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Aspects of ecotoxicology of sulphur in the Harz region – a guided excursion

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Abstract

Sulphur has become a major limiting factor for plant production during the last decades. In its initial stages, an insufficient S supply can only be detected by quantification of S in plant tissue with chemical methods. Severe S deficiency, however, can be identified by visual symptoms. An excursion to the Harz Mountains region not only provides the opportunity to study various visual symptoms of S deficiency in the field, but also provides insight into aspects of the ecotoxicology of sulphur. Oilseed rape fields around Silstedt and Ilsenburg display a variety of typical symptoms of S deficiency such as chlorosis starting from the leaves'edge and spreading over into intercostal areas, reddish purple colouring due to the enrichment of anthocyanins, spoonlike deformations of leaves, succulence of leaves, reduced petal size or white blooming. S deficiency also affects yield structure, which is revealed in a reduced number of seeds per pod. Decreasing concentrations of airborne sulphur over the past few decades may have an impact on the composition of plant communities, which is displayed by epiphytic lichen communities near the Kästeklippen at Romkerhall. On the other hand, a surplus of sulphur may impair plant performance, too. An example for this can be studied on mosses growing in bogs in the High Harz Mountains. A soil of calcium-sulphate origin may also give rise to the development of a specialised plant community, with plant specimens being able to store up to three times the amount of sulphur in their leaves compared to specimens growing on calcium carbonate soils. Plant communities on gypsum soils can be seen in the Hainholz near Hörden. A geogenic source of sulphur exists at Rhumspringe at the southern Harz rim, where the Rhume karst spring delivers up to 5500 L of sulphur enriched water per second after high precipitation. The total annual discharge amounts to 7092 t S.

Key words: Harz, sulphur deficiency, sulphur surplus, oilseed rape, epiphytic lichens, Torfhaus bog, gypsiferous vegetation

Zusammenfassung

Aspekte der Ökotoxikologie von Schwefel in der Harzregion – eine geführte Exkursion

In den letzten Jahrzehnten ist Schwefel (S) zu einem der wichtigsten limitierenden Faktoren für die Pflanzenproduktion geworden. Eine unzureichende Schwefelversorgung lässt sich im Anfangsstadium nur über die Quantifizierung der S-Konzentration im Pflanzengewebe mit Hilfe chemischer Methoden feststellen. Starker S-Mangel ist jedoch anhand visueller Symptome erkennbar. Eine Exkursion in die Harzregion gibt Gelegenheit, nicht nur verschiedene visuelle S-Mangelsymptome im Feld zu studieren, sondern bietet auch einen Einblick in ökotoxikologische Aspekte des Schwefels. Rapsfelder in der Umgebung von Silstedt und Ilsenburg zeigen eine Vielfalt typischer S-Mangelsymptome wie an den Blatträndern ansetzende, sich interkostal ausbreitende Chlorosen, rötliche bis lila Blattfärbung durch Anthocyane, löffelförmige Blattdeformationen, Blattsukkulenz, reduzierte Größe der Blütenblätter und weiße Blüten. S-Mangel beeinflusst auch die Ertragsstruktur, was sich bei Raps vor allem in einer reduzierten Samenzahl in den Schoten niederschlägt. Die in den vergangenen Jahren abnehmende S-Konzentration in der Luft hat auch Auswirkungen auf die Zusammensetzung von Pflanzengemeinschaften, wie epiphytische Flechtengesellschaften in der Nähe der Kästeklippen bei Romkerhall verdeutlichen. Andererseits kann sich auch ein Überschuss an Schwefel nachteilig auf Pflanzen auswirken. Ein Beispiel hierfür bieten Moose, die in Mooren des Hochharzes wachsen. Ein auf Calciumsulfat gewachsener Boden kann zur Herausbildung spezialisierter Pflanzengesellschaften mit Individuen führen, die bis zu dreimal so viel Schwefel in ihren Blättern speichern wie Vertreter der gleichen Art, welche auf Calciumcarbonatböden wachsen. Pflanzengesellschaften auf Gipsböden sind zum Beispiel "im Hainholz" bei Hörden zu finden. In Rhumspringe am südlichen Harzrand ist schließlich eine geogene Schwefelquelle zu sehen. Hier fördert die Rhume-Karstquelle nach starken Niederschlägen bis zu 5500 L mit S angereichertes Wasser pro Sekunde zu Tage, insgesamt 7092 t S kommen so im Jahr an die Oberfläche.

Schlüsselwörter: Harz, Schwefelmangel, Schwefelüberschuss, Raps, epiphytische Flechten, Torfhausmoor, Vegetation auf Gipsböden

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Introduction[4]

In the past, the Harz region was characterized by extremely high atmospheric SO_2 concentrations. This was because, in addition to ubiquitous atmospheric SO_2 loads from industrial burning processes and exhaust fumes from motorized traffic, the atmosphere was further enriched with sulphur emissions from ore processing. The situation changed over the last few decades due to desulphurisation of exhaust gases and the use of fuel with reduced S contents. Thus, atmospheric sulphur input into soils was reduced by as much as a factor of 10 over the last 25 years. With decreasing atmospheric inputs (Daemmgen et al., 1997) and the shift towards low or no sulphur (S) containing sources for nitrogen (N) and phosphorus (P) (Ceccotti et al., 1997), S has become a major limiting factor for plant production in industrialised as well as remote rural areas. But although today there are only a few places left where the average S input from atmospheric and fertiliser sources satisfies the demand of crops, not all sites with a negative S balance show S deficiency symptoms, and crop response to S fertilisation is not universal. This is because S is a geogenic abundant element (Clark, 1979) compared for instance to nitrogen, the origin of which in agro-ecosystems is predominantly anthropogenic. Vast amounts of S are bound in minerals (e.g. gypsum and pyrite) and delivered to the surface by ground water. The Rhume spring (see chapter 4.2) in the Harz mountain area in Northern Germany (51°35'N, 10°17'E), for example, delivers 7092 t T of S in the form of gypsum each year (Herrmann, 1969), which is twice the amount of S sold in the whole country as potassium-sulphate fertilisers today, and theoretically enough to fertilise 10 % of all oilseed rape cropped in Germany with S. But also sites without access to mineral bound S sources may have sufficient S dissolved in soil water and shallow groundwater bodies available to plant roots (Eriksen et al., 1997;, Bloem et al., 1997,; Duyniveld et al., 1993). This is because soil water and shallow groundwater have much higher sulphate concentrations than precipitation water, which is due to natural S sources in the ground or due to the charging by atmospheric sources (Eriksen et al., 1997).

