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Towards threshold values for nutrients

Petrifying springs in South-Limburg (NL) in a Northwest European context

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Towards threshold values for nutrients; Petrifying springs in South-Limburg (NL) in a Northwest European context

Final report

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Voorwoord

Het doel van het Kennisnetwerk Ontwikkeling en Beheer Natuurkwaliteit (OBN[1]) is het ontwikkelen, verspreiden en benutten van kennis voor terreinbeheerders over natuurherstel, Natura 2000, PAS, leefgebiedenbenadering en ontwikkeling van nieuwe natuur.

In het kader van Natura 2000 zijn in Europees perspectief zeldzame soorten en vegetatietypen in Nederland beschermd. In dit rapport staan de (prioritaire) "Kalktufbronnen" (H7220) centraal. Dit bijzondere habitat type, dat in ons land uitsluitend in enkele Natura2000 gebieden in Zuid-Limburg voorkomt, ligt veelal ingebed in bronbossen (H91Eo-c). Omdat dit type hier zelden grote oppervlakten inneemt waren tot voor kort de kalktufbronnen voor veel mensen een onbekend fenomeen. Kalktufvorming, het neerslaan van kalk op van alles dat met het bronwater in aanraking komt, kent diverse, soms wat bizarre maar altijd fotogenieke verschijningsvormen, zelfs binnen Zuid-Limburg. De bronnen vormen bovendien het leefgebied van bijzondere planten en dieren. De van nature vaak geringe oppervlakte van de verschillende locaties draagt echter bij aan hun kwetsbaarheid. Daarbij springt vooral de hoge stikstof belasting van de bronnen in Zuid-Limburg in het oog. Tot nu toe was het echter onduidelijk welke concentraties al of niet toelaatbaar waren in onze kalktufbronnen.

In dit project, dat geheel met steun van de Provincie Limburg is uitgevoerd, is het gelukt om drempelwaarden voor de toelaatbare nitraat- en fosfaatbelasting van het bronwater te bepalen. Dat is mede gelukt door de Zuid-Limburgse kalktufbronnen in een veel breder perspectief te plaatsen door in aansluiting op de beschikbare literatuurgegevens ook in België, Luxemburg, Frankrijk en Duitsland op tal van plaatsen kalktufbronnen te onderzoeken en te bemonsteren. Afgezien van de vastgestelde drempelwaarden, laten de verzamelde gegevens ook een relatie zien met de (historische) aanwezigheid van Kalkmoerassen (H7230). Helaas moet eveneens worden geconstateerd dat voor het herstel van onze kalktufbronnen er nog een lange weg te gaan is.

De verzamelde informatie die in dit rapport is opgenomen, is afkomstig uit maar liefst 11 landen in Noordwest - en Oost Europa. Gezien dit internationale karakter, het belang van de toegankelijkheid van de verzamelde gegevens over dit habitattype (H7220) ditmaal *ook* buiten ons land, en de specifieke aard van dit onderzoek, waarin niet zozeer beheervraagstukken centraal stonden maar bovenal het bepalen van drempelwaarden, heeft er toe geleid dat voor het eerst een Engelstalig OBN-rapport wordt gepresenteerd. Dit maal is een uitgebreide Nederlandse samenvatting beschikbaar.

Ik wens u veel leesplezier!

Teo Wams

Voorzitter van de OBN Adviescommissie

[1] For English information on OBN Knowledge Network see: http://dt.natuurkennis.nl/uploads/OBN_English_Brochure_2016.pdf

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In the implementation of a research project like this many people and agencies are directly or indirectly involved. The authors would like to thank everyone who contributed to this. In particular the authors would like to thank the following people. First of all we would like to thank Gareth Farr (British Geological Survey, Cardiff) and Piet de Becker (INBO, Brussel) who delivered data sets and related publications on petrifying springs respectively in Wales and in Flanders. The scope and content of their information formed an important basis for this research.

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The scientific guidance of this research project was given by the members of the OBN-Expert Team 'Colline Areas' (Heuvelland)[2]. Overall supervision lay at the Association of Forest and Nature site owners (VBNE) in the person of Mark Brunsveld.

[2] For further information on OBN Expert Team 'Colline Areas' please contact the secretary: friso.vanderZee@wur.nl or the VBNE: m.brunsveld@vbne.nl
See also http://dt.natuurkennis.nl/uploads/OBN_English_Brochure_2016.pdf

Towards threshold values for nutrients: petrifying springs in South-Limburg (NL) in a Northwest European context

Summary

Petrifying springs with tufa formation (*Cratoneurion*) are an endangered rare habitat throughout Europe. Therefore this habitat type is now protected under the Habitat Directive (code 7220) with sense of urgency. In Netherlands the habitat is only found in South Limburg. The habitat type is thought to be sensitive to nitrogen. However the South-Limburg petrifying springs suffer from high nitrate loads in groundwater but a scientifically based threshold value was missing. This threshold value is the concentration above which adverse ecological effects in this habitat type occur, or no longer can be excluded so special measures must be taken to preserve at least the present state of conservation. The aim of this study was to establish this threshold value for nitrate.

