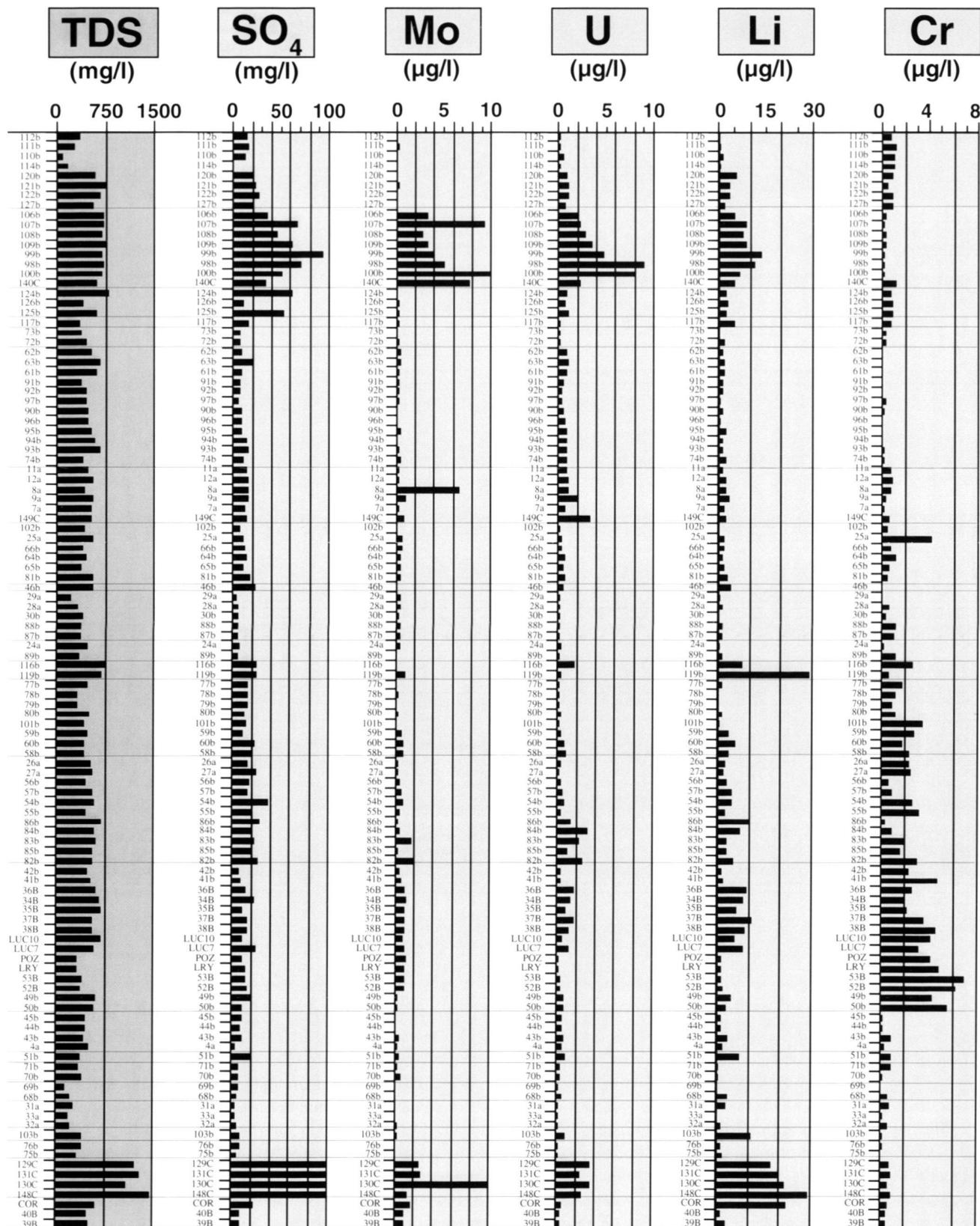
The particular water chemistry of the association of the elements Mo, U and Li, reflecting acid source rocks, can be explained by the lithological and hydrological conditions prevailing in the "Glimmersande" aquifers. Looking at sedimentary petrography, detrital sulfurous ore minerals and muscovite are abundant in the quartz-rich arenites (Hofmann 1960). Tuschschmid (1995), reported also higher molybdenum contents in this kind of mica sands compared to the psammitic rocks of the Swiss Molasse. Likewise, Dubois (1992) found considerable molybdenum and uranium anomalies in groundwater related to hydrothermal veins of fracture zones in granitic host-rocks. Hence, the increased water concentrations of molybdenum and sulfate might be produced by oxydation of sulfurous ore minerals, particularly pyrite and molybdenite, by acid rain, whereas lithium anomalies might originate from micas.

Effects of the late-Miocene Hegau volcanism on water geochemistry is unlikely because of the predominance of basaltic rock petrography. Phonolithe extrusions, as another possible lithogenic source, on the other hand, have a very small, local distribution.

From a hydrogeological point of view, mineral solution is enhanced in the "Glimmersande" by the intergranular porosity of the well sorted and almost unconsolidated aquifer sands providing a slow groundwater flow and a relatively high water-rock interaction surface. Residence times between 4 and 20 years have been reported (Geolog. Landesamt Baden-Württemberg 1990, 1992). Furtheron, the well washed sands contain low contents of absorbing material, such as clay minerals and organic matter. Accordingly, this fact favours the mobility of anions such as molybdate, MoO_4^{2-} and uranyl complexes, $\text{UO}_2(\text{CO}_3)_4^{4-}$, which are very soluble and mobile components under oxydating conditions and can easily circulate in aquifers.

Fig. 5. Semi-stratigraphical water composition profiles. Component analyses of 112 spring waters are arranged in geological order with respect to the stratigraphical position of the corresponding aquifer hostrock. This procedure allows to check spatial variations of water geochemistry with aquifer geology. The diagram illustrates that total mineralization (TDS) does not allow a good distinction of Molasse groundwater whereas trace elements such as molybdenum (Mo), uranium (U), lithium (Li) and chromium (Cr) serve as distinctive markers linked to aquifer geology. – Data used in this graphic can be found in Appendix 1. The geological units are named according to the stratigraphical lexica by Habicht (1987).

		"Schüttung"	Depositional facies (aquifer sub-type)	Spring number	Aquifer hostrock: geological unit lithology	
OSM		"Ost-West"	proximal	112b 111b 110b 114b 120b 121b 122b 127b	Hausruck-Schotter Obere Kobernausserswald-Schotter Munderfing-Schotter Mittlere Serie	quartz-crystalline-rich gravel sandy quartz-crystalline-rich gravel quartz-crystalline-rich gravel sandy quartz-gravel reworked sands
				106b 107b 108b 109b 99b 98b 100b 140C	Glimmersande	quartz-rich micaceous sands
			distal	124b 126b 125b	Nördliche Vollschorer	quartz-rich gravel
				117b 73b 72b	Ortenburger Schotter Sommersberg-Zone	quartz-rich gravel calcareous conglomerates, sandstones and marls
			proximal	62b 63b 61b 91b 92b 97b 96b 95b 94b 93b	Konglomerat-Fazies	calcareous and dolomitic conglomerates
		Sommersberg		74b	Oberaquitane Mergelzone	marls and sandstones
		Hörnli	proximal	11a 12a 8a 9a 7a	"Tortonian"	marls and sandstones
				149C		
				102b 25a 66b 64b 65b 81b	Napf-Schichten Belpberg-Schichten	polygenetic conglomerates tabular sandstones, marls tabular sandstones
				46b 29a 28a 30b 88b 87b	"Aquitanian" Gabelspitz-Schichten Wachthubel-Schichten	granitic sandstones and marls polygenetic quartzite-rich conglomerates
OMM		Napf	distal	24a 89b 116b 119b 77b	Kalchstätten-Formation Guggershorn-Formation Ottmanger Schlier Glaukomsand/Blättermergel	calcareous sandstones, marls and conglomerates calcareous conglomerates siliceous-rich, sandy marls siliceous-rich, sandy marls
				78b 79b 80b 101b 59b 60b 58b	Plattensandsteine/Seclaffen Luzerner Schichten	calcareous, tabular sandstones calcareous, glauconitic, tabular sandstones
				26a 56b 57b 54b 55b 86b 84b 83b 85b 82b	Oberer Muschelsandstein "Burdigalian" "Burdigalian/Helvétian" "Burdigalian"	glauconitic sandstones calcareous, glauconitic sandstones calcareous sandstones, marls
				41b 36b 34b 35b 37b 38b	"Burdigalian"	glauconitic sandstones
				LUC10 LUC7 POZ LRY 53b 52b 49b 50b	"Burdigalian/Helvétian"	
			brackish	45b 44b 43b 4a	Poudingue de la Sappalaz	quartzitic conglomerates
			shoreline	51b 71b 70b 69b 68b	Molasse grise de Lausanne Gäbris-Nagelfluh Granitische Molasse	marls, sandstones polygenetic conglomerates granitic sandstones, conglomerates, marls
				31a 33a 32a	Loseneegg-Schichten	polygenetic conglomerates
			open sea	103b 76b 75b	Bunte Serie s.l. Speer-Schichten	kristallinführende Kalk-Dolomit-Nagelfluh calcareous conglomerates
				129C 131C 130C 148C	Molasse à gypse	gypsum bearing sandstones and marls
USM		Guggisberg	estuary	COR 40b 39b	Grès de la Cornalle Conglomérats du Mont-Pélerin	calcareous sandstones and marls calcareous conglomerates
USM		marine OMM	proximal			
USM		Gibloux	proximal			
USM		Gäbris	proximal			
USM		Höhronen	proximal			
USM		Honegg	proximal			
USM		Rigi	proximal			
USM		Speer	proximal			
USM		"Chattian"	brackish			
USM		Mont-Pélerin	distal proximal			