Thus, any S fertilisation claiming to be efficient in terms of supplying S-deficient plants and to be environmentally acceptable in terms of no unneccessary discharge of plant nutrients into ecosystems outside agriculture (Kluge and Embert, 1996) needs to be based on a proper diagnosis of the S nutritional status.

Plants can be assessed for their nutritional status visually or by means of chemical tissue analysis. Visual diagnosis of plants primarily allows the identification of symptoms of severe nutrient deficiency caused by physiological disorders, and altered or damaged tissues. A lack of nutrients without producing deficiency symptoms, but already limiting growth and yield, requires the quantification of nutrients in tissues by means of chemical methods.

1 Sulphur deficiency in oilseed rape – visual symptoms

Literature describes symptoms of S deficiency as being less specific and more difficult to identify than other nutrient deficiency symptoms (Bergmann, 1992 & 1993; Chapman, 1966; Robson and Snowball, 1986; Saalbach, 1970b). In a perfect diagnostic system, visual diagnosis must always come together either with soil or with plant analysis (Bennett, 1993).

In contrast to most other agricultural crops, *Brassica* species such as oilseed rape develop a very distinctive expression of symptoms. A visit to the north-eastern part of the Harz area (Silstedt, 51°52'N, 10°51'E and Ilsenburg, 51°52'N, 10°41'E, see Figure 1) gives the opportunity to study fields of *Brassica napus* and the weedy *Capsella bursa-pastoris* with symptoms of sulphur deficiency.

1.1 Macroscopic symptoms in single plants

In oilseed rape, the total S concentration in tissue corresponding to the first appearance of deficiency symptoms is about 3.5 mg g^{-1} S. The symptoms are very specific and thus are a reliable guide towards S deficiency. There is no difference in the symptomatology of S deficiency in varieties containing high or low amounts of glucosinolate (= S-containing secondary metabolite of *Brassica* species, which is responsible for the high S demand of oilseed rape) (Schnug, 1988). Even at very early growing stages leaves of oilseed rape start to develop symptoms of S starvation. As S is fairly immobile within the plant (Cram, 1990), symptoms always show up first in the youngest leaves. However, when the plants are still small, symptoms can cover the entire plant (Figure 2). Deficiency symptoms in young foliar tissue of oilseed rape begin to appear when the total S concentrations drop below 2.8 mg g^{-1} and 3.5 mg g^{-1} S in high glucosinolate respectively low glucosinolate containing cultivars (Schnug and Haneklaus, 1994a, b).

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[4] Prior and after the last COST Action 829 at Braunschweig, two excursions were guided into the Harz mountains and their surroundings to demonstrate the impact of the former mining and processing of sulphurous ores on ecosystems, the adaptation to heavy metal enriched substrates and gypsiferous soils, and the consequences of a lack of sulphur fertilization on oilseed crops and associated weed communities. The present report is part 2 of the excursion guide, which gives analytical data of materials collected during the excursions to support the effects shown in the field and compares them with published data. Part 1 on the ecotoxicology of heavy metals was published in the previous issue.