The research was conducted in two steps: at first a review of scientific publications and reports was carried out. The focus was on the collection of data on water chemistry of petrifying springs of North Western Europe (< 500 m) in combination with (qualifying) mosses. Also some data files originating from Wales, South-Limburg and Flanders were made available as was additional information acquired from Eastern Europe (Poland, Slovakia and Latvia).
Not all information appeared to be complete with regard to water quality parameters and the qualifying mosses. Therefore, an additional one-off sampling was carried out (step 2) in petrifying springs in the Euregio, Wallonia, Luxembourg, Northern France and the German Teutoburg Forest and Saarland (n=51). In combination with the other data from step one a robust dataset was obtained (n=158). This dataset contains a hydro-chemical range of virtually non-polluted springs to severely polluted springs.

Analysis of the dataset reveals that within the Northwest European research area the petrifying springs of South-Limburg have by far the highest contaminations with nitrate and phosphate. As a result, also the total hardness of the spring water here is usually higher than in surrounding countries.

The presence and abundancy of Fern-leaved Hook-moss (*Cratoneuron filicinum*) turned out to be significantly positively correlated with nitrate pollution and the related increased hardness of the water. Therefore this species is not considered to be an indicator of good habitat quality. On the other hand especially Curled Hook-moss (*Palustriella commutata*) and to a lesser extend Whorled Tufa-moss (*Eucladium verticillatum*) and River Feather moss (*Brachythecium rivulare*) exhibit a preference for nutrient poorer conditions associated with less hardness of the water. Therefore these species are considered to be indicators of a good habitat quality.

On the basis of the collected data threshold values were determined for nitrate and ortho-phosphate in 7220 petrifying springs. The threshold value for this habitat type for nitrate is 28 mg/l (450 µmol/l NO_3^-) and for ortho-phosphate 0.05 mg/l (0.53 µmol/l ortho-PO_4^{3-}). However, for reference situations these values are more strictly; for nitrate 18 mg/l (288 µmol/l NO_3^-) and phosphate 0.04 mg/l (0.42 µmol/l ortho-PO_4^{3-}).

The current, average nitrate concentration in petrifying springs in South-Limburg is about 85 mg/l (1360 µmol/l NO_3^-) thus far above the threshold value. The least contaminated locations in South-Limburg [23-28 mg/l = 370-450 µmol/l NO_3^-] were found near Epen.

This research project was initiated and financed by the Province of Limburg (NL) and was supervised by the VBNE (OBN-program).

Kalktufbronnen in Zuid-Limburg (NL) vanuit Noordwest Europees perspectief: naar grenswaarden voor nutriënten in het bronwater

Samenvatting

Deze samenvatting beschrijft de uitkomsten van het onderzoek naar de maximaal toelaatbare concentraties nitraat en fosfaat in het bronwater van de zogenaamde Kalktufbronnen. Dit is een bijzonder brontype, opgenomen in de Habitatrichtlijn (H7220) en komt binnen Nederland alleen voor in Zuid-Limburg. Omdat dit brontype in Limburg zelden grote oppervlakten inneemt, waren tot voor kort de kalktufbronnen voor de meeste mensen een onbekend fenomeen.

Het onderzoek vond plaats in het kader van het onderzoeksprogramma van het Kennisnetwerk Ontwikkeling en Beheer Natuurkwaliteit (OBN). Dit kenniswerk en de uitvoering van het wetenschappelijke onderzoeksprogramma wordt gecoördineerd door de VBNE (Vereniging van Bos- en Natuurterrein-eigenaren) in opdracht van en gefinancierd door het Ministerie van Economische Zaken en de Samenwerkende Provincies (BIJ12).

Eén van de speerpunten van het OBN-programma betreft het ontwikkelen van - en adviseren over - instandhoudingsmaatregelen ten behoeve van de N2000-beheerplannen en de PAS (Programmatische Aanpak Stikstof). Dat en het feit dat de kalktufbronnen alleen in Limburg voorkomen heeft de Provincie Limburg er toe gebracht het Kennisnetwerk OBN speciaal te verzoeken om de bestaande kennislacunes in te vullen rond de nutriëntenbelasting van deze bronnen.

Wat zijn kalktufbronnen

Een kalktufbron is een brontype waar in het afstromende water als gevolg van specifieke milieuomstandigheden actief kalk neerslaat. Er zijn verschillende mechanismen waardoor kalktufvorming op gang komt en het kan daarbij verschillende verschijningsvormen hebben. Dit brontype biedt plaats aan bijzondere levensgemeenschappen. Vooral de mosflora valt hierbij op.

In kalktufbronnen vormt zich kalktuf door het neerslaan van kalk ($CaCO_3$) op alles dat met het bronwater in aanraking komt. Het kent diverse, soms wat bizarre maar altijd fotogenieke verschijningsvormen. In hydro-morfologisch goed ontwikkelde kalktufsystemen komen de verschillende vormen vaak naast elkaar voor.

Bij de meest eenvoudige verschijningsvorm, de klastische vorm, wordt al het losse materiaal (takjes, stenen, bladresten) in en op de oever van de bronbeek bedekt met een laagje kalktuf. Dit materiaal kan eenvoudig verspoeld raken. Er kunnen zich echter ook volledig verkalkte bodems en drempels vormen, waar erosie veel minder grip op krijgt. Soms raken zelfs (steile) hellingen waarover het bronwater afstroomt er helemaal mee ingepakt (cascade-vorm).