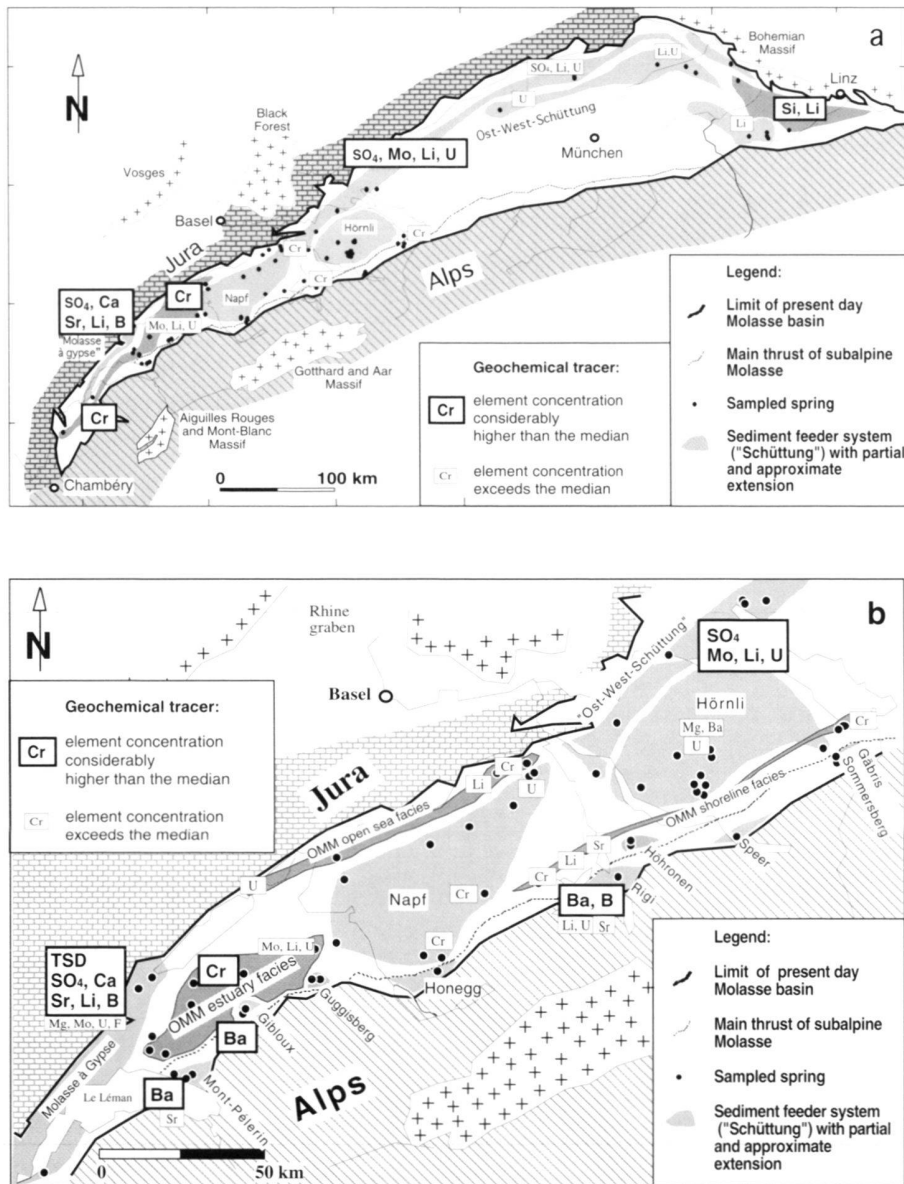


Fig. 6. Geochemical tracer distribution in the springwaters of the Molasse basin between Chambéry (France) and Linz (Austria; Fig. 6a) and of the Swiss basin (Fig. 6b). The relatively higher element concentrations are determined with respect to the median values of the whole water data set ($n=112$). This pictorial overview is based on the data of Appendix 1 and on the evaluation proceeding as shown in Fig 5.

3.2.2 OMM sandstones: $\text{Ca-Mg-HCO}_3\text{-Cr}$

Figures 5, 6a and b summarize the chromium (Cr) content distribution in the sampled Molasse aquifers. It reveals that increased chromium concentrations in groundwater cover remarkably the whole part of the OMM aquifers consisting of glauconitic and calcareous arenaceous rocks. In fact, while the median value of all sampled Molasse springwaters is $0.7 \mu\text{g Cr/l}$ ($n=112$), those of the 36 OMM water samples originating from marine sandstones, is considerably higher with $2.5 \mu\text{g Cr/l}$.

In order to confirm the characterization of OMM sandstones by increased chromium contents, the analysis of the for-

est spring LRY, belonging to the AQUITYP monitoring network, has been repeated regularly between April 1982 and May 1995. While the discharge rates vary considerably between 1 and 73 l/min and the electrical conductivity between 193 and 362 $\mu\text{S/cm}$ at the spring, the corresponding chromium concentrations remain in the range of 2.9 to 7.1 $\mu\text{g Cr/l}$ with a median concentration of 4.5 $\mu\text{g Cr/l}$ ($n=29$). Thus, this spring, also emerging from OMM-sandstones, confirms the representativeness of the single chromium measurement of 4.8 $\mu\text{g Cr/l}$ used for the present study of spatial geochemical variation in springwater.

Tab. 1a. Geochemical markers detected in springwaters from the “Glimmersande” aquifer sub-types, composed of micaceous sands of the “Ost-West-Schüttung” (OSM).

Num ber	Spring name, location	Water type	TDS (mg/l)	SO ₄ (mg/l)	U (µg/l)	Mo (µg/l)	Li (µg/l)
98b	Gemeindequelle, Diessenhofen	Ca-Mg-HCO ₃ -(SO ₄)	656	69.2	9.0	5.0	11
99b	Schupfenquelle, Diessenhofen	Ca-Mg-HCO ₃ -(SO ₄)	618	92.6	4.8	3.8	13
100b	Heubergrüti B., Winkel	Ca-Mg-HCO ₃ -(SO ₄)	640	50.8	8.0	-	7
106b	Soss, Owingen- Hohenbodmann	Ca-Mg-HCO ₃ -(SO ₄)	653	34.7	2.0	3.2	5
107b	Mösser, Owingen- Hohenbodmann	Ca-Mg-HCO ₃	656	66.1	2.3	9.2	9
108b	Hattental Nr. 1, Sipplingen	Ca-Mg-HCO ₃ -(SO ₄)	623	45.2	2.8	2.6	8
109b	Nonnenebene Nr. 4, Sipplingen	Ca-Mg-HCO ₃ -(SO ₄)	685	61.8	3.4	3.2	9
140C	Waldbrunnen, Stallikon	Ca-Mg-HCO ₃	560	32.9	2.2	7.7	5

Tab. 1b. Comparison of the median values of typical marker element concentrations in different aquifer lithologies.

Aquifer lithology	TDS (mg/l)	SO ₄ (mg/l)	U (µg/l)	Mo (µg/l)	Li (µg/l)
“Glimmersande” (OSM)	646 (n=8)	56.3 (n=8)	3.1 (n=8)	3.8 (n=7)	8 (n=8)
Gypsum bearing Molasse	1154 (n=4)	386.5 (n=4)	3.0 (n=4)	2.6 (n=4)	20 (n=4)
Molasse	447 (n=104)	12.9 (n=104)	0.5 (n=104)	0.3 (n=104)	2 (n=104)

Aquifer lithology	EC (µS/cm, 20°C)	SO ₄ (mg/l)	U (µg/l)	Mo (µg/l)	Li (µg/l)
Carbonated rocks (Dematteis 1995)	346 (n=110)	9.7 (n=112)	0.3 (n=112)	0.3 (n=112)	1 (n=112)
Evaporites (Mandia 1991)	1710 (n=92)	1060 (n=91)	5.4 (n=87)	-	20 (n=91)
Flysch (Basabe 1992)	291 (n=70)	10.9 (n=70)	0.3 (n=70)	-	4 (n=70)
Cristalline rocks (Dubois 1992)	75 (n=339)	9.0 (n=117)	8.2 (n=117)	5.4 (n=117)	3 (n=345)

These high chromium contents are also outstanding values compared to other aquifer types. Indeed, the median concentrations in groundwater originating from carbonated rocks (0.3 µg/l, n=112, Dematteis 1995), from evaporitic rocks (0.1 µg/l, n=82, Mandia 1991) and from flysch rocks (0.2 µg/l, n=69, Basabe 1992) are considerably lower than those in the OMM-sandstones.

The lithogenic origin of chrome in these groundwaters is assumed for several reasons. In deep formation waters of the OMM, having longer residence times than springwaters, the concentrations attained up to 16.5 µg Cr/l (borehole Zürich-Tiefenbrunnen, Hesske 1995). As seawater is poor in chromium (0.2 µg/l, Turekian 1969), the increased contents in groundwater of marine sandstones do not show a marine origin. This

suggestion is supported by the following sedimentological observation. Within this OMM-aquifer sub-type, chromium concentrations attain their greatest values close to the Prealps, in the western part of the Swiss Molasse basin (up to 7.0 µg Cr/l), whereas they decrease in an easterly direction along the basin axis (Fig. 5 and 6). We therefore suppose ophiolitic source terranes in the Prealps, as chromiferous-spinel associations derived from ophiolitic source areas are still found today in the Simme-Flysch of the Prealps (Wildi 1985). Fluvial systems transported the eroded rock material to the adjacent Molasse basin, where marine currents deviated it in easterly direction. The mixing up of these clastic sediments with non chromiferous sediments originating e.g. from the “Napf-Schüttung” can explain the decreasing chromium concentrations in the water within the aquifer sub-type in the eastern Swiss basin.

Concerning non-lithogenic influences, a systematic chemical bias due to chromiferous metal tubes at the spring catchment can be excluded, because 21 samples out of 36 could be sampled straight from the hostrock or from polyethylene (PE) and polyvinylchloride (PVC) tubes. Moreover, Cr contents in atmospheric and soil water are generally low, not passing 0.2 µg Cr/l (Atteia 1992, Hesske 1995, Dalla Piazza 1996). Only water from soils developed from OMM sandstones show values up to 2.0 µg Cr/l (Atteia 1992). The liberation of chromium in the soil seems to be related to weathered ophiolitic detritus, more precisely to the dissolution of a serpentinite phase-type in the bottom of the soil (Dalla Piazza 1996). Once liberated from the rock, chromium forms less adsorbed chromate anions under the alkaline and oxygenated conditions of shallow groundwaters. They are therefore quite soluble in water (Matzat & Shiraki 1978, Drever 1982, Bodek 1988).