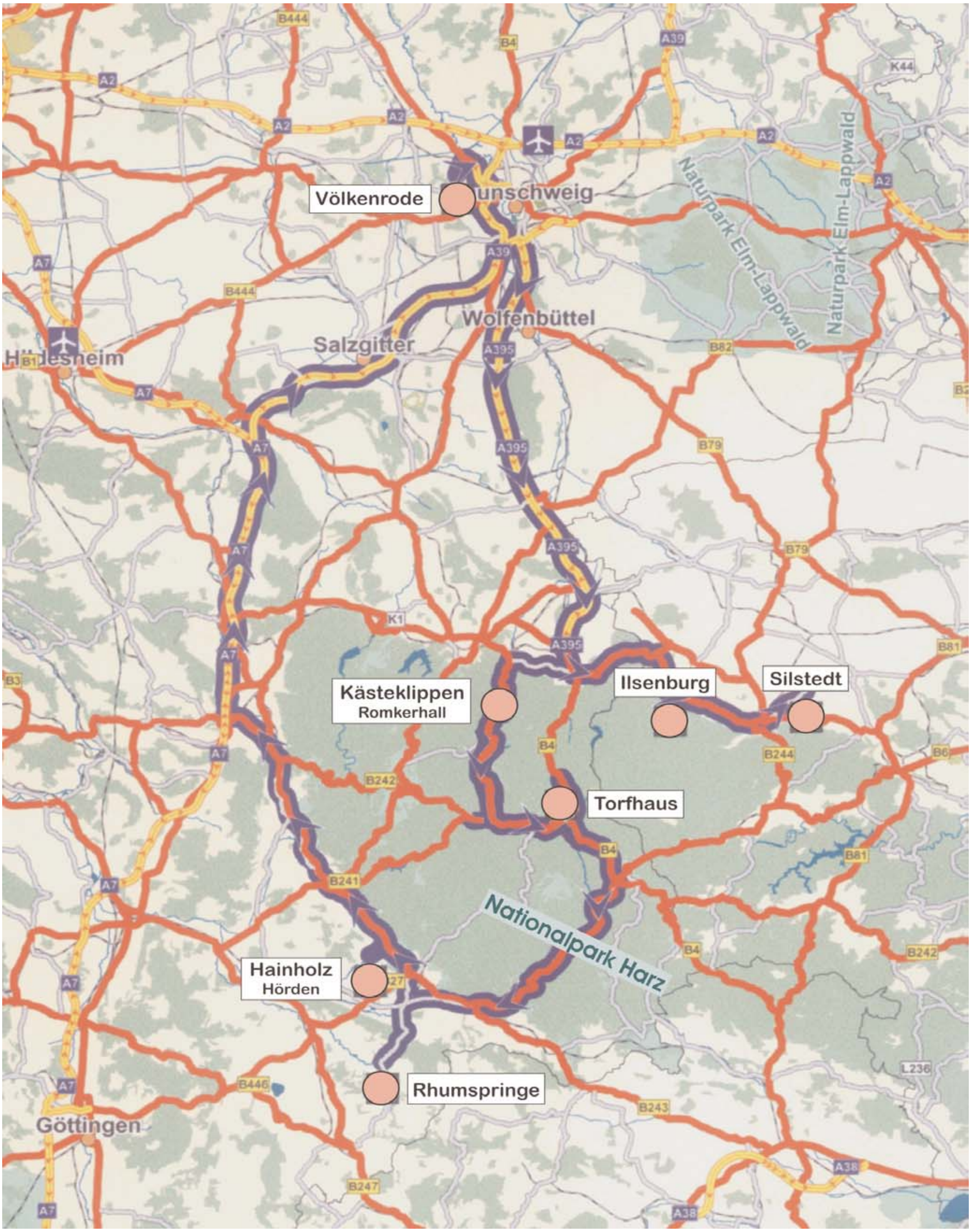

Figure 1:
Suggested excursion route on aspects of ecotoxicology of sulphur in the Harz mountain region. Map produced with KlickRoute 2003©

Figure 2:
Sulphur deficiency on younger and older leaves. (Photo: Schnug)

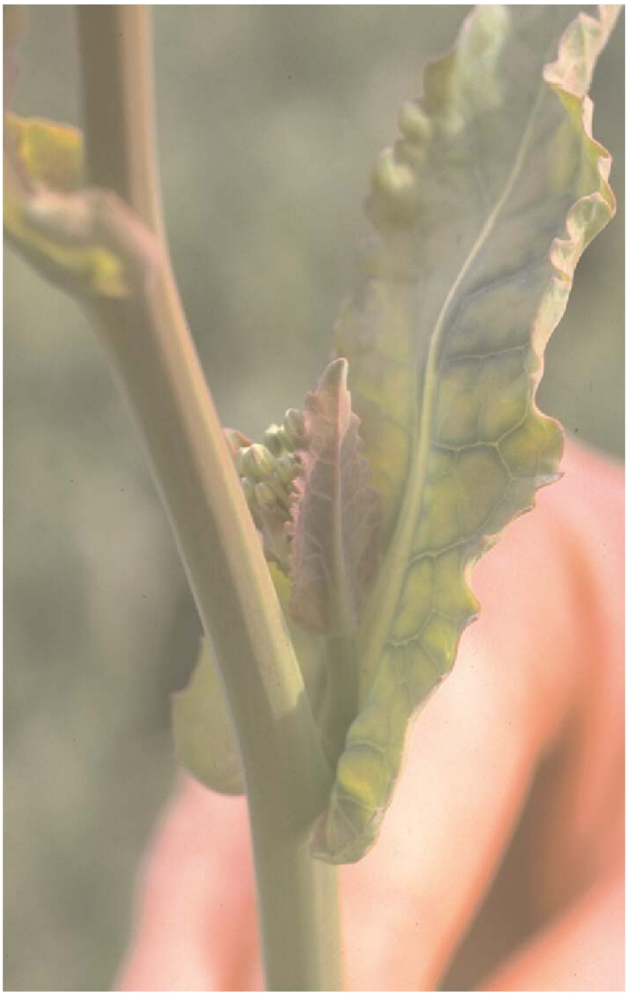

Figure 3:
Effect of sulphur deficiency on intercostal areas of an oilseed rape leaf, leaving zones along the veins green. (Photo: Schnug)

In plants suffering from severe S deficiency, leaves begin to develop chlorosis (Burke et al., 1986; Dietz, 1989 a & b; Ergle and Eaton, 1951; Haq and Carlson, 1993; Stuiver et al., 1997). The chlorosis starts from the leaf's edge spreading over intercostal areas but leaving the zones along the veins always green (Lobb and Reynolds, 1956; Schnug, 1988) (Figure 3). The reason for the green areas around the veins is most likely the reduced intercellular space in that part of the leaf tissue resulting in shorter transport distances and a more effective transport of sulphate. However, high anthocyanin contents in leaves, naturally occurring in some varieties of oilseed rape (e.g. Bronowsky) may mask this symptom, but they are still easy to recognise in translucent light.

Chlorosis caused by S deficiency very rarely turns into necrosis (Schnug, 1988; Ulrich et al., 1993) as it does with nitrogen and magnesium deficiency, which is an important criterion for differential diagnosis. Even under extreme S deficiency where an oilseed rape plant shows severe disorders it will not wither.

The intensity of S deficiency symptoms on leaves depends on the nitrogen supply of the plants (Figure 4). In general a high nitrogen supply promotes the expression of S deficiency symptoms and vice versa (Walker and Booth, 1994).

With duration of severe S deficiency the chlorotic parts of *Brassica* leaves acquire a reddish purple colour due to the enrichment of anthocyanins (Figure 5). Under field conditions, the formation of anthocyanins starts 4-7 days after chlorosis. Conditions for high photosynthetic activity promote the process. The phenomenon is initialised by the enrichment of carbohydrates in the cells following the

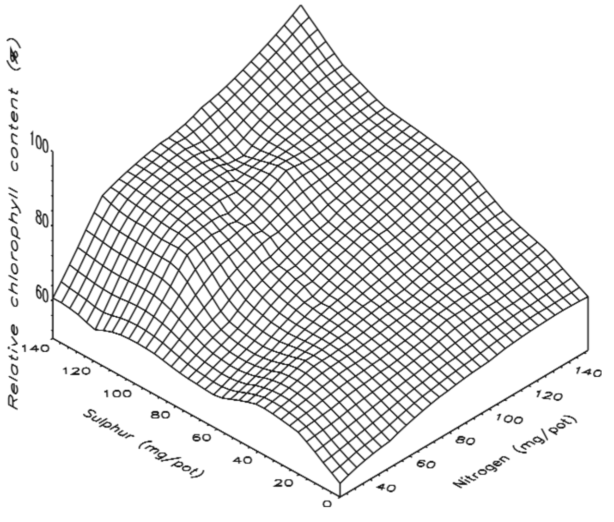

Figure 4:
Chlorophyll content of younger, fully differentiated leaves of oilseed rape as influenced by nitrogen and S supply (Schnug and Haneklaus, 1994b)