Kalktufvorming doet zich alleen voor wanneer basisch grondwater (pH 7-8,5) met hoge calcium- en bicarbonaat concentraties aan de dag treedt. Deze componenten vormen een labiel evenwicht met kalk ($CaCO_3$) en opgeloste hoeveelheden koolzuur (CO_2) in het water volgens het chemische evenwicht:

$$Ca^{2+} + 2(HCO_3^-) \leftrightarrow CaCO_3 + CO_2 + H_2O$$

Twee verschijningsvormen van kalktuf

A: Klastische vorm,

B: Cascade-vorm

De koolzuurconcentraties in het grondwater zijn hierbij beduidend hoger dan die in de atmosfeer. Onder de grond kan dat koolzuurgas echter niet ontwijken, maar komt dat water eenmaal in de open lucht dan begint koolzuur (CO_2) alsnog te ontwijken naar de atmosfeer. Het directe gevolg daarvan is dat het bronwater oververzadigd raakt met kalk dat vervolgens begint neer te slaan.

Het gaat in beginsel dus om een eenvoudige, puur hydrochemische reactie. Echter, hierop werken een aantal factoren in die de mate van kalktufvorming beïnvloeden. Zo speelt de watertemperatuur een rol, omdat warm water minder koolzuur kan bevatten. In (op)warmend bronwater slaat kalktuf daardoor sneller neer dan in koud water. De mate van kalkneerslag kan dus zelfs verschillen per seizoen. Een andere factor is de verhouding tussen het contactvlak met de atmosfeer en het betreffende volume water. Hoe groter dat contactvlak verhoudingsgewijs is, des te makkelijker het koolzuur kan ontwijken uit het water met als gevolg een snellere kalktufvorming. Sterke kalktufvorming kan zich dus voordoen in ondiepe, snelstromende (spetterende), snel opwarmende bronbeekjes, mits de bron sterk koolzuurhoudend water levert.

Tot slotte kan er ook nog een ecologische component betrokken zijn bij kalktufvorming. Algen en mossen die in de bronnen groeien, kunnen actief en passief de vorming van kalktuf bespoedigen. Actief door het opnemen van koolzuur uit het bronwater. Ze beïnvloeden daarmee het labiele chemische evenwicht, waardoor dus extra kalktuf neerslaat. In passieve zin zorgen vooral mossen door hun groeivorm voor een uitgebreid fijnmazig raamwerk waarop zich makkelijk kalktuf kan afzetten. Groeien ze echter te langzaam dan lopen ze kans te worden bedolven. Slechts een vrij beperkt aantal mossoorten is daarom in staat onder die vrij extreme, kalktufvormende omstandigheden te groeien. Daarvan zijn *Palustriella commutata* (Geveerd diknerfmos) en *Eucladium verticillatum* (Tufmos) wel de meest typerende. De bronnen vormen daarnaast ook het leefgebied van andere bijzondere vaatplanten en dieren (m.n. macrofauna).

Kalktufbronnen als Habitattype

In Europees verband zijn zeldzame soorten en vegetatietypen conform de Habitatrichtlijn ook in Nederland beschermd, zo ook het habitattype Kalktufbronnen.

Overal in Europa worden de levensgemeenschappen van dit bijzondere habitattype bedreigd in hun voortbestaan door grondwatervervuiling, verdroging en verstoring of combinaties daarvan. De van nature vaak geringe oppervlakte van de verschillende locaties draagt bij aan hun kwetsbaarheid. Daarom zijn Kalktufbronnen (H7220) met een karakteristieke mosflora (*Cratoneurion commutati*) zelfs aangemerkt als Prioritair habitattype, habitattypen waar met voorrang gewerkt moet worden aan duurzaam behoud en herstel.

Karakteristieke mos- en kranswiersoorten van de Europese Kalktufbronnen (laagland)

Palustriella commutata	*Philonotis calcarea*
Palustriella falcata	*Pellia endiviifolia*
Eucladium verticillatum	*Scorpidium cossonii*
Bryum pseudotriquetrum	*Cratoneuron filicinum*
Bryum rivulare	
Campylium stellatum	*Chara vulgaris*
Drepanocladus vernicosus	

Opgesteld op basis van de Vlaamse, Franse, Duitse, Luxemburgse en de Europese beschrijving van het habitattype

In Nederland is het voorkomen van kalktufbronnen beperkt tot Zuid-Limburg. Hier komt het vooral voor in het Bunder- en Elslooërbos, de Noorbeemden en op verschillende plaatsen in het stroomgebied van de Geul en, incidenteel, de Geleenbeek. De meeste locaties liggen binnen Natura2000-gebieden. De kalktufbronnen in het Bunder- en Elslooërbos, de Noorbeemden en het Geuldal vallen onder de Europese bescherming van Natura2000. Hiervoor zijn instandhoudingsdoelen vastgesteld. Het habitattype ligt daar vaak ingebed in zogenaamde Alluviale (bron)bossen, eveneens een bedreigd habitattype (H91E0-C). In het buitenland kan het ook wel worden aangetroffen te midden van basenrijke veenmoerassen waaronder kalkmoeras (H7230). Omgekeerd worden sommige soorten van het kalkmoeras ook wel aangetroffen in kalktufbronnen.