3.2.3 Brackish OMM (“Ottangian”): Ca-Mg-HCO₃-Si

The brackish OMM of the Paratethys, deposited during Ottangian-time, is only found in the eastern part of the Bavarian Molasse basin. The sediments are composed of quartz-rich, thinly stratified marls and sandstones, called “Schlier” in Austria. The fine grained sediments are of low permeability and produce waters with an increased total mineralization of around 650 mg TDS/l compared to the mean Molasse value of 450 mg TDS/l (n=112; Appendix 1 sample no 116b and 119b). This increased mineralization is a characteristic feature of the so-called “Schlierwässer” (Schramm 1986).

One of the most conspicuous elements found in the “Schlierwässer” is silicon (Si), rising up to 19.0 mg Si/l, naturally occurring in water as silicic acid, H₄SiO₄. Generally, the mean value for Molasse springwaters is 6.2 mg Si/l (n=112). In Figure 7, silicon concentrations have been plotted against temperature. The highest values (> 10 mg Si/l) are in agreement with the occurrence of quartz-rich aquifer hostrocks and only found in the Bavarian Molasse basin. Maximum concentrations were measured at the “Unterkienberg-spring” in Wolfs-egg am Hausruck (Austria) with 17.7 mg Si/l and at the natural spring of the “Teufelsmühle” in Griesbach i.R. (Bavaria) with

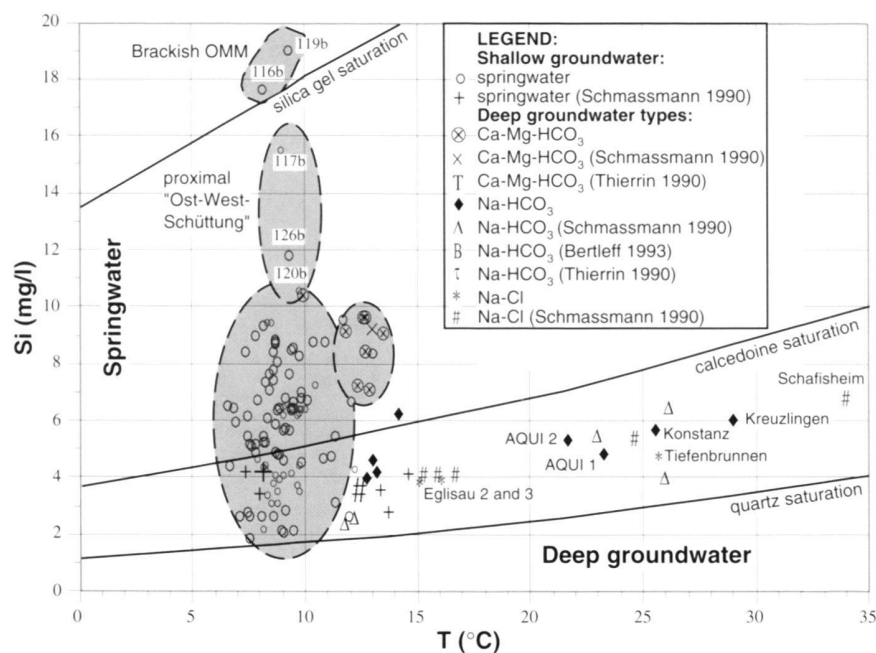


Fig. 7. Relationship between water temperature and silicon concentrations in various molassic groundwaters (modified after Hesske 1995). The saturation curves have been calculated with WATEQ4F which is based on the thermodynamical data of Nordstrom et al. (1990).

19.0 mg Si/l. For the latter, Unger (1984) reported also a high value of 14.7 mg Si/l, which confirms the order of magnitude of this Si-anomaly. On the diagram of Figure 7, these waters are found in vicinity of the silica gel saturation curve.

In order to compare Si concentrations with respect to water temperature, thermal and subthermal deep groundwaters, characterized by tritium activities generally below about 1 tritium unit (TU), have also been plotted in Figure 7. These are saline formation waters of the sodium-chloride type occurring in the pores of deeply buried Molasse sediments and show long residence times of the water (Schmassmann et al. 1984). Even so, their Si contents are situated below the range of the shallow Ottnangian groundwaters and do not exceed 7.0 mg Si/l (6.9 mg Si/l in the borehole "Schafisheim"; Schmassmann et al. 1984). Moreover, the reworked quartzitic and unconsolidated OSM pebble deposits of the Bavarian basin with important intergranular porosity (with K-values of $9 \cdot 10^{-4}$ to $2 \cdot 10^{-6}$ m/s, Egger 1985), such as the "Ortenburger Schotter", the "Nördliche Vollsotter" and the "Mittlere Serie", also show high Si concentrations in groundwater (ranging between 4.0 and 15.4 mg Si/l, Appendix 1) but lower ones than the marly Ottnangian sediments. That means, that, besides of a slow groundwater flow, high Si concentrations in water are mainly dependent on both, high silica content in the hostrock and a large water-rock reaction surface provided by a fine grained sediment.

3.2.4 "Molasse à gypse" (USM): $\text{Ca-Mg-SO}_4\text{-HCO}_3\text{-Sr-Li-B}$

The Chattian Molasse of the USM represents a particular aquifer sub-type which occurs in western Switzerland. The sediments consist of gypsum-bearing marls and sandstones, the so-

called "Molasse à gypse". Emerging springwaters are highly mineralized (>1000 mg TSD/l) due to leaching of sulphate and calcium ions resulting from dissolution of gypsum (Tab. 2). They are generally of the $\text{Ca-Mg-SO}_4\text{-HCO}_3$ type. Additionally, a variety of trace elements in water were greatest in these aquifer sub-types, containing strontium (Sr), lithium (Li; Fig. 5) and boron (B) in characteristic amounts, but also distinctive concentrations of magnesium (Mg), molybdenum (Mo), uranium (U) and copper (Cu; Tab. 2). Thus, water composition of molassic sulphate waters is quite similar to those issued from Triassic evaporitic rocks studied by Mandia 1991 (Tab. 2). Nevertheless, natural trace element marking might be disturbed by the quaternary cover of these aquifers, but also by the agricultural land use of the recharge area. The latter is obviously indicated by high contents of nitrates, often accompanied by increased chloride and bromide concentrations (Appendix 1).

3.2.5 Fracture dominated aquifers: $\text{Ca-Mg-HCO}_3\text{-Ba}$

Considering barium (Ba) concentrations in Molasse waters, showing a median value of $27 \mu\text{g/l}$ ($n=112$), variation of contents does not correlate with sedimentary petrography as in the previous cases. High concentrations exceeding $150 \mu\text{g/l}$ and attaining a maximum value up to $334 \mu\text{g/l}$ occur in spring waters issued from the quartzitic conglomerates of the Gibriloux fan deposits ("Poudingue de la Sappalaz"), from the "kristallinführende Kalk-Dolomit-Nagelfluh" of the Rigi fan and from calcareous sandstones and marls of the Pélerin fan ("Grès de la Cornalle", Appendix 1). Nevertheless, it is interesting to note, that all of these aquifer sub-types have in com-

No	Spring name, location	Water type	TDS (mg/l)	SO ₄ (mg/l)	Ca (mg/l)	Sr (μg/l)	Li (μg/l)	B (μg/l)	Mg (mg/l)	Mo (μg/l)	U (μg/l)	Cu (μg/l)
129C	Bel Air, Yverdon	Ca-(Mg)-SO ₄ -HCO ₃	1121	364.0	231.1	4.71	17	20	35.4	2.6	3.5	2.3
130C	Ferme Perrin, Ependes *	Ca-Mg-HCO ₃ -SO ₄ -(Cl)	989	255.0	168.5	4.68	21	31	43.2	-	3.5	3.1
131C	Beauregard, Yverdon	Ca-Mg-SO ₄ -HCO ₃	1187	409.0	237.4	4.03	19	12	39.9	2.7	2.4	2.8
148C	Fontaine, Choulex	Ca-(Mg)-SO ₄ -HCO ₃	1353	445.0	289.2	4.80	29	52	39.0	1.3	2.5	49.5
	Spring group											
	Molassic sulphate springs	median (n=4)	1154	386.5	234.3	4.69	20.3	26	39.5	2.6	3.0	2.9
	Evaporite springs (Mandia 1991)		1710 (n=92)	1060 (n=91)	442.0 (n=91)	8.24 (n=91)	20 (n=91)	20 (n=86)	57.1 (n=91)	- (n=87)	5.4 (n=88)	3.0 (n=88)
	Molasse springs	median (n=112)	446	13.4	86.2	0.23	2.2	3.3	14.9	0.4	0.5	0.2

Tab. 2. Geochemical markers detected in spring-waters from gypsum-bearing aquifer sub-types, composed of marls and sandstones (USM). They are compared with median concentrations of Molasse and Evaporite springs (lower part). (The outstanding copper (Cu) value of 49.5 μg/l measured at the spring in Choulex GE is supposed to be the result of manmade vineyard treatment.)

mon to be situated in the subalpine or folded Molasse where aquifer permeabilities are dominated by fractures.

Looking at the origin of barium, this trace element may reflect the presence of the barium mineral barytes, BaSO₄. Initially dissolved from weathered potassium feldspars and mica (Dalla Piazza 1996), barium tends to precipitate in fractures of molassic rocks as post-tectonic and authigenous barytes as reported by von Moos (1935), Gasser (1966) and Maurer et al. (1978). The presence of barium in groundwater might therefore be the response of the dissolution of barytes in water circulating through these fractures. Therefore, our preliminary findings leads us to the hypothesis, that high barium contents in water are a hydrogeological marker for a dominantly fissural flow system in the aquifer.