Figure 5:
Anthocyanin enrichment following extreme sulphur deficiency. (Photo: Schnug)

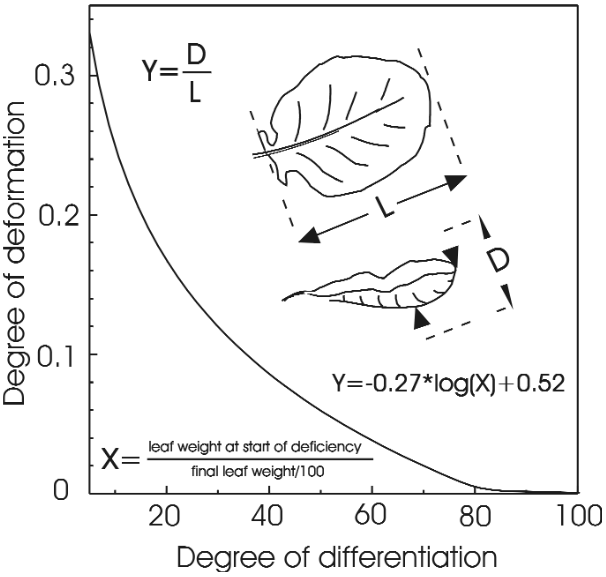

Figure 6:
Deformation of oilseed rape leaves depending on degree of expansion at which the plant is struck by severe S deficiency (Schnug and Haneklaus, 1994b)

inhibition of the protein metabolism. To avoid physiological disorders caused by too high carbohydrate concentrations, plants detoxify them in anthocyanates derived from the reaction with cell borne flavonols (Deloch and Bussler, 1964; Eaton, 1935, 1941, 1951; Harborne, 1967, & 1988; Nightingale et al., 1932). Many other nutrient deficiencies are also accompanied by formation of anthocyanins, which therefore is a less specific indicator of S deficiency.

Not fully expanded leaves in particular produce spoonlike deformations when struck by S deficiency. The reason for that is a reduced cell growth rate in the chlorotic areas along the edge of the leaves, while normal cell growth continues in the green areas along the veins. The grade of deformation turns up stronger the less expanded the leaf is when it is struck by S deficiency (Figures 6 and 7).

Figure 7:
Spoonlike deformations caused by limited sulphur supply early in the growth period. (Photo: Schnug)

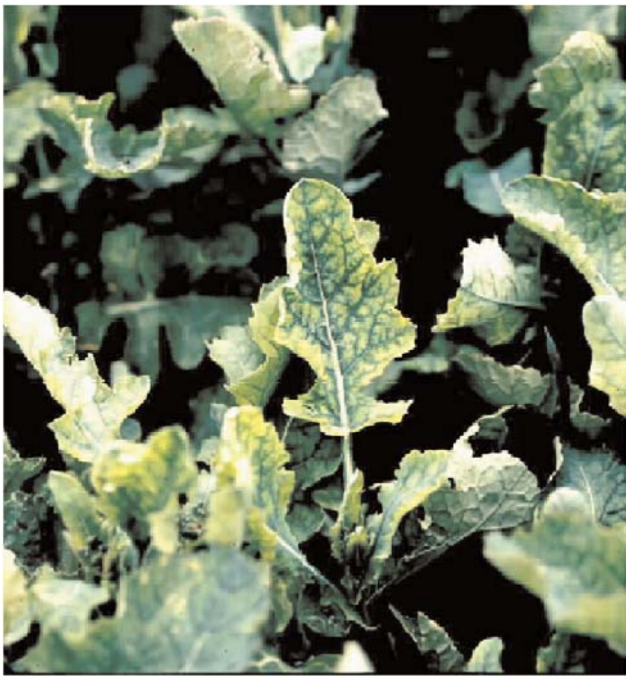

Figure 8:
Deformation and marbling in youngest leaves caused by sulphur deficiency. (Photo: Schnug)

Figure 9:
“White blooming” of oilseed rape flowers. (Photo: Schnug)

Figure 10:
White blooming oilseed rape plants painted by Lincoln (1995)

Marbling, deformation and anthocyanin accumulation can be detected up to the most recently developed small leaves inserted in forks of branches (Figure 8).

Leaves of S deficient plants appear to have a higher succulence (Bermann, 1983; Bugakova et al., 1969). Deloch and Bussler (1964) suspected an increase in chloride uptake caused by lack of sulphate as the physiological background for this phenomenon. But with an increase of chloride concentrations by 0.4 mg g^{-1} Cl on the account of a decrease of S concentrations by 1 mg g^{-1} in leaves, this effect seems to be too small to justify this hypothesis (Schnug, 1988). It is more likely that the appearance of increased succulence is caused by the above explained mechanical effects of distortion together with a cell wall thickening from the accumulation of starch and hemicellulose (Sinclair, 1993).

S deficiency causes one of the most impressive symptoms of nutrient deficiency: the “white blooming” of oilseed rape flowers (Figure 9). Since the beginning of the 1990s, this symptom has become so widespread in Northern Europe that it is accidentally picked up by artists (Lincoln, 1995; Figure 10) or photographers attracted by the beauty of an oilseed rape field in full bloom (Anon, 1996b). However, detecting this symptom in the field requires some patience, because the human eye needs at least 10-15 minutes to identify the white colour within a yellow background.