Instandhoudingsdoelen Kalktufbronnen (H7220) in de daarvoor aangewezen Nederlandse N2000-gebieden.

N2000-gebied	***Doel areaal***	***Doel kwaliteit***
Bunder- & Elslooërbos	Behoud	Verbetering
Noorbeemden & Hoogbos	Behoud	Verbetering
Geuldal	Behoud	Behoud

Doel van het onderzoek

Kalktufbronnen gelden als stikstofgevoelig en de Zuid-Limburgse kalktufbronnen hebben te maken met een hoge tot zeer hoge nitraatbelasting van het grondwater. Voor het toekomstige beheer is het cruciaal om te weten welke concentraties nog toelaatbaar zijn voor onze kalktufbronnen.

Het Prioritaire habitattype Kalktufbronnen (H7220) staat te boek als stikstofgevoelig. Daarom wordt de grote nitraatbelasting van het bronwater in Zuid-Limburg gezien als een probleem; op dit moment is die gemiddeld 85 mg/l (1360 µmol/l NO_3^-) en ligt daarmee ruim boven de geldende Europese Nitraatrichtlijn (=50 mg/l NO_3^-) voor grondwater. Dat betekent dat er ook door middel van de PAS, met voorrang maatregelen genomen moeten worden om te zorgen dat de staat van instandhouding minstens geborgd blijft. Bij onduidelijke normering blijft het echter onzeker welke maatregelen genomen moeten worden en met welke urgentie.

Doel van het uitgevoerde onderzoek was dan ook het vaststellen van een in Nederland te hanteren grenswaarde voor nitraat en fosfaat in het bronwater van kalktufbronnen.

De grenswaarde is die concentratie waarboven negatieve effecten op de staat van in stand houding van het habitattype optreden, of niet langer uitgesloten kunnen worden.

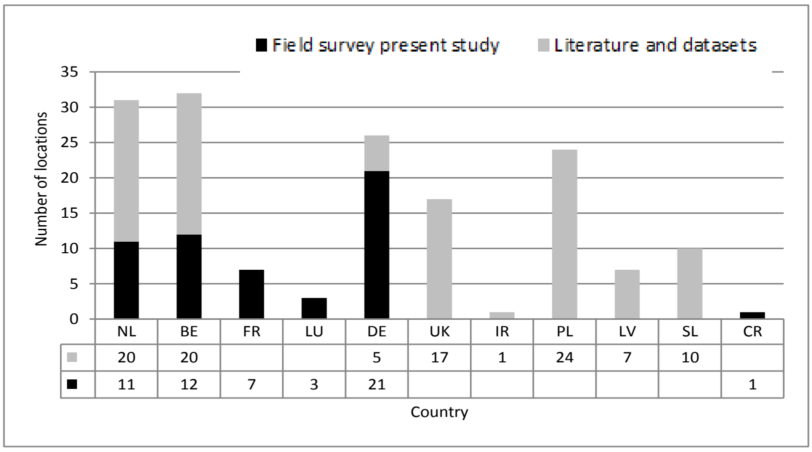
Het onderzoek heeft als achterliggend doel om onzekerheden weg te nemen, zodat de aandacht ten volle op de uitvoering van maatregelen kan worden gezet. De verwachting is dat daarmee een cruciale bijdrage kan worden geleverd aan het bereiken van de instandhoudingsdoelen van de desbetreffende N2000-gebieden.

Opzet van het onderzoek

Het onderzoek kent twee invalshoeken. Enerzijds zijn gegevens verzameld ontleend aan wetenschappelijke publicaties. Daarnaast heeft een aanvullende bemonstering van vergelijkbare bronnen in binnen- en buitenland plaatsgevonden. Zo werd een evenwichtige dataset verkregen om de voorliggende vraag te kunnen beantwoorden.

In eerste instantie is een wetenschappelijke literatuurstudie uitgevoerd. Hierbij lag de focus op het verzamelen van beschikbare gegevens over de waterkwaliteit van kalktufbronnen uit het laagland van Noordwest Europa (<500m) in combinatie met de aanwezigheid van voor dit brontype karakteristieke mossen. In het verlengde daarvan konden enkele grotere databestanden worden verkregen afkomstig uit Zuid-Limburg (Waterschap Roer & Overmaas, Sittard), Vlaanderen (INBO, Brussel), Wales (British Geological Survey, Cardiff), Polen en Letland (West Pomeranian University of Technology, Szczecin).

Niet alle, aldus verzamelde gegevens bleken helemaal compleet. Zo ontbraken geregeld voor dit onderzoek gewenste waterkwaliteitsparameters en / of de combinatie met opnamen met (kwalificerende) mossen. Daarom is in het vroege voorjaar van 2016 een eenmalige, aanvullende bemonstering uitgevoerd van 51 verschillende kalktufbronnen in Noordwest Europa. Hierbij zijn gegevens over waterkwaliteit en het voorkomen van mossen op uniforme wijze verzameld. De locaties lagen in Zuid-Limburg, de Voerstreek, Wallonië, Luxemburg, Noord-Frankrijk en in het Duitse Teutoburgerwoud, de Eifel en het Saarland. Vanuit Zuid-Limburg gezien gaat het hierbij om de meest dichtstbijzijnde, klimatologisch en landschappelijk vergelijkbare gebieden in het Europese laagland met kalktufbronnen met een overeenkomstige ecohydrologische systeemwerking. Zowel op het oog goed ontwikkelde bronsystemen als zichtbaar verstoorde bronsystemen zijn hier bemonsterd.