4. Conclusions

Molasse aquifers have been subdivided into about 30 aquifer sub-types with respect to their varying sedimentary petrography, hydraulic conductivity and grain size distribution. Such a geological and hydrogeological approach shows, that the great variety of the Molasse basin sediments forming aquifer host-rocks is reflected by the groundwater geochemistry. Thus, a great number of springwaters, usually classified as calcium-magnesium-bicarbonate type, can chemically be clearly distinguished using trace elements, such as chromium, uranium, lithium, molybdenum and barium.

Naturally occurring mineral constituents in water must fulfill four conditions when serving as lithogenic tracers: first, typically marking elements must occur in the hostrock minerals of the aquifer. Second, they should be soluble in prevailing water conditions, third, be present in measurable amounts, and finally they should allow a clear distinction from other aquifer water types.

Despite the lack of further statistical proof and a possible chemical bias due to anthropogenic influences, our finding confirms the idea that trace element analyses can provide a new tool in applied geology when concerned with the determination of geological water origin in Molasse deposits in underground works and boreholes. Presented data contribute as well

to a georeference for naturally occurring element contents in groundwater which helps to assess water quality criteria. Subsequently, field geologists might use trace element analyses of springwater in order to check subsurface geology in a hilly recharge area with poor outcrop conditions.

There exists an analogy between clastic sedimentology and hydrochemistry. Thus, the study of heavy minerals within a great bulk of clastic sedimentary material enabled sedimentologists to determine more precisely the source terrane of a deposit. Similarly, trace element contents in groundwater contain more information on water origin as major water constituents which often do not allow any differentiation.

Although considerable research has been done on Molasse deposits, much less is known on their geochemical and mineralogical sedimentary composition. Such a gap of knowledge, in turn, makes it difficult to explain geochemical markers in groundwater in many greater details. Additionally, a full understanding of the complexity of groundwater geochemistry can only be achieved by a sufficient knowledge of element variability in space and time (long term monitoring) and further investigations of water-rock interaction processes in a natural environment, including rock leachate tests in laboratory.

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Number	Spring name	Location	Coordinates Y	X	Elevation m a.s.	Water Type
OMM, brackish facies						
116b	Unterkienberg	Wolfsegg a. Hausruck (A)	L775.519	B5329.274	555	Ca-Mg-HCO3
119b	Teufelsmühle	Griesbach i. Rottal (D)	R4586.740	H5367.110	360	Ca-Mg-HCO3
OMM, shoreline facies						
77b	Vogelherd-Quelle	Rorschacherberg	756.860	259.370	650	Ca-Mg-HCO3
78b	Hobrüti-Quelle	Rorschacherberg	756.140	258.860	700	Ca-Mg-HCO3
79b	Hasenhus-Buob-Quelle	Rorschacherberg	755.280	258.500	715	Ca-(Mg)-HCO3
80b	Ulmann-Quelle	Rorschacherberg	754.980	258.040	765	Ca-(Mg)-HCO3
101b	Steintobel-Q. Nr.1, links	Risch (ZG)	675.270	219.735	590	Ca-Mg-HCO3
58b	Tobel-Quelle	Malters (LU)	660.780	210.030	600	Ca-Mg-HCO3
59b	Steinbruch-Quelle	Kriens	660.820	209.750	620	Ca-Mg-HCO3
60b	Loch- und Täli-Quelle	Malters	660.820	210.090	550	Ca-Mg-HCO3-(SO4)
OMM, open sea facies						
26a	Kobi-Quellstollen	Biezwil (SO)	598.330	217.920	600	Ca-HCO3
27a	Holen-Quellstollen	Biezwil (SO)	598.430	217.770	620	Ca-HCO3
54b	Hohlgasse	Oberentfelden	647.480	244.620	520	Ca-Mg-HCO3-(SO4)
55b	Waldgraben	Uerkheim	642.550	240.350	570	Ca-(Mg)-HCO3
56b	Ob. Wildenstein-Stollen	Lenzburg (AG)	657.080	247.770	470	Ca-Mg-HCO3
57b	Lütisbuech-Stollen Nr.3	Lenzburg-Lütisbuech	656.870	246.830	450	Ca-Mg-HCO3
82b	Quellstollen Nr.12	Gals	571.570	208.960	535	Ca-Mg-HCO3
83b	Quellstollen Nr.7	Gals	571.860	209.220	540	Ca-Mg-HCO3
84b	Quellstollen Nr.1	Gals	572.080	209.440	500	Ca-Mg-HCO3
85b	Quelle Entschertz	Tschugg	571.770	208.330	555	Ca-Mg-HCO3
86b	Quellstollen Rappenried	Tschugg	572.470	208.900	520	Ca-Mg-HCO3
OMM, estuary facies						
34B	Creux de Nervaux	Payeme	563.720	183.550	605	Ca-Mg-HCO3
35B	Petite source	Payeme	563.720	183.550	605	Ca-Mg-HCO3
36B	Maison Rouge	Onnens	569.500	181.810	655	Ca-Mg-HCO3
37B	regard 2, drain 2	Cheiry	553.800	178.640	627	Ca-Mg-HCO3
38B	regard 1	Cheiry	553.670	178.600	646	Ca-Mg-HCO3-(Cl)-(NO3)
41b	Rüti	Albigen	591.180	189.050	735	Ca-Mg-HCO3
42b	Hargart	Albigen	591.340	189.690	770	Ca-Mg-HCO3
LUC7	drain 7 sous forêt	Lucens	553.180	172.040	600	Ca-Mg-HCO3
LUC10	drain 10 sous cultures	Lucens	553.180	172.040	600	Ca-Mg-HCO3
URY	Bois du Grand Jorat	Savigny	544.620	157.350	878	Ca-(Mg)-HCO3
POZ	Pierre Ozaire	Savigny	544.860	156.690	855	Ca-(Mg)-HCO3-(Cl)
52B	regard 2, drain 10	Lausanne	540.060	158.060	810	Ca-(Mg)-HCO3
53B	regard 1, drain 3	Lausanne	540.100	158.150	810	Ca-(Mg)-HCO3-(NO3)
49b	Chez Davy	Menthonnex s. Cl. (F)	F879.80	F112.98	600	Ca-(Mg)-HCO3
50b	Chainaz	Menthonnex s. Cl. (F)	F880.16	F113.09	560	Ca-(Mg)-HCO3
"Gibloux-Delta"						
4a	chambre 53, drain b	Sorens	568.730	169.680	1050	Ca-(Mg)-HCO3
43b	chambre 1a, drain A	Villarod	569.200	171.150	985	Ca-Mg-HCO3
44b	chambre 123C, drain 2	Sorens	569.370	169.750	1030	Ca-(Mg)-HCO3
45b	ch. 123C, "nouveau drain"	Sorens	569.670	170.020	1130	Ca-(Mg)-HCO3
Molasse grise de Lausanne						
51b	Galerie "La Mine"	Bottens	540.760	162.580	745	Ca-Mg-HCO3-(SO4)
"Gäbris-Schüttfächer"						
70b	ob. Gigerquelle	Gais	753.560	249.540	1150	Ca-Mg-HCO3
71b	unt. Gigerquelle	Gais	753.960	249.560	1110	Ca-Mg-HCO3
"Höhronen-Schüttung"						
68b	Itten-Hausquelle	Oberägeri	689.660	222.520	975	Ca-Mg-HCO3
69b	Militärquelle	Oberägeri	689.740	223.070	1140	Ca-Mg-HCO3-(SO4)
"Honegg-Nagelfluh"						
31a	Nr.1, Hofbr.	Eriz	629.420	183.650	1415	Ca-Mg-HCO3
32a	Nr.2, Reservoir	Eriz	629.380	183.700	1430	Ca-Mg-HCO3
33a	abreuvoir	Eriz	629.400	183.320	1320	Ca-Mg-HCO3
"Rigi-Schüttung s.l."						
103b	Grisselen	Arth	685.440	211.920	555	Ca-Mg-HCO3
"Speer-Schüttfächer"						
75b	Geissrüti	Schänis	722.780	223.710	560	Ca-Mg-HCO3
76b	Rüti	Schänis	722.950	224.970	550	Ca-Mg-HCO3
Molasse à gypse						
129c	Bel Air	Yverdon	540.660	180.700	484	Ca-(Mg)-SO4-HCO3
130c	Ferne Perrin	Ependes	536.810	177.090	470	Ca-Mg-HCO3-SO4-(Cl)
131c	captage de M. Willer	Yverdon	540.290	180.570	475	Ca-Mg-SO4-HCO3
148c	Fontaine publique	Choulex	506.600	120.210	435	Ca-(Mg)-SO4-HCO3
Grès de la Cornalle						
CCR	Comalle	Eppesses	547.420	149.240	597	Ca-Mg-Na-HCO3
Conglomerats du Mont-Pélerin						
39b	galerie de Longive	Puidoux	551.450	149.370	836	Ca-(Mg)-HCO3
40b	tranchée	Chardonne	552.510	150.420	935	Ca-(Mg)-HCO3

Appendix 1. Location of the individual springs sampled within the Molasse Basin. The water samples are grouped according to aquifer sub-types, defined on the basis of the sedimentary petrography, hydraulic conductivity and grain size distribution of the aquifers. Description of the water type based on milliequivalent concentrations of major ions according to Jäckli (1970) and Schmassmann et al. (1984).