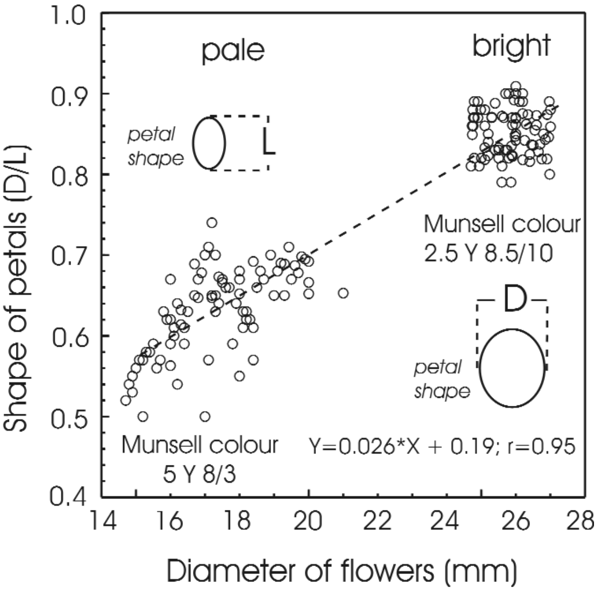

Figure 11:
Change of size and colour of oilseed rape petals at different S supply (Schnug and Haneklaus, 1994b)

The white colour develops from an overload of petal cells with carbohydrates caused by disorders in the protein metabolism which finally ends up in the formation of leuco-anthocyanins (Schnug and Haneklaus, 1995). As with anthocyanins in leaves, the symptoms develop strongest during periods of high photosynthetic activity. Besides the remarkable change in colour, size and shape of oilseed rape petals change, too (Figure 11).

Figure 12:
Reduced petal size resulting from sulphur deficiency. (Photo: Kirschnick)

Figure 13:
Smaller pods and reduced number of seeds (upper half of figure) in sulphur deficient oilseed rape. (Photo: Schnug)

The petals of S deficient oilseed rape flowers are smaller and oval shaped compared to the larger and rounder shape of plants without S deficiency symptoms (Figure 12). The fertility of flowers of S deficient oilseed rape plants is not inhibited. But with the change in size and colour their ability to attract honey bees is apparently reduced. This is significant in the case of the yield of non-restored hybrids which need pollination by insect vectors (Schnug and Haneklaus, 1995).

Flowers of severely S deficient oilseed rape plants develop no pods or pods with significantly lower numbers of seeds than normal (Figure 13). The leaves as well as the branches and pods of S deficient plants are often red or purple coloured caused, as explained above, by the accumulation of anthocyanins.

Though not many investigations report on the influence of S supply on root development, there is sufficient evidence that S deficiency reduces root mass and increases the number of secondary roots (Holobrada, 1969; Rivero, 1996; Smith et al., 1993).

1.2 Infrared imaging

In 1910, five years after the invention of infrared sensible dyes by Koenig and Philips, Wood detected that the leaves of trees appear on infrared images “white as snow” (Wagner, 1970). The “Wood-Effect”, also called “Chlorophyll-Effect”, has also been tried as a means for an early diagnosis of biotic and abiotic plant damage (Bowden, 1933, Gibson et al., 1965), especially after the invention of “false colour films” (Fritz, 1967). The principal reasons for the “Wood Effect” are the strong reflection of chlorophyll in the infrared range (Tkachuk and Kuzina, 1982) and the reflection of infrared light at the leaves’ inner parenchymal boundary (Wagner, 1970). Changes in the infrared image for the latter reason are related to a breakdown of this boundary which is caused by loss of turgor in the leaf and thus have no meaning for the detection of early S deficiency. A reduction of chlorophyll concentrations within the chloroplasts (Hu et al., 1991; Burke et al., 1986; Stuiver et al., 1997) may also change the infrared image of a leaf. This is obviously the reason why in oilseed rape the very early beginning of S deficiency symptoms is visible earlier on an infrared than on a common colour image under controlled conditions (Schnug, 1988). Due to the very minor changes in the image, the practical value of infrared imaging for an earlier identification of S deficiency is, still, questionable.

1.3 Yield structure

Visual diagnosis of plants is commonly concentrated on changes in the appearance of individual plant organs and, as mentioned before, only applicable to identify severe deficiency. Severe deficiency is characterised by blocking or breakdown of certain metabolic pathways, which finds its final expression in physiological disorders and visible symptoms. But long before true metabolic calamities occur, a shortage of S supply will limit the ability of plants to produce yield.

Yield, however, is a combination of individual parameters (Geisler, 1983), and abnormal changes in the yield structure of a crop may indicate any shortage of growth factors earlier than first visible deficiency symptoms appear. Changes in yield structure can be identified by visual assessment, too. Although changes in yield structure might not be specific at all, they provide a valuable piece of information for differential diagnosis of S deficiency especially when symptomatic interferences of diseases may occur.

The strongest yield component affected by S deficiency in oilseed rape is the number of seeds per pod, which very significantly decreases with S deficiency (Schnug, 1988). The number of branches per plant, flower insertion, fertility and seedweight are nearly unaffected even by severe S deficiency (Schnug, 1988; Schnug and Haneklaus, 1994a, b). Abnormally low numbers of seeds per pod, down to seedless “rubberpods”, are a characteristic hint towards S deficiency particularly in late growth stages, when no photosynthetically active leaves for visual assessment or chemical analysis are available. Under conditions of S starvation, plants may also fail to commence pod growth after fertilisation. The little remains of the fertilised stigmata fall off after some time, faking an image of sterility of flowers or a lowered degree of fertilisation (Figure 14).

The final number of seeds per pod is determined immediately after fertilisation and maintained irrespectively of the nutritional status of the plant. Even if sufficient S was available for the plant after pollination, the pods would not be able to benefit from it. Thus the distribution of failed pod insertion and pods with abnormally low seed numbers along the branch is also a record of the time when S starvation hit the plant previously.

Figure 14:
Remains of fertilised stigmata in S deficient oilseed rape. (Photo: Schnug)

Another very typical indicator for an S deficient site is the so called “second flowering” of the oilseed rape crop. Up to approximately one week after blooming, even oilseed rape plants starving of S are able to restart and continue with flowering, pod insertion and seed filling and can regain full yield if sufficient S is supplied (Schnug, 1988). A natural trigger for second flowering is sudden warm and dry weather following a wet and rainy spring season up to the end of blooming. During the wet period, precipitation water, which has 10 to 100 times lower S concentrations than the entire soil solution, dilutes or leaches the sulphate in the rooting area of the plants, finally causing S starvation. With the beginning of warmer weather, evaporation increases and S rich subsoil water becomes available to the plant, causing the second flowering of the crop. The ability of oilseed rape to compensate fully for earlier S deficiency makes correct visual diagnosis in that crop vital, as it allows in principle the correction of S deficiency at any time during the main vegetative period. Practical limits under field conditions, however, are technical constraints for fertiliser application and the problem that there might not be enough vegetative time left to complete the delayed vegetation cycle of the plant and to allow seeds to mature.