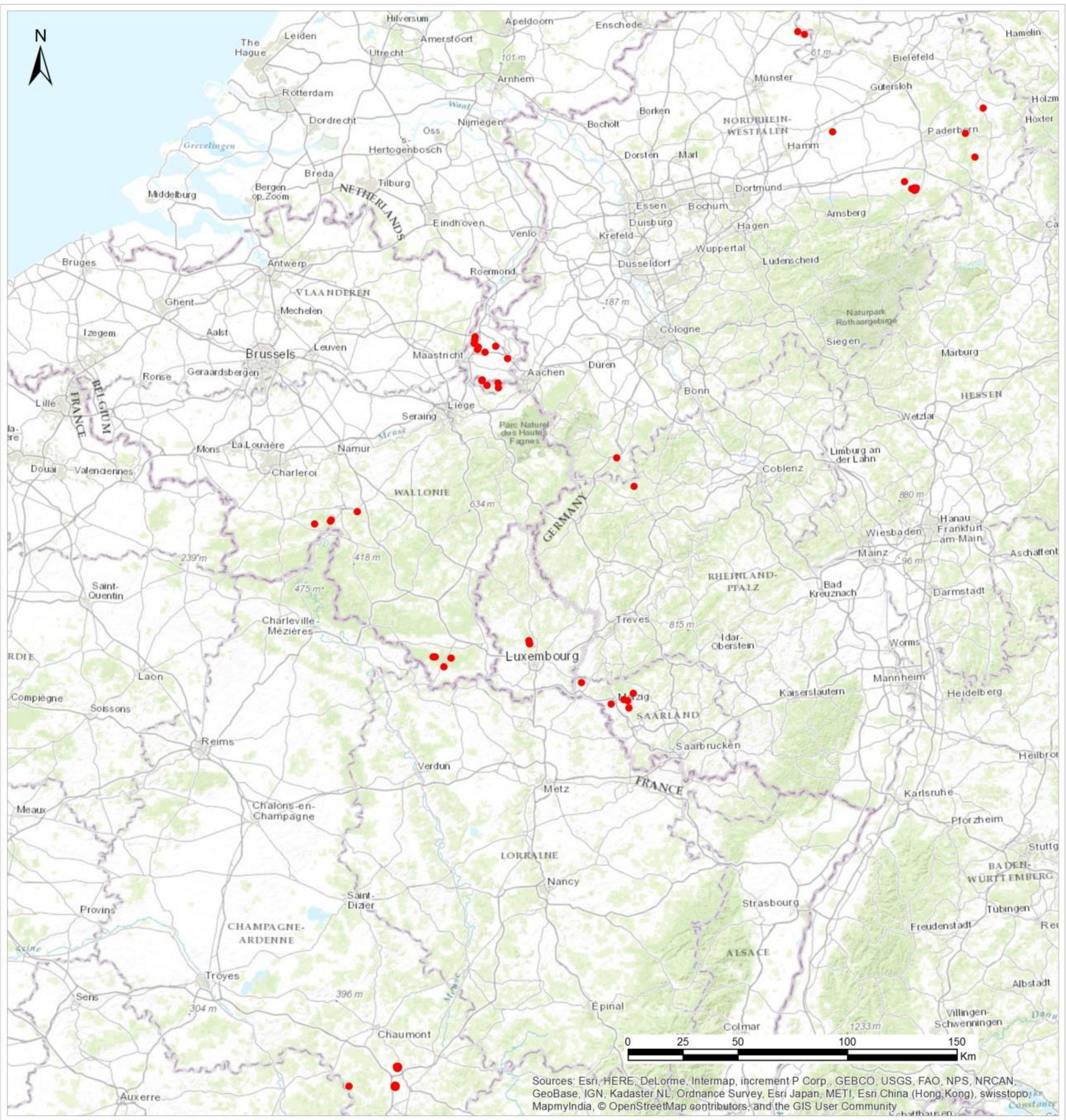
	NL	BE	FR	LU	DE	UK	IR	PL	LV	SL	CR
■ (grey)	20	20			5	17	1	24	7	10	
■ (black)	11	12	7	3	21						1

NL: The Netherlands; BE: Belgium; Fr: France; LU: Luxembourg; DE: Germany; UK: United Kingdom; IR= Ireland; PL: Poland; LV: Latvia; SL: Slovakia; CR: Croatia;

Het per land verzamelde aantal voor deze studie bruikbare monsterlocaties.
Grijze kolom: het aantal monsterpunten uit datasets en uit literatuurbronnen.
Zwarte kolom: het aantal aanvullend bemonsterde locaties.

Het landgebruik binnen de intrekgebieden van deze bemonsterde bronnen loopt uiteen van grotendeels agrarisch gebied tot gebieden die soms grotendeels een natuurbestemming (bos, zeer extensieve landbouw) hebben.