Number	Spring name	Location	Coordinates Y	X	Elevation m a.s.	Water Type
Hausruck-Schotter						
112b	Hochlehen-Quelle	Fornach (A)	L757.150	B5322.550	680	Ca-HCO3
Kobernausserwald-Schotter						
110b	Fornacher Redl	Fornach (A)	L755.100	B5327.200	660	Ca-(Mg)-SO4-HCO3-(NO3)
111b	S Redlthal	Fornach (A)	L756.050	B5323.500	590	Ca-Mg-HCO3-(SO4)
Munderfing Schotter						
114b	Kolming	Mattighofen (A)	L741.050	B5322.600	493	Ca-Mg-HCO3
Mittlere Serie						
120b	Simbacher Wiesen	Simbach (D)	R4554.400	H5380.980	420	Ca-Mg-HCO3
121b	Schellmühle	Mammig (D)	R4541.500	H5389.400	380	Ca-Mg-HCO3
122b	Moosthann	Postau-Moosthann (D)	R4521.440	H5392.160	410	Ca-Mg-HCO3-(Cl)
Erolzheimer Sande (L3)						
127b	Fleinhausen/Kobel	Dinkelscherben (D)	R4392.050	H5359.110	490	Ca-Mg-HCO3
Glimmersande						
106b	Soss	Owingen-Hohenbodmann (D)	R3515.500	H5297.880	615	Ca-Mg-HCO3
107b	Mösser	Owingen-Hohenbodmann (D)	R3515.190	H5297.810	618	Ca-Mg-HCO3-(SO4)
108b	Hattental Nr.1	Sipplingen (D)	R3508.129	H5295.837	592	Ca-Mg-HCO3-(SO4)
109b	Nonnenebene Nr.4	Sipplingen (D)	R3507.860	H5295.998	598	Ca-Mg-HCO3-(SO4)
98b	Rodenberg	Diessenhofen	701.020	281.190	440	Ca-Mg-HCO3-(SO4)
99b	Rodenberg	Diessenhofen	701.560	281.070	440	Ca-Mg-HCO3-SO4
100b	Heubergrüti	Winkel	684.861	260.223	535	Ca-Mg-HCO3-(SO4)
140c	Müli-Waldbrunnen	Stallikon	678.420	244.260	530	Ca-Mg-HCO3
Nördliche Vollschotter						
124b	Hohenried	Brunnen (D)	R4454.010	H5388.470	440	Ca-Mg-HCO3-NO3-(SO4)
125b	Rettenbach	Schrobenhausen (D)	R4444.780	H5376.290	430	Ca-Mg-HCO3-(NO3)-(SO4)-(Cl)
126b	Sattelberg	Gachenbach (D)	R4446.990	H5371.520	460	Ca-Mg-HCO3-(Cl)-(NO3)
Ortenburger Schotter						
117b	Edelsbrunn	Aldersbach (D)	R4581.600	H5383.780	340	Ca-(Mg)-HCO3-(NO3)-(Cl)
"Sommersberg-Zone"						
72b	Rietlihof-Quelle	Gais	754.630	247.710	955	Ca-HCO3
73b	Quelle Hofgut 3a	Gais	754.670	248.800	960	Ca-HCO3
"Hörnli-Schüttung"						
61b	Schulhaus-Quelle	Fischingen	714.370	251.070	735	Ca-Mg-HCO3
62b	Böhi-Quelle	Fischingen	714.820	249.800	825	Ca-Mg-HCO3
63b	Klosterblick	Fischingen	714.580	251.770	752	Ca-Mg-HCO3
90b	Bachtelweid-Quelle	Wald (ZH)	709.930	238.630	915	Ca-Mg-HCO3
91b	Beizi	Wald (ZH)	712.720	240.680	820	Ca-Mg-HCO3
92b	Sagenrain	Wald (ZH)	712.200	237.950	650	Ca-Mg-HCO3
93b	Herrliberg-Quelle	Herrliberg	692.290	239.890	820	Ca-Mg-HCO3
94b	Hohwacht	Russikon	703.670	250.170	750	Ca-Mg-HCO3
95b	Girriet	Hinwil	708.730	241.120	840	Ca-Mg-HCO3
96b	Hörnli/Allmen	Hinwil	709.620	240.860	1010	Ca-Mg-HCO3
97b	Würz	Fischenthal	711.350	243.800	910	Ca-(Mg)-HCO3
Oberaquitane Mergelzone						
74b	Steineggwald	Teufen	749.760	252.140	910	Ca-Mg-HCO3
"Tortonian"						
7a	Stöckhof	Lenzburg	658.250	244.630	585	Ca-(Mg)-HCO3
8a	Eichberg	Seengen	658.340	243.340	660	Ca-Mg-HCO3
9a	Eichberg	Seengen	658.340	243.340	660	Ca-Mg-HCO3
11a	Grossmoos	Villmergen	659.330	244.400	610	Ca-(Mg)-HCO3
12a	Grossmoos	Villmergen	659.330	244.400	610	Ca-Mg-HCO3
149C	Schwarzenberg	Gontenschwil (AG)	652.890	234.390	610	Ca-Mg-HCO3
Napf-Schichten						
102b	Weierhüsli	Romoos	644.070	206.720	785	Ca-HCO3
Belalp Schichten						
25a	Spycher-Quellstollen	Oberbalm (BE)	597.820	191.260	830	Ca-(Mg)-HCO3
64b	Brunnstube b. Reservoir	Altishofen (LU)	639.070	227.660	590	Ca-Mg-HCO3
65b	Schlosshof-Waldquelle	Altishofen (LU)	638.980	227.880	600	Ca-Mg-HCO3
66b	Kiesgruben-Stollen	Altishofen (LU)	639.240	227.450	595	Ca-Mg-HCO3
81b	Käser-Quellstollen	Kleindietwil (BE)	627.230	221.800	620	Ca-(Mg)-HCO3
"Aquitani"						
46b	Rufer-Stollen	Bangerten	600.350	210.920	600	Ca-HCO3
Gabelspitz Schichten						
28a	Fassung Nr.3	Röthenbach i.E.	625.080	187.680	1180	Ca-(Mg)-HCO3
29a	Brunnstube 3, Quelle 5	Röthenbach i.E.	625.242	187.466	1155	Ca-HCO3
30a	Friedli-Hofbrunnen	Schangnau	631.040	186.130	1000	Ca-HCO3
87b	untere Eggli-Quelle	Schangnau	630.670	187.080	1055	Ca-HCO3
88b	obere Eggli-Quelle	Schangnau	630.770	186.990	1060	Ca-HCO3
Kalchstätten-Formation						
24a	Gemeinschaftsquelle	Guggisberg - Chrüz	590.710	180.200	1070	Ca-HCO3
Guggershorn-Formation						
89b	Sternen-Quelle	Guggisberg	592.250	180.020	1180	Ca-Mg-HCO3

Number	Sampling date	TDS (mg/l)	Hardn. (°f)	Q (l/min)	EC (µS/cm) (20°C)	T (°C)	pH	Eh (mV) (H corr.)	Ca (mg/l) 2 to 4	Mg (mg/l) 0.2	Na (mg/l) 0.2	K (mg/l) 0.2	Sr (mg/l) 0.01	Si (mg/l) 0.5
Detection limit														
Hausrück-Schotter														
112b	12.11.93	302	16.5	3	303	8.8	7.1	437	70.3	1.2	0.9	0.5	0.07	5.0
Kobenausserwald-Schotter														
110b	12.11.93	57	1.2	31	22	6.5	6.5	462	6.5	0.7	1.7	0.5	0.07	6.7
111b	12.11.93	224	19.8	24	212	7.3	7.5	449	37.6	8.5	1.0	0.5	0.43	8.6
Munderfing Schotter														
114b	12.11.93	146	7.8	48	143	7.7	7.8	427	20.2	5.4	1.7	0.4	0.06	9.1
Mittlere Serie														
120b	16.11.93	541	30.5	66	553	9.8	7.2	432	89.8	28.1	6.1	0.8	0.11	10.5
121b	16.11.93	677	39.9	1260	705	9.7	7.1	439	115.1	34.0	5.3	2.5	0.16	8.4
122b	16.11.93	612	37.5	45	661	8.5	7.4	432	103.8	28.1	4.2	0.5	0.16	9.3
Erolzheimer Sande (L3)														
127b	18.11.93	501	29.7	5	536	9.1	7.2	484	97.2	19.7	3.9	0.4	0.13	4.0
Glimmersande														
106b	29.10.93	656	37.3	27	679	9.4	7.5	403	122.7	25.3	5.8	0.7	0.29	6.8
107b	29.10.93	653	39.4	127	698	9.7	7.6	403	123.7	27.2	4.7	0.7	0.29	6.1
108b	29.10.93	623	36.5	30	619	9.1	7.6	423	109.4	26.2	2.6	0.6	0.24	7.0
109b	29.10.93	685	39.1	26	679	9.3	7.6	440	122.7	30.8	2.4	0.7	0.30	8.6
98b	30.9.93	656	37.9	4	641	9.8	8.1	337	121.8	26.0	2.4	0.9	0.22	6.9
99b	30.9.93	618	37.8	13	617	9.8	7.8	377	111.0	27.0	2.4	0.9	0.16	7.2
100b	30.9.93	640	38.4	19	643	10.5	8.1	352	112.7	25.7	2.6	0.8	0.22	7.2
140c	5.8.94	560	16.7	2	561	11.9	7.8	398	94.7	25.9	8.5	0.8	0.68	2.8
Nördliche Vollsotter														
124b	17.11.93	726	43.3	17	806	8.6	7.2	397	117.4	36.1	10.5	1.3	0.10	8.8
125b	17.11.93	561	31.5	13	607	8.7	7.0	288	90.5	29.1	6.2	2.4	0.13	8.2
126b	17.11.93	347	18.8	360	354	9.2	7.1	402	54.9	16.7	4.1	0.8	0.07	12.0
Ortenburger Schotter														
117b	15.11.93	297	15.1	66	310	9.0	6.6	422	49.0	6.5	5.1	0.7	0.07	15.4
"Sommersberg-Zone"														
72b	8.9.93	411	25.0	280	410	9.7	7.3	383	92.7	3.1	2.4	4.2	0.46	3.7
73b	8.9.93	333	19.8	30	328	7.0	7.3	386	79.3	1.2	0.3	0.5	0.32	2.8
"Hörnli-Schüttung"														
61b	25.8.93	547	30.4	26	525	8.7	7.2	361	103.6	23.2	1.1	0.6	0.25	4.0
62b	25.8.93	488	29.0	>6	473	9.8	7.2	374	88.3	22.7	1.1	0.5	0.22	3.4
63b	25.8.93	604	29.6	7	568	8.6	7.3	375	105.3	27.3	1.7	0.5	0.32	5.1
90b	27.9.93	441	25.8	77	440	8.4	7.9	368	85.3	14.5	1.3	0.5	0.16	3.3
91b	27.9.93	334	18.9	160	330	7.4	7.3	349	59.9	14.6	1.0	0.6	0.11	2.9
92b	27.9.93	396	22.0	65	393	8.8	7.6	403	72.0	12.0	1.4	0.5	0.12	3.0
93b	28.9.93	603	34.2	27	583	7.7	7.7	423	108.8	25.2	1.4	0.4	0.23	5.0
94b	28.9.93	530	31.2	7	526	9.4	7.6	407	90.4	25.0	1.3	0.6	0.19	4.1
95b	29.9.93	491	28.3	49	485	8.9	7.7	410	89.8	21.0	2.5	0.5	0.24	3.9
96b	29.9.93	428	25.8	2	430	8.0	8.1	395	75.2	20.2	0.8	0.7	0.01	2.8
97b	29.9.93	407	22.8	5	389	12.2	7.6	385	82.0	12.1	1.1	0.4	0.11	4.2
Obersäutane Mergelzone														
74b	8.9.93	350	21.0	72	355	8.6	7.0	373	56.6	13.6	7.0	0.9	0.35	3.7
"Tortonian"														
7a	13.5.93	482	20.5	14	470	6.9	6.9	372	103.0	9.4	2.1	0.6	0.29	6.1
8a	14.5.93	387	23.2	10	374	8.2	6.7	419	73.9	14.6	2.3	0.8	0.12	7.5
9a	14.5.93	497	29.3	32	479	7.8	6.7	426	90.1	21.1	2.4	0.9	0.38	6.9
11a	14.5.93	442	26.1	39	431	6.8	6.8	399	93.3	7.3	2.2	0.9	0.20	6.6
12a	14.5.93	508	30.4	22	491	7.4	6.8	396	99.0	17.3	2.1	0.6	0.33	6.3
149C	10.9.94	485	27.9	2	479	8.8	7.7	411	89.6	18.7	3.2	0.8	0.62	3.4
Napf-Schichten														
102b	4.10.93	395	19.5	194	394	8.3	8.1	445	86.2	3.9	1.7	2.4	0.25	4.4
Belpberg Schichten														
25a	21.7.93	496	27.8	20	467	8.4	6.9	430	95.8	13.4	3.2	1.2	0.27	7.8
64b	28.8.93	408	23.8	10	412	8.4	7.2	369	72.5	13.2	2.2	0.8	0.19	7.2
65b	28.8.93	324	17.4	10	307	8.5	7.0	377	55.2	13.3	1.2	0.6	0.14	7.9
66b	28.8.93	365	20.3	18	356	9.2	7.1	379	67.0	12.2	1.9	0.9	0.17	7.8
81b	11.9.93	498	27.6	3	486	12.9	7.3	377	88.6	13.5	2.9	1.8	0.23	8.5
"Aquitani"														
46b	16.8.93	506	28.1	9	472	8.5	7.3	375	105.6	7.0	3.6	0.6	0.14	8.6
Gabelspitz Schichten														
28a	29.7.93	279	14.6	15	260	8.8	7.7	440	59.1	5.4	1.3	0.9	0.11	6.4
29a	29.7.93	193	10.0	95	183	7.7	7.2	458	38.2	1.3	0.5	0.8	0.04	5.4
30a	29.7.93	368	20.4	21	370	11.1	7.3	461	80.4	1.3	2.6	2.1	0.13	4.9
87b	20.9.93	324	18.6	40	320	8.2	7.3	373	71.0	1.6	1.8	1.3	0.15	4.3
88b	20.9.93	330	18.4	71	323	8.3	7.3	379	72.0	2.3	1.7	1.0	0.12	4.2
Kalchstätten-Formation														
24a	21.7.93	421	23.8	24	407	10.7	6.9	430	96.5	1.3	1.6	0.8	0.16	4.8
Guggershorn-Formation														
89b	20.9.93	300	18.5	130	300	6.6	7.6	387	57.7	9.2	0.6	0.6	0.17	4.6