Figure 15:
Irregularly shaped areas with lighter green colour in an early oilseed rape crop. (Photo: Schnug)

1.4 Field-scale symptoms

Symptoms of nutrient deficiency are usually described for individual plants or plant parts. However, there are some characteristic features in the appearance of fields which can provide an early evidence of S deficiency.

S deficiency develops first on the light textured sections within a field. From a bird’s eye view these areas appear as irregularly shaped plots with lighter green colour (“wash outs”) in an early oilseed rape crop (Figure 15). The irregular shape distinguishes the phenomenon from the regular shape of areas deficient in nitrogen, which are normally caused by inaccurate fertiliser application. Due to frequent soil compaction and limited root growth, S deficiency develops first along the headlands and tramlines or otherwise compacted areas of a field (Figure 16).

The appearance of S deficient oilseed rape fields is more obvious at the beginning of blooming: white flowers of oilseed rape are distinctively smaller and therefore much more of the green undercover of the crop is shining through the canopy of the crop (Figure 17). On an infrared

Figure 16:
S deficiency develops first along the headlands and tramlines of a field. (Photo: Schnug)

Figure 17:
Green undercover shining through the canopy of the oilseed rape crop due to reduced size of flowers. (Photo: Schnug)

Figure 18:
Colour of green leaves shining through the S deficient flowers as red on an infrared ("false colour") air photograph. (Photo: Schnug)

Figure 19:
In mature oilseed rape, S deficiency is revealed by a sparse, upright standing crop. (Photo: Schnug)

("false colour") air photograph, the infrared reflectance (red colour) of green leaves is usually covered by the yellow flower canopy (white colour on infrared image). Only where, due to S deficiency, the flowers are reduced in size, the red colour of leaves is shining through (Figure 18). In mature oilseed rape crops, S deficiency is revealed by a sparse upright standing crop (Figure 19).

2 Response of epiphytic lichens to changing air quality in the Harz Mountains

During the period of high SO_2 emissions, a lot of epiphytic lichen species, e.g. *Hypogymnia physodes*, *Evernia prunastri*, *Usnea*- and *Parmelia*-species disappeared (Hauck et al., 2002). SO_2-resistant lichens such as *Lecanora conizaeoides*, however, expanded. Only where SO_2 deposition was highest, the resistance of *Lecanora conizaeoides* was not strong enough to withstand the degree of air pollution (Hauck et al., 2001). Nowadays, with declining SO_2 concentrations, this lichen species is disappearing (Wirth, 1993; Bates et al., 2001), and species more sensitive to air pollution are recovering (Figure 20). In addition to SO_2, high concentrations of manganese in the stemflow of Norway spruce are thought to be responsible for the decrease in the vitality of SO_2-sensitive epiphytic lichens (Hauck et al., 2001; 2002). Lichen vegetation on tree trunks can be inspected in a Norway spruce forest near the Kästeklippen at Romkerhall.

Romkerhall (51°51'N, 10°26'E) was built as a hunting lodge by King Georg V. in the 19th century. Once belonging to the properties of the kingdom Hannover, the recent owner claims it was forgotten to attach it to a parish after monarchy had ceased in 1918 in Germany, and again after a general reformation of the parishes in Lower Saxonia in 1970. He succeeded to attract the princess of Saxonia who had her enthronisation as Queen of Romkerhall in 1988. That day, Romkerhall was exclaimed "the smallest kingdom of the world"! (http://www.koenigreich-romkerhall.de/) German aristocracy and government are in continuous quarrels with Romkerhall and tourism marketing… .

Figure 20:
SO_2-sensitive lichens such as *Evernia prunastri, Parmelia subaurifera* and *Physcia ascendens* are recovering as epiphytes on trunks after the strong reduction of SO_2 emissions (Photo: Ernst, 2003)

3 Bogs in the High Harz Mountains around Torfhaus (51°48'N, 10°32'E)[5]

In the High Harz Mountain region, between ca. 700 and 1100 m a.s.l., more than 30 slope mires have developed since the Younger Dryas period around 12000 BP. These mires have peat layers up to 8 m in thickness and include ombrotrophic raised bogs and minerotrophic mires (fens); they are surrounded by forested mires (spruce carr) and cover an area of more than 1600 ha (Beug et al., 1999). Beug and his co-workers gave a detailed monograph on the spatio-temporal development of the mires in the West and East Harz Mountains, based on analysis and interpretation of 12 pollen diagrams with ^{14}C dates and over 3200 pollen samples of the transition peat - mineral subsoil. Also, the impact of early mining and smelting was detected in these mires.

A visit to the raised bog "Grosses Torfhausmoor" shows the specific bog vegetation and the gradient from a rain-fed bog to woodland and forests on mineral soil (Figure 21).

The dominant plant species in the wet parts (gullies) of the bog are peat-mosses, mostly *Sphagnum cuspidatum, Sphagnum magellanicum, Sphagnum palustre, Sphagnum papillosum, Sphagnum rubellum,* and *Sphagnum tenellum*, together with the insect-catching herb *Drosera rotundifolia*. *Sphagnum magellanicum*, however, tends to grow in the drier parts of the gullies. The peat mosses solely depend on the water and nutrient supply from dry and wet precipitation. These oligotrophic peat mosses concentrate the nutrients by capillary transport into the growing "moss heads" (Brehm, 1971). In general, the concentration of calcium and sulphur in these *Sphagnum* species is below 1200 mg kg^{-1} dry mass (Malmer and Sjörs, 1955). Therefore, they are very sensitive to a chemical enrichment by deposition, especially to a surplus of calcium and sulphur compounds (Ferguson et al., 1978; Baxter et al., 1989, 1991), which may lead to a reduction in shoot growth (Table 1). Under persistent exposure to a surplus of SO_2, resistant *Sphagnum cuspidatum* populations have evolved (Baxter et al., 1991).

At higher and thus drier parts of the bogs, the humps, a heather vegetation is growing with *Andromeda polifolia, Calluna vulgaris* and *Vaccinium oxycoccus*. The accompanying sedges *Eriophorum vaginatum* and *Trichophorum caespitosum* are very sensitive to eutrophication of their environment with nitrogen and phosphorus.