In combinatie met de verzamelde literatuurgegevens ontstond zo de gewenste robuuste en bovendien (geografisch) evenwichtiger opgebouwde dataset, met in totaal 158 verschillende locaties. Binnen de verzamelde dataset is een hydrochemische range van nagenoeg onbelast tot sterk belast aanwezig.



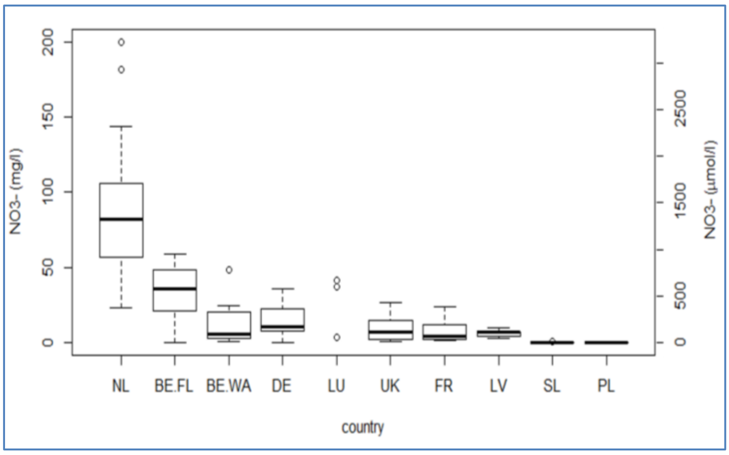
Globale ligging van de aanvullend bemonsterde locaties in Zuid-Limburg, België, Duitsland, Frankrijk en Luxemburg.

Resultaten

Mede dankzij de verzamelde gegevens uit tal van ons direct omringende landen konden grenswaarden voor nitraat en fosfaat worden bepaald. Uit het onderzoek komt duidelijk naar voren dat binnen het Noordwest Europese onderzoeksgebied onze Zuid-Limburgse kalktufbronnen veruit de hoogste concentraties nitraat en fosfaat hebben. Het leidt bovendien tot de constatering dat onze Kalktufbronnen er slecht voor staan.

Een eerste analyse van het verzamelde databestand wees uit dat de nitraatgehalten in het bronwater in vrijwel alle Zuid-Limburgse kalktufbronnen beduidend hoger liggen dan in ons omringende landen. In Oost-Europa (LV, SL, PL) wordt amper nitraat aangetroffen in de bronnen.

De gemiddelde nitraatconcentratie in het Zuid-Limburgse bronwater ligt momenteel op 85 mg/l (1360 µmol/l NO_3^-). De minst vervuilde locaties in Zuid-Limburg [23-28 mg/l = 370-450 µmol/l NO_3^-] zijn te vinden in het Terzieter bronnetjesbos bij Epen.



Boxplots van het nitraatgehalte in het water van kalktufbronnen per deelgebied/land (n=98)

Aantal locaties per land: NL=31, Be=32 (BE-FL=20 en BE-WA=12), DE=23, LU=3, UK=12, FR=5, LV=7, SL=10, PL=24.

Ook voor ortho-fosfaat blijken de concentraties in de Limburgse kalktufbronnen duidelijk hoger te zijn dan elders in het onderzoeksgebied, ondanks de kalkrijke milieuomstandigheden.

Verder komt naar voren dat de overvloedige uitspoeling van nitraat in de ondergrond voor allerlei bodemchemische vervolgreacties kan zorgen. Dat leidt er toe dat de samenstelling van het grondwater verandert. Zo zorgt de uitspoeling en afbraak van nitraat ook nog voor hogere concentraties calcium, magnesium en soms sulfaat in het bronwater.

Bepalen van grenswaarden

Tijdens het veldonderzoek zijn in totaal 45 mossoorten aangetroffen in en vlak langs kalktufbronnen. Daaronder bevonden zich vijf karakteristiek geachte soorten van kalktufbronnen die in voldoende mate vertegenwoordigd zijn in het databestand om te kunnen worden gebruikt voor nadere analyses en het bepalen van de grenswaarden, te weten:

- Gewoon diknerfmos (*Cratoneuron filicinum*)
- Geveerd diknerfmos (*Palustriella commutata*)
- Tufmos (*Eucladium verticillatum*)
- Beekdikkopmos (*Brachythecium rivulare*)
- Gekroesd plakkaatmos (*Pellia endiviifolia*)

Om te komen tot de afleiding van grenswaarden is eerst onderzocht hoe de individuele mossoorten reageren op de samenstelling van het bronwater en vooral de nutriëntenbelasting daarvan. Hiertoe werd een zogenaamde Redundancy analyse (RDA) uitgevoerd. Hieruit kwam naar voren dat Gewoon diknerfmos en Geveerd diknerfmos zich gedragen als elkaars tegenpolen. Een nadere analyse wees uit dat de presentie en abundantie van Gewoon diknerfmos significant toenemen met de nitraatbelasting! Hoewel deze soort deel uitmaakt van het gangbare soortenpalet van de Noordwest Europese Kalktufbronnen, kan Gewoon diknerfmos dus niet worden gebruikt als indicator voor een voldoende of goede habitatkwaliteit. Zonder de aanwezigheid van andere karakteristieke soorten wijst ze eerder op een habitat onder zware stress, waar nog alleen deze mossoort rest en nog wel kalktuf wordt gevormd. De soort is niet specifiek gebonden aan kalktufbronnen maar wordt ook nog in allerlei, vochtige tot natte, en matig voedselarme tot voedselrijke biotopen gevonden.