Appendix 2. Field parameters and major cation chemistry of spring waters from Molasse aquifers. The water samples are grouped according to aquifer sub-types, defined on the basis of the sedimentary petrography, hydraulic conductivity and grain size distribution of the aquifers.

Multielement analyses have been performed with the High Resolution Inductively Coupled Plasma Source Mass Spectrometry (HR-ICP-MS) of VG/FISONS Instruments. Silicon were determined by using colorimetry. Total concentrations, i.e. including the particle-bound fraction are reported.

(Q: spring discharge; EC: Electrical conductivity corrected for 20°C)

Number	Sampling date	TDS (mg/l)	Hardn. (°f)	Q (l/min)	EC (µS/cm) (20°C)	T (°C)	pH	Eh (mV) (H corr.)	Ca (mg/l) 2 to 4	Mg (mg/l) 0.2	Na (mg/l) 0.2	K (mg/l) 0.2	Sr (mg/l) 0.01	Si (mg/l) 0.5
Detection limit														
OMM, brackish facies														
116b	14.11.93	683	37.4	25	637	8.1	7.4	419	116.4	32.6	3.4	2.1	0.38	17.7
119b	15.11.93	629	33.2	8	570	9.4	6.8	395	99.2	31.5	4.5	1.8	0.27	19.0
OMM, shoreline facies														
77b	10.9.93	426	23.5	15	422	8.8	7.4	375	83.0	15.4	2.2	0.9	0.30	6.6
78b	10.9.93	295	16.9	116	301	8.2	7.2	367	52.9	13.8	2.0	0.6	0.27	5.4
79b	10.9.93	273	15.3	95	277	8.7	7.2	394	52.8	7.1	1.5	0.6	0.19	5.0
80b	10.9.93	454	25.0	16	447	8.1	7.4	391	90.3	12.7	2.3	0.7	0.40	5.6
101b	1.10.93	384	20.5	24	387	9.8	7.6	399	72.7	12.3	1.8	0.9	0.33	6.3
58b	24.8.93	380	22.0	n.m.	381	9.4	7.2	374	59.0	21.2	4.5	1.4	0.56	6.6
59b	24.8.93	428	23.7	20	418	12.0	7.2	377	79.3	16.3	4.3	1.8	0.52	6.8
60b	24.8.93	380	21.0	200	381	9.4	7.2	372	52.5	23.4	6.7	1.3	0.70	6.4
OMM, open sea facies														
26a	26.7.93	490	27.2	3	463	9.2	7.0	n.m.	102.4	4.6	4.4	0.8	0.23	5.8
27a	26.7.93	514	30.3	2	515	9.0	7.4	n.m.	109.0	5.4	2.9	0.8	0.23	4.8
54b	23.8.93	526	31.0	30	511	8.5	7.2	363	94.1	18.3	2.1	1.1	0.24	7.6
55b	23.8.93	397	21.0	26	397	8.1	7.3	354	74.5	8.1	2.2	0.6	0.21	9.5
56b	23.8.93	419	23.3	45	399	8.6	7.4	363	72.4	17.4	3.1	0.9	0.21	9.0
57b	23.8.93	518	30.6	46	500	9.4	7.2	393	75.0	25.0	4.5	1.2	0.34	8.8
82b	15.9.93	517	31.5	15	503	8.3	7.2	378	89.1	16.7	3.0	1.4	0.16	6.2
83b	15.9.93	552	33.6	11	530	8.7	n.m.	396	86.1	27.7	3.6	1.2	0.16	6.5
84b	15.9.93	536	31.2	17	503	8.4	n.m.	396	87.5	23.2	2.4	0.9	0.27	9.3
85b	15.9.93	516	30.8	38	493	9.1	7.3	397	87.3	21.9	2.8	1.1	0.12	5.9
86b	15.9.93	635	38.0	50	599	8.6	7.3	394	100.0	35.0	4.3	0.9	0.25	8.9
OMM, estuary facies														
34B	5.8.93	593	37.4	50	597	9.8	7.2	398	102.0	22.9	5.4	1.7	0.29	6.2
35B	5.8.93	639	34.6	1	607	10.0	7.3	399	113.0	18.3	3.8	1.3	0.29	6.3
36B	5.8.93	552	32.2	95	542	9.1	7.0	396	86.8	28.0	5.0	1.5	0.33	6.4
37B	9.8.93	518	30.8	60	547	9.3	7.3	390	80.4	22.3	3.7	1.5	0.23	6.6
38B	9.8.93	513	30.5	60	551	9.3	7.3	373	80.7	23.7	4.8	1.6	0.23	6.6
41b	12.8.93	487	34.2	9	484	10.8	7.0	367	87.0	14.8	4.6	2.9	0.20	8.9
42b	12.8.93	444	27.6	4	429	11.6	7.0	367	78.1	18.8	5.0	2.0	0.23	9.7
LUC7	13.9.93	542	32.8	3	543	9.9	7.2	442	82.4	23.7	3.4	1.3	0.23	6.3
LUC10	13.9.93	642	40.0	3	662	10.0	7.2	427	110.0	20.7	5.1	1.1	0.31	6.9
LRY	14.9.93	291	16.7	14	287	9.0	7.2	459	54.8	5.5	2.1	0.5	0.16	5.8
POZ	14.9.93	285	15.7	66	300	9.8	7.3	448	59.6	6.8	4.5	1.7	0.18	4.7
52B	19.8.93	333	25.0	2	347	9.1	7.0	364	64.5	7.6	3.4	0.6	0.13	6.1
53B	19.8.93	358	22.5	9	385	8.6	7.0	352	65.3	9.1	3.4	0.7	0.18	6.1
49b	18.8.93	551	31.9	20	516	10.3	7.2	379	99.2	13.6	2.9	1.5	0.22	8.9
50b	18.8.93	537	31.8	16	521	11.3	7.2	383	101.4	14.9	3.1	2.1	0.22	5.6
"Gibloux-Delta"														
4a	19.4.93	464	28.5	30	466	8.1	7.5	352	100.0	8.7	2.6	0.4	0.25	5.4
43b	12.8.93	386	22.9	95	375	7.4	7.2	368	65.4	15.8	3.1	1.3	0.41	5.6
44b	12.8.93	416	23.9	27	407	7.5	7.3	374	90.0	7.0	1.9	0.3	0.21	5.3
45b	12.8.93	415	25.0	8	404	7.6	7.3	384	87.4	9.7	1.6	0.7	0.27	5.2
Molasse grise de Lausanne														
51b	19.8.93	328	25.1	15	318	8.4	7.0	373	52.8	15.3	4.5	0.8	0.65	7.8
"Gäbris-Schüttfächer"														
70b	8.9.93	352	21.0	18	340	7.5	7.6	379	69.1	12.7	1.3	0.5	0.20	2.8
71b	8.9.93	318	21.0	18	314	8.5	7.6	388	58.4	13.2	1.5	0.8	0.15	2.8
"Höhronen-Schüttung"														
68b	7.9.93	183	9.6	6	188	9.8	6.8	371	32.3	7.4	2.1	0.4	0.10	4.3
69b	7.9.93	121	5.8	3	114	7.9	6.8	372	19.1	3.4	1.3	0.3	0.04	4.5
"Honegg-Nagelfluh"														
31a	29.7.93	227	12.6	11	223	8.5	7.2	428	43.0	7.7	1.2	0.6	0.18	3.0
32a	29.7.93	175	8.2	5	179	8.1	6.9	432	33.8	5.4	1.1	0.4	0.12	2.9
33a	29.7.93	154	9.6	2	157	9.1	7.0	419	27.7	5.0	1.0	0.5	0.08	3.0
"Rigi-Schüttung s.l."														
103b	4.10.93	366	19.9	284	360	8.9	7.8	414	61.5	18.7	2.8	1.8	0.86	2.3
"Speer-Schüttfächer"														
75b	9.9.93	287	18.4	150	285	8.2	7.2	385	55.0	10.9	0.5	0.2	0.24	2.1
76b	9.9.93	364	21.9	10	361	9.0	7.4	382	71.1	12.0	0.5	0.2	0.23	2.3
Molasse à gypse														
129c	20.7.94	1121	70.9	40-80	1141	10.7	7.5	333	231.1	35.4	10.0	4.3	4.71	7.4
130c	22.7.94	989	55.2	6	1008	9.8	7.4	424	168.5	43.2	29.5	3.5	4.68	3.7
131c	22.7.95	1187	75.7	0	1141	12.1	7.5	434	237.4	39.9	7.6	2.0	4.03	3.9
148c	2.9.94	1353	86.0	1	1326	16.3	7.8	409	289.2	39.0	9.2	8.1	4.80	6.0
Grès de la Cornallie														
COR	14.9.93	547	22.2		562	11.3	7.8	439	66.6	22.0	30.1	1.3	0.69	3.3
Conglomerats du Mont-Pélerin														
39b	10.8.93	449	26.8	29	460	9.4	7.0	375	82.8	12.0	3.1	1.1	0.33	2.3
40b	10.8.93	429	25.6	1	435	7.5	7.0	381	87.5	10.6	1.3	0.5	0.24	2.0
n		112	112	108	112	112	110	110	112	112	112	112	112	112
min		57	1.2	0.4	22	6.5	6.5	288	6.5	0.7	0.3	0.2	0.01	2.0
max		1353	86.0	1260	1326	16.3	8.1	484	289.2	43.2	30.1	8.1	4.80	19.0
median		446	25.7	20	444	8.8	7.3	394	86.2	14.9	2.5	0.8	0.23	6.1
mean		467	27.1	53	463	9.1	7.3	396	85.6	16.5	3.5	1.1	0.40	6.2
s		193	12.1	132	194	1.4	0.3	32	37.9	9.9	4.1	1.0	0.82	2.8