At the borderline between these rain-fed ecosystems and the mineral soils, swamp woodlands with dwarfed trees of the species *Betula pubescens* and *Picea abies* established (Figure 21). The dwarfed growth is caused not only by oxygen deficiency of the water-saturated soil, but also by low availability of nutrients, especially potassium, phosphorus, iron, and zinc (Table 2).

Up to now, the High Harz bogs seem to remain quite stable under the long lasting atmospheric immissions, but we do not know for how long.

Table 1:
Impact of SO_2 (131 mg m^{-3}) on the performance of *Sphagnum* species. Data are based on Ferguson et al. (1978). The values of the control are set to 100 %.

	Relative growth	Relative chlorophyll concentration
Sphagnum species	(% of control)	(%)
S. imbricatum	-18.7	+3.7
S. magellanicum	-3.7	+36.4
S. flexuosum	-8.5	-27.4
S. tenellum	-26.9	+19.4

Figure 21:
A view onto the raised bog "Grosses Torfhausmoor" (Photo: Hagen, 2003)

Table 2:
The nutrient concentration of 1st year needles of *Picea abies* growing at the margin of a bog at Torfhaus, collected on May 15, 2003, in comparison to Norway spruce on neighbouring schists

	Element concentration in mg kg^{-1} dry matter							
Substrate	K	Ca	Mg	P	Cu	Fe	Mn	Zn
Bog	3128	3287	778	619	10.5	50.8	179	30.1
Schist	5200	3206	511	867	9.6	67.6	269	167

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[5] Please note that the bogs around Torfhaus are protected as part of the Harz National Park. This implies that visitors may walk along the marked paths only. It is not allowed to pick plants or collect insects or other animals in this area.

4 Gypsum, dolomite and karst at the southern Harz rim

4.1 Vegetation on gypsum rocks (Hainholz near Hörden, 51°40'N, 10°17'E)[6]

During the geological period of the Perm nearly 253 million years ago, under a hot and dry climate with constant evaporation, huge amounts of calcium sulphate ($CaSO_4 \cdot 2\ H_2O$ = gypsum) and calcium carbonate ($CaCO_3$) were precipitated as white, soft sediments in the Permian "Zechstein" sea (Figure 22). Due to continental drifting, the nowadays middle European area moved from what is now the Canary islands latitude northwards to 51° latitude. The gypsum sediments were 20 to 200 m thick in the Harz region. In later geologic periods, they dehydrated to anhydrite, forming hard grey-blue rocks. The calcium carbonate turned into dolomite ($CaMg(CO_3)_2$) by diagenetic processes. One of the sites where gypsum is exposed at the surface layer is the Hainholz near Osterode-Düna and Hörden at the southern Harz rim. This area was endangered by gypsum quarrying for many years (Knolle and Vladi, 1999) – a threat still present for many of the gypsum outcrops in the Southern Harz area (see www.naturschatz.org).

The soils which developed on gypsum belong to the rendzina (syroseme) type with low concentrations of iron, nitrogen, phosphorus and potassium and with variable concentrations of sulphate, calcium and magnesium (Table 3). They have a low water-holding capacity. On sites where loess as a periglacial remnant is overlying the gypsum, the soil is richer in nutrients and has an improved water-holding capacity supporting thermophilic shrubs. The mosaic pattern of dolomite, gypsum and loess has resulted in a high diversity of plant communities, however, without a specific gypsum-indicating species.

Figure 22:
The vegetation on the gypsum soil in the South Harz region is similar to that of chalk grassland. Where gypsum was removed for industrial purposes, the steep part of the quarry is colonised by thermophilic vegetation (Photo: Ernst, 2003)

One plant genus named after the gypsum soils is *Gypsophila.* Due to continental climate with hot and dry summers at the south and south-east rim of the Harz Mountains the species *Gypsophila fastigiata* does occur there, but is missing at the south-western Harz rim with its cooler and wetter atlantic climate. Most plant species of the gypsum vegetation have a broad ecological amplitude and also grow on calcium carbonate soils. The populations on gypsum are obviously not highly differentiated from those on calcium carbonate if the results with some populations of *Gypsophila* can be generalised (Fiedler et al., 1987). Plants growing on gypsum soils have up to threefold higher sulphur levels in their leaves, as shown for *Cynanchum vincetoxicum* (0.8 to 1.04 % S), when compared to plants growing on calcium carbonate. Most of the leaf sulphur is present as sulphate (Heinze et al., 1982). The high sulphur concentration in *Arabis hirsuta*, however, is not necessarily caused by the increased sulphate level of these gypsum soils, because plant species belonging to the family Brassicaceae are generally high in sulphur.

The carbonate and sulphate chemistry of the karstic groundwater in the Hainholz area was described in great detail by Kempe (1982).

4.2 Rhume spring (Rhumspringe, 51°35'N, 10°17'E)

Once upon a time, the giant Romar met Ruma, daughter of the king of dwarfs. They fell in love and had a child. Unfortunately, their fathers were enemies, so the king of dwarfs didn't want them to marry, killed the little child and locked his daughter Ruma in a subterranean dungeon. Being the daughter of a water-nymph, Ruma turned herself into a spring and thus was

Figure 23:
Gypsiferous vegetation at Hainholz near Hörden. (Photo: Ernst, 2003)

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[6] Please note that the "Gipskarstlandschaft Hainholz" is a protected area ("Naturschutzgebiet"). This implies that visitors may walk along the marked paths only. It is not allowed to pick plants or collect insects or other animals in this area. Attractive hiking routes are suggested at http://ext-lk-osterode.advantic.de/Natur/index.htm.