Geveerd diknerfmos maar ook Tufmos en Beekdikkopmos indiceren vaak een rijkere en gewoonlijk een goed ontwikkelde mosflora. Vooral Geveerd diknerfmos en Tufmos zijn in NW Europa en daarbuiten vrijwel beperkt tot de biotoop van kalktufbronnen. Deze drie soorten kunnen daarom dienen als positieve kwaliteitsindicatoren van het habitattype. Met andere woorden, ze zijn indicatoren van een goede staat van instandhouding en van een stabiele situatie die noodzakelijk is voor het behoud van het habitattype. Ze vertonen een voorkeur voor wat voedselarmere condities. Geveerd diknerfmos is zelfs significant positief gecorreleerd met nitraatarm bronwater.
Gekroesd plakkaatmos vertoont een meer ambivalent gedrag. Deze soort wordt ook volgens de literatuur geregeld op (tijdelijk) verdroogde kalktuf aangetroffen.

Om drie kwaliteitsklassen te kunnen onderscheiden resteren daarmee drie relatief kritische mossoorten: Geveerd diknerfmos, Beekdikopmos en Tufmos.

Classificatie van de mosvegetaties in kalktufbronnen op basis van de drie geselecteerde kritische mossen.

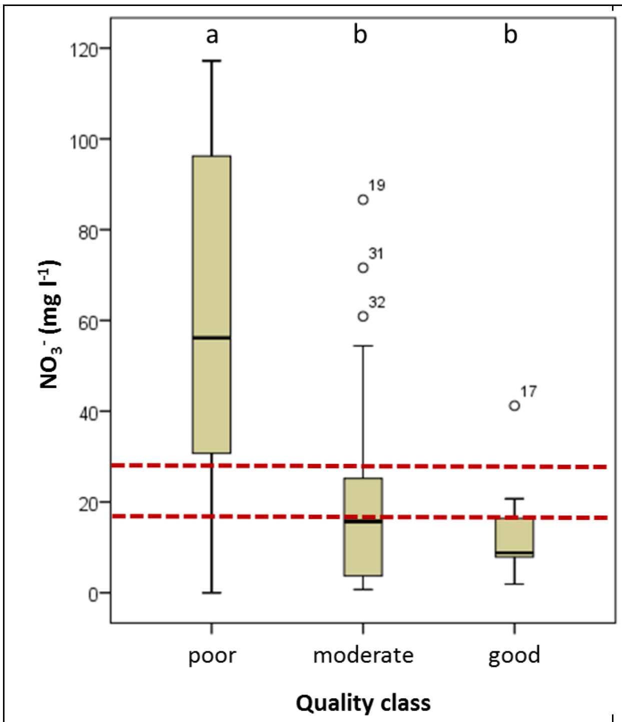
Kwaliteitsklasse	***Criteria***
Slecht (verarmd) [poor]	*Afwezigheid van de drie geselecteerde kritische mossen*
Matig [moderate]	*Aanwezigheid van tenminste 1 van de drie soorten: bedekking < 50 %*
Goed (referentie) [good]	*Aanwezigheid van tenminste 1 van de drie soorten: bedekking > 50 %*

De kwaliteitsklasse 'Goed' kan ook als de natuurlijke referentie worden opgevat.

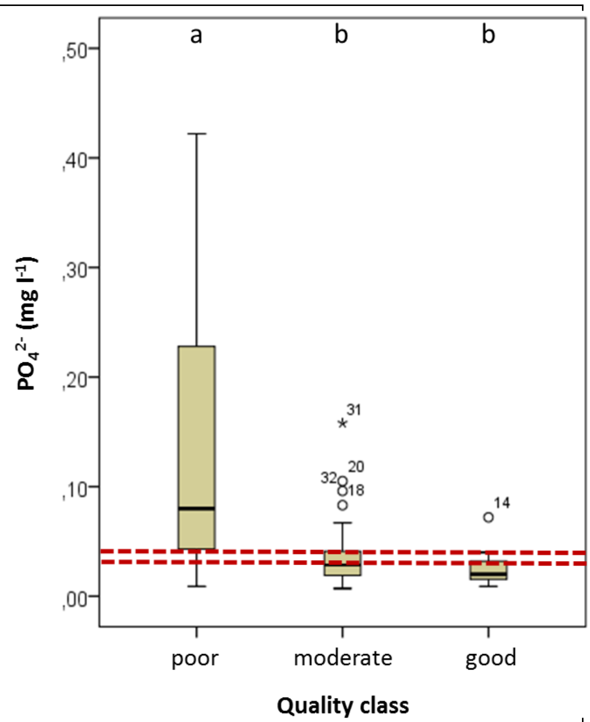
Alle 51 bemonsterde kalktufbronnen (systemen met actieve kalktufvorming) zijn op basis van de geselecteerde mossen toegedeeld aan één van de drie aldus gedefinieerde kwaliteitsklassen. Om vervolgens grenswaarden te bepalen voor deze classificatie is de methode van de Britse Technische Adviescommissie voor de Kaderrichtlijn Water (UKTAG) gehanteerd. Om grenswaarden af te leiden gaat men als volgt te werk:

- De grenswaarde van een klasse moet tenminste onder het gemiddelde en bij voorkeur onder de 25-percentielwaarde van de groep met een slechte conditie.
- De grenswaarde moet tenminste boven het gemiddelde en bij voorkeur boven 75-percentielwaarde liggen van de groep met een goede conditie.
- De grenswaarde weerspiegelt de beschikbare kennis uit de literatuur en kennis uit de onderzoeksgebieden.