Number	HCO ₃ (mg/l)	SO ₄ (mg/l)	NO ₃ (mg/l)	Cl (mg/l)	B (µg/l)	Ba (µg/l)	Br (µg/l)	Cr (µg/l)	Cu (µg/l)	Li (µg/l)	Mo (µg/l)	U (µg/l)
Det.lim.	2 to 4	2.0	2.0	1.0	1 to 10	0.2	1 to 10	0.2	0.2	1 to 10	0.2	0.2
Hausruck-Schotter												
112b	190.3	14.0	7.1	0.5	1.3	8.5	5	0.7	0.2	0	0.1	0.2
Kobernausserwald-Schotter												
110b	7.3	11.5	5.2	0.7	1.7	4.8	14	1.0	0.0	1	0.1	0.4
111b	128.7	14.3	2.4	1.6	1.1	13.4	11	1.1	0.4	1	0.2	0.1
Munderfing-Schotter												
114b	80.6	0.0	6.2	0.4	1.0	5.1	14	1.0	0.9	1	0.1	0.2
Mittlere Serie												
120b	315.4	18.6	25.9	20.2	3.6	21.2	26	0.8	0.5	5	0.1	0.9
121b	405.7	21.7	35.3	28.1	6.5	37.3	34	0.5	0.2	3	0.2	1.1
122b	349.9	25.2	40.6	27.5	1.4	22.4	33	0.8	0.3	4	0.1	1.0
Erolzheimer Sande (L3)												
127b	300.4	20.1	33.5	12.4	3.3	14.3	22	0.8	0.3	2	0.1	0.7
Glimmersande												
106b	386.5	34.7	32.3	24.3	3.7	49.8	34	0.2	0.3	5	3.2	2.0
107b	374.2	66.1	7.3	27.7	3.4	37.3	37	0.2	0.2	9	9.2	2.3
108b	402.0	45.2	2.7	9.6	1.8	30.4	21	0.3	0.2	8	2.6	2.8
109b	430.1	61.8	0.0	6.9	2.1	31.9	14	0.2	0.1	9	3.2	3.4
98b	409.9	69.2	0.0	2.0	2.1	11.4	11	0.2	1.1	11	5.0	9.0
99b	357.7	92.6	0.0	2.0	1.9	10.1	23	0.2	<0.20	13	3.8	4.8
100b	408.3	50.8	4.3	9.6	3.3	24.5	26	0.2	1.2	7	140.3	8.0
140c	367.8	32.9	14.3	4.7	7.3	65.3	2	1.1	2.8	5	7.7	2.2
Nördliche Vollsotter												
124b	279.4	60.6	157.9	32.0	10.1	16.4	126	0.7	0.8	2	0.1	0.9
125b	242.8	51.4	83.6	26.4	6.9	25.8	110	0.8	0.4	2	0.2	1.0
126b	177.5	9.6	27.5	15.2	3.0	9.1	24	0.9	0.9	3	0.2	0.7
Ortenburger Schotter												
117b	118.3	15.1	34.3	15.2	3.1	15.8	20	0.8	3.7	5	0.2	0.2
"Sommersberg-Zone"												
72b	273.9	6.4	13.3	2.4	8.0	63.3	6	0.3	15.2	2	0.2	0.1
73b	228.8	6.5	5.7	1.1	3.5	28.2	3	0.3	<0.10	0	0.1	0.1
"Hörmil-Schüttung"												
61b	388.8	7.5	6.7	1.2	3.8	89.4	4	<0.20	0.1	2	0.2	0.9
62b	347.7	7.6	7.4	1.0	2.7	74.6	1	<0.20	<0.20	1	0.4	0.9
63b	426.8	17.8	5.2	1.3	5.5	73.5	8	<0.20	0.1	2	0.4	1.1
90b	309.0	7.5	9.0	2.8	3.6	29.6	9	0.1	<0.20	1	0.1	0.5
91b	233.3	6.1	6.6	1.2	2.0	38.4	1	<0.20	0.0	1	0.3	0.5
92b	284.5	6.5	6.9	1.5	1.9	42.1	3	<0.20	0.1	1	0.2	0.4
93b	417.9	15.8	14.4	1.9	4.7	43.8	11	0.1	<0.20	1	0.2	0.9
94b	368.1	12.6	15.3	2.3	6.2	46.7	7	<0.20	0.1	1	0.1	0.8
95b	337.3	8.3	13.8	3.8	4.1	76.6	7	<0.20	<0.20	2	0.4	0.8
96b	300.1	7.5	12.2	1.2	3.5	28.3	8	<0.20	0.5	1	0.1	0.6
97b	283.0	4.5	7.5	1.7	2.9	15.0	0	0.3	<0.20	1	0.2	0.4
Oberaquitane Mergelzone												
74b	238.7	9.0	7.6	3.5	7.1	81.0	7	0.1	0.1	2	0.4	0.8
"Tortonian"												
7a	324.5	12.4	6.2	2.9	2.6	43.5	16	0.2	3.7	2	0.3	0.7
8a	236.7	14.8	14.6	2.9	1.6	33.5	18	0.7	0.3	2	6.5	1.0
9a	329.6	15.0	10.7	2.8	2.1	97.8	19	0.3	3.4	3	1.0	1.9
11a	292.7	13.0	7.2	3.1	2.2	27.4	21	0.7	1.2	1	0.2	0.9
12a	342.2	16.0	6.4	2.7	2.2	47.1	14	0.8	<0.20	2	0.2	1.1
149C	338.6	13.3	5.0	3.7	2.6	68.6	2	0.6	2.5	3	0.8	3.3
Napf-Schichten												
102b	264.3	5.8	11.8	3.4	4.6	52.9	1	0.4	5.6	0	0.1	0.1
Beipberg Schichten												
25a	331.2	10.5	8.0	5.6	3.2	18.1	3	4.1	0.1	2	0.5	0.3
64b	264.3	13.4	15.1	1.8	1.6	2.4	9	1.1	<0.10	2	0.4	0.6
65b	208.3	9.8	6.6	1.7	1.1	3.2	9	0.6	<0.10	2	0.4	0.5
66b	233.0	11.7	10.1	1.5	1.8	3.6	13	0.7	<0.10	2	0.5	0.3
81b	334.9	17.2	6.6	2.9	2.0	14.0	16	0.4	0.3	3	0.4	0.6
"Aquitani"												
46b	329.3	21.9	6.8	1.3	2.5	24.0	7	<0.10	0.8	4	<0.10	0.5
Gabelspitz Schichten												
28a	172.9	4.2	11.2	2.2	1.4	12.9	11	0.6	<0.10	1	0.4	0.2
29a	123.9	2.6	6.2	1.2	0.8	3.7	<0.10	<0.10	0.5	1	0.4	0.1
30a	241.2	4.1	15.5	4.0	2.0	40.5	4	0.3	<0.10	0	0.3	0.1
87b	217.8	4.0	9.0	2.6	2.9	74.9	4	1.0	<0.10	1	0.4	0.2
88b	223.8	4.9	7.4	2.5	2.0	57.9	11	1.1	<0.10	1	0.4	0.2
Kalchstätten-Formation												
24a	287.1	5.5	8.8	2.5	2.5	89.4	6	0.1	<0.10	1	0.4	0.3
Guggershorn-Formation												
89b	203.4	4.1	7.2	1.5	2.0	37.5	4	1.1	<0.10	1	0.1	0.1