Table 3:
Element concentrations in rock material and leaves of plant species from the gypsum site at Hörden in comparison with plant species from four different sites of gypsum soils in the Kyffhäuser. Data from the Kyffhäuser (Heinze et al., 1982) are indicated by an asterisk (*)

	Element concentration in mg kg^{-1} dry matter									
	Ca		Mg		K		P		S	
	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
Gypsum rock	21363		340		7.82		31.0			
Festuca ovina on										
- gypsum soil	8898		997		5943		799		513	
- carbonate soil	3206	842	1143	292	9619	1642	1205	201	353	64.1
Arabis hirsute on										
- gypsum soil	42685		1775		17087		870		22770	
Thymus praecox on										
- gypsum soil	20802	3687	2990	462	14663	2190	1369	146		
Cynanchum vincetoxicum on										
- gypsum soil*	13988	1002	3890	899	39256	12786	1874	746	8787	1122
- carbonate soil*	13266	4008	4424	2382	24086	4457	1799	279	5420	2694
Festuca cinerea on										
- gypsum soil*	3206	561	802	194	9306	3832	700	353	577	192

	Fe		Mn		Cu		Zn	
	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E.
Gypsum rock	61.4		3.30		1.65		1.31	
Festuca ovina on								
- gypsum soil	648		53.3		12.2		83.0	
- carbonate soil	274	39.1	79.1	20.3	8.71	1.59	170	43.8
Arabis hirsute on								
- gypsum soil	559		86.3		4.96		47.1	
Thymus praecox on								
- gypsum soil	262	22.3	63.2	10.4	14.5	1.46	85.7	16.3
Cynanchum vincetoxicum on								
- gypsum soil*	173	16.8	56.0	17.0	7.12	4.58	70.0	7.85
- carbonate soil*	179	22.3	63.7	13.7	9.09	0.83	54.9	3.92
Festuca cinerea on								
- gypsum soil*	162	67.0	13.7	7.69	5.40	1.72	45.8	23.5

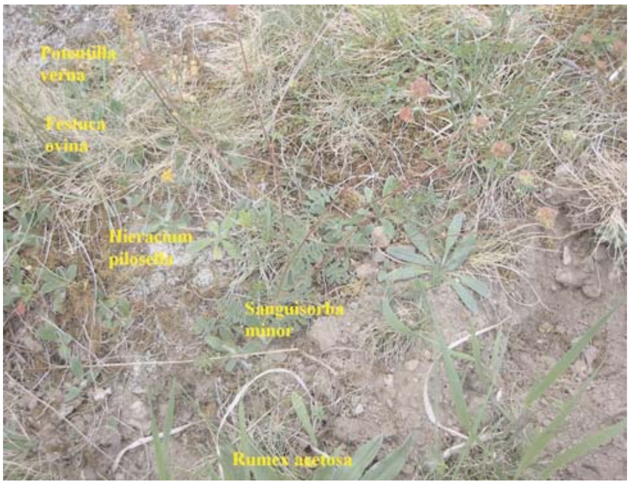

Figure 24:
Plant community on gypsum soil with *Potentilla verna, Festuca ovina, Hieracium pilosella, Sanguisorba minor* and *Rumex acetosa*. (Photo: Ernst, 2003)

able to find her way out through the rocks and reunite with Romar again. People say that the killed child's blood gives the water of the Rhume spring a red colour from time to time… (http://www.harzlife.de/harzrand/rhume.html).

Apart from this legend, there is also a geological explanation for the existence of the Rhume spring: The karstified and water-permeable anhydrite and dolomite layers of the Southern Harz rim are slightly dipping in south-west direction. At their borderline, the karstic water flow is blocked by water-impermeable sandstone layers (Figure 25). This resulted in the emergence of one of the greatest well heads of Central Europe, the karst spring of the Rhume (Figures 26 and 27), which delivers 900 L water per second in dry periods and up to 5500 L after high precipitation. Most of the water is derived from oozing away of the rivers Oder and Sieber (Herrmann, 1969). Dolomite ($CaMg(CO_3)_2$) and gypsum ($CaSO_4 \cdot 2\ H_2O$) are water-soluble. Subsurface leaching produced a typical karst

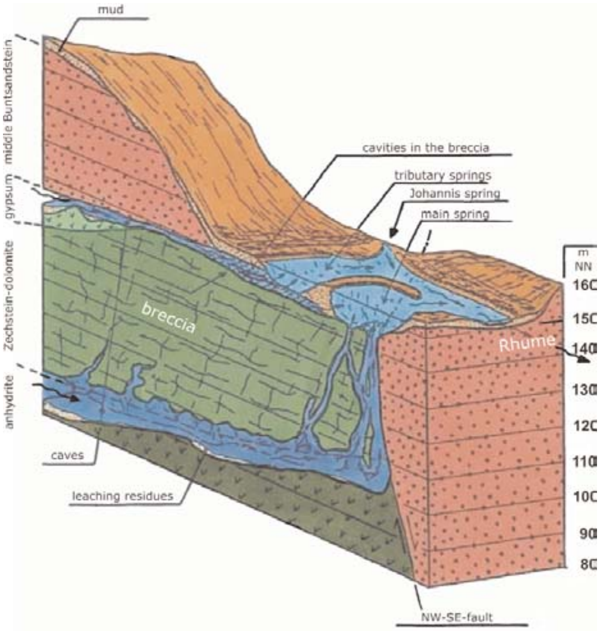

Figure 25:
Geological and hydrological situation of the Rhume spring. (From: http://www.karstwanderweg.de/rhumequelle/3.htm)

morphology, often combined with the disappearance of brooks and rivers at the surface.

The Rhume spring has one main spring which is about 20 m in diameter, and up to 360 small springs. The water is rich in calcium and sulphates, the average sulphate concentration of the main spring is growing with declining water delivery (Ricken and Knolle, 1986). The smell of sulphides indicates that also other sulphur species are released. Specific sulphur bacteria have evolved in these karst aquifers. From the Rhume spring, a strain (DSM 3910) of the chemolithoautotrophic *Ancylobacter* (Herbst et al., 1987) has been isolated.

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Figure 26:
A view onto the Rhume spring at Rhumspringe. (Photo: Ernst, 2003)

Figure 27:
Alnus woodland bordering the Rhume spring. (Photo: Ernst, 2003)

Table 4:
Chemistry of the water of the Rhume karst spring in comparison to wells from calcium carbonate areas in the Teutoburg forest

	Element concentration in mg L^{-1}							
	Ca mean	S.E.	Mg mean	S.E.	S mean	S.E.	Zn mean	S.E.
Rhume karst spring	140		21		68		0.008	
Calcium carbonate wells	117	58	8.2	2.6	8.5	1.4	0.025	0.007

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