Appendix 3. Chemistry of spring waters from Molasse aquifers. The water samples are grouped according to aquifer sub-types, defined on the basis of the sedimentary petrography, hydraulic conductivity and grain size distribution of the aquifers. Anions were determined by using standard methods such as ionic chromatography for chloride, sulfate, nitrate, specific electrode for fluorine, and titration for alkalinity. Trace elements were measured with a HR-ICP MS of VG/Fisons. General detection limit is around 0.2 ppb. For the elements lithium and iodine it was varying between 2 and 10 ppb. Total concentrations, i.e. including the particle-bound fraction are reported. Standard major-ion analyses were checked by ion balance methods accepting an error up to 5%. The complete water data set can be found in Hesske (1995).

Number	HCO ₃ (mg/l) 2 to 4	SO ₄ (mg/l) 2.0	NO ₃ (mg/l) 2.0	Cl (mg/l) 1.0	B (μg/l) 1 to 10	Ba (μg/l) 0.2	Br (μg/l) 1 to 10	Cr (μg/l) 0.2	Cu (μg/l) 0.2	Li (μg/l) 1 to 10	Mo (μg/l) 0.2	U (μg/l) 0.2
Det.lim.												
OMM, brackish facies												
116b	416.4	24.4	19.7	6.9	6.6	14.7	5	2.5	<0.10	8	0.1	1.8
119b	397.3	24.5	0.0	4.3	3.2	16.7	5	0.5	<0.10	29	1.0	0.3
OMM, shoreline facies												
77b	266.3	14.6	16.5	3.6	5.3	12.2	7	1.7	<0.10	1	0.1	0.1
78b	184.8	15.0	4.4	3.2	3.9	10.4	4	1.1	<0.10	0	0.2	0.1
79b	167.1	15.7	8.1	3.0	2.5	6.9	5	0.9	<0.10	0	0.1	0.1
80b	305.0	11.1	7.9	3.9	4.3	17.6	4	1.1	<0.10	1	0.3	0.3
101b	236.7	13.0	20.2	4.0	3.6	15.9	7	3.4	<0.10	1	0.1	0.1
58b	234.6	20.6	13.4	2.3	7.0	25.8	10	2.2	<0.10	3	0.7	0.9
59b	276.7	9.9	10.3	5.7	11.4	26.2	3	2.7	<0.10	3	0.5	0.3
60b	235.1	22.2	14.1	2.2	9.1	29.1	8	1.7	<0.10	6	0.7	0.6
OMM, open sea facies												
26a	328.0	15.2	11.3	3.4	20.4	22.2	9	2.2	5.5	2	0.2	0.4
27a	333.0	24.1	18.8	3.7	1.8	28.6	19	2.4	0.1	2	0.2	0.2
54b	338.3	35.5	7.2	3.0	1.8	8.5	18	2.5	<0.10	4	0.7	0.7
55b	236.4	20.1	17.6	4.8	1.9	3.3	27	3.1	<0.10	2	0.4	0.3
56b	264.4	17.4	10.1	2.3	1.6	5.8	22	0.6	<0.10	3	0.4	0.3
57b	349.3	16.0	8.2	8.0	2.5	14.1	18	0.9	<0.10	4	0.5	0.5
82b	353.1	26.3	2.2	4.0	3.3	15.3	10	2.9	1.8	5	1.9	2.6
83b	385.0	21.7	0.2	3.6	3.2	24.1	6	1.9	4.4	3	1.7	2.2
84b	366.2	18.3	2.0	3.2	3.2	53.0	12	0.9	7.2	7	0.4	3.1
85b	355.1	20.2	4.3	3.4	2.8	17.4	7	1.5	1.1	3	0.2	1.0
86b	425.5	26.8	6.6	4.9	3.8	45.1	14	0.3	<0.10	10	0.2	1.3
OMM, estuary facies												
34B	361.6	21.5	31.9	24.7	3.7	17.7	29	1.9	1.5	8	1.1	1.4
35B	432.9	9.3	24.2	14.7	3.9	27.3	17	2.1	0.2	6	0.9	0.9
36B	368.3	12.8	17.1	10.2	8.2	47.8	17	2.5	0.6	9	1.0	1.8
37B	319.9	14.4	32.1	20.7	3.3	11.9	20	3.5	1.5	11	0.9	1.7
38B	292.4	15.0	46.7	25.2	4.0	7.3	27	4.5	0.5	8	0.9	1.1
41b	297.2	8.6	33.3	7.6	6.8	14.3	15	4.6	0.1	2	0.5	0.4
42b	274.7	6.7	15.6	9.2	2.8	20.8	16	2.3	0.3	1	0.4	0.3
LUC7	369.7	23.5	11.2	4.5	3.1	19.2	11	3.1	<0.20	8	0.9	1.2
LUC10	414.5	10.4	41.7	14.2	6.9	38.7	15	4.1	0.8	6	0.7	0.5
LRY	183.6	13.1	9.3	1.8	6.3	8.4	8	4.8	0.9	1	1.0	0.2
POZ	154.1	10.1	16.3	15.7	6.5	14.9	6	4.1	4.3	1	1.1	0.1
52B	193.0	15.5	21.0	6.1	2.9	10.5	6	6.2	0.4	2	1.0	0.3
53B	204.0	13.9	30.6	10.1	3.9	16.9	18	6.9	0.7	1	0.9	0.4
49b	376.6	18.3	3.5	4.1	5.4	9.3	8	4.2	0.1	4	0.3	0.6
50b	377.3	10.4	3.9	4.0	6.2	11.4	7	5.5	<0.10	3	0.2	0.7
"Giboux-Delta"												
4a	307.2	3.6	18.5	4.1	4.0	50.5	10	0.3	0.3	2	0.2	0.5
43b	263.0	9.0	7.7	1.1	6.0	193.4	14	0.8	0.3	3	0.4	0.7
44b	280.0	8.8	8.0	1.2	1.7	225.1	11	0.1	0.1	1	0.1	0.5
45b	271.4	9.9	14.7	1.4	5.5	333.7	20	0.2	0.1	1	0.1	0.5
Molasse grise de Lausanne												
51b	198.8	21.2	2.4	4.7	4.6	53.5	7	0.9	0.3	7	0.4	0.9
"Gäbris-Schüttfächer"												
70b	247.4	6.4	3.1	1.2	2.5	28.9	4	0.2	1.5	1	0.5	0.4
71b	224.9	5.5	2.0	2.4	4.5	30.6	5	0.9	1.9	1	0.3	0.3
"Höhronen-Schüttung"												
68b	113.0	4.1	5.8	2.7	2.8	29.3	3	0.5	1.3	4	0.1	0.5
69b	65.9	6.9	7.0	1.1	0.4	14.5	4	<0.10	0.1	0	0.1	0.1
"Honegg-Nagelfluh"												
31a	157.2	3.4	2.6	0.9	2.3	53.4	1	0.7	1.3	3	0.1	0.1
32a	116.9	4.1	2.4	0.8	2.3	46.9	3	0.6	0.1	1	0.2	0.2
33a	102.4	3.5	2.7	0.6	1.6	28.2	2	0.1	0.4	0	<0.10	0.1
"Rigi-Schüttung s.l."												
103b	257.5	8.8	4.8	1.1	28.2	244.2	3	0.1	1.7	11	0.3	0.8
"Speer-Schüttfächer"												
75b	203.1	4.4	4.5	0.5	5.0	35.0	3	<0.1	5.5	2	<0.10	0.1
76b	258.4	7.6	5.6	0.9	5.8	18.7	4	0.1	0.5	1	0.1	0.2
Molasse à gypse												
129c	375.8	364.0	35.0	35.0	20.2	20.7	28	0.7	2.3	17	2.6	3.5
130c	389.8	255.0	32.0	50.0	31.1	35.4	45	0.6	3.1	21	16.0	3.5
131c	417.9	409.0	28.0	28.0	11.9	30.5	31	0.8	2.8	19	2.7	2.4
148c	463.5	445.0	40.0	34.0	52.4	43.0	43	0.8	49.5	29	1.3	2.5
Grès de la Cornaille												
COR	370.5	21.6	11.4	11.5	55.7	150.0	6	0.5	2.8	22	1.7	0.5
Conglomerats du Mont-Pélerin												
39b	319.9	8.4	8.2	4.8	8.0	74.1	5	0.4	1.2	3	1.0	0.3
40b	305.3	7.8	7.4	1.1	5.7	39.4	4	0.4	0.2	1	1.0	0.3
Summary statistics												
n	112	112	112	112	112	112	110	100.0	110.0	112	110.0	112.0
min	7.3	0.0	0.0	0.4	0.4	2.4	0	0.1	0.0	0	0.1	0.1
max	463.5	445.0	157.9	50.0	55.7	333.7	45	6.9	7.2	29	9.2	9.0
median	295.0	13.4	8.2	3.3	3.3	27.4	9	0.8	0.2	2	0.4	0.5
mean	288.0	29.3	14.5	7.1	5.5	39.3	12	1.4	0.9	4	0.8	1.0
s	93.0	68.6	18.5	9.3	8.0	48.2	10	1.5	1.4	5	1.4	1.4