Op basis van de verzamelde gegevens zijn grenswaarden afgeleid voor nitraat en fosfaat in het bronwater. De grenswaarde voor de referentie (goed) is voor nitraat in kalktufbronnen vastgesteld op 18 mg/l (288 µmol/l NO_3^-). Voor ortho-fosfaat ligt de grenswaarde voor de referentie op 0,04 mg/l (0,42 µmol/l ortho-PO_4^{3-}).



Box plots van het nitraatgehalte (NO_3^-) in bronwater voor de drie kwaliteitsklassen
In rood zijn de twee kritische concentraties weergeven (zie tekst).
Indien letters bovenaan de kolommen verschillen is sprake van een significant verschil tussen de betreffende klassen



Box plots van het ortho-fosfaatgehalte (ortho-PO_4^{3-}) in bronwater voor de drie beschreven kwaliteitsklassen
In rood zijn de twee kritische concentraties weergeven (zie tekst).
Indien letters bovenaan de kolommen verschillen is sprake van een significant verschil tussen de betreffende klassen

In Zuid-Limburg komen helaas geen kalktufbronnen voor die tot de referentieklasse 'goed' kunnen worden gerekend. Wel kan een aantal bronnen worden toegedeeld aan de klasse 'matig'. Het zwaartepunt daarvan ligt in het zuidoosten van Zuid-Limburg (o.a. Noorbeemden, omgeving Epen). De overige bronnen zijn te rekenen tot de sterk verarmde klasse, waaronder de kalktufbronnen in het Bunder- en Elslooërbos.

Kalktufbronnen van de referentieklasse, bronnen met vaak hoge bedekkingen aan Geveerd diknerfmos, zijn uitsluitend in de direct ons omringende landen te vinden (o.a. in Zuid-België, Eifel etc). Ook het zwaartepunt in het voorkomen van de klasse 'matig' ligt in het buitenland. Het gaat steeds om locaties waar de nitraatconcentraties in het bronwater beduidend lager zijn dan in Zuid-Limburg.

Hoe de grenswaarden te gebruiken

Uit de voorgaande analyse zijn verschillende grenswaarden af te leiden. Welke waarde moet men nu hanteren, mede in het licht van de Europese Nitraatrichtlijn en de N2000 doelstellingen.

De klassen 'matig' en 'goed' zijn, zoals in de bovenstaande figuren te zien is, voor wat betreft het nitraat- en fosfaatgehalte onderling niet significant verschillend, maar samen wel ten opzichte van de verarmde klasse. De klassen 'matig' en 'goed' verschillen dan vooral in mosbedekking van de bronnen. Deze twee klassen kunnen, mede gezien de aanwezige, kritische mos-combinaties, tot het habitattype H7220 worden gerekend. In navolging daarvan gelden dan voor het bronwater de volgende grenswaarden voor het habitattype:
- voor ortho-fosfaat: **0,05 mg/l** (0,53 µmol/l ortho-PO_4^{3-})
- voor nitraat: **28 mg/l** (450 µmol/l NO_3^-).

Voor nitraat voldoen in Limburg alleen enkele kalktufbronnen nabij Epen aan deze grenswaarde. De overige Zuid-Limburgse kalktufbronnen zitten hier wat betreft nitraat vaak een factor twee tot vier boven!

Voor Kalktufbronnen met een matige habitatkwaliteit moet er eventueel door middel van maatregelen wel voor worden gezorgd dat te hoge nitraatconcentraties op korte termijn worden teruggebracht tot onder de 28 mg/l NO_3^-, om de staat van instandhouding te kunnen garanderen. Ligt de doelstelling op verbetering van de habitatkwaliteit, dan moet worden gestreefd naar het bereiken van de referentiewaarde.

De sterk verarmde klasse ('poor') mist de kritische mossoorten. Binnen deze groep kan dan nog wel Gewoon diknerfmos aanwezig zijn. Zoals hiervoor is aangetoond, wordt deze soort juist gestimuleerd door toenemende nitraatgehalten. Ze kan daarom worden beschouwd als negatieve kwaliteitsindicator voor het habitattype. Vanwege die negatieve trend is de bovengrens van deze verarmde klasse, circa 95 mg/l NO_3^-, niet bruikbaar als grenswaarde/norm, omdat daarmee het behoud van deze verarmde situatie niet kan worden gegarandeerd, laat staan verbetering van de kwaliteit. Als het gaat om 'behoud' is een lagere waarde een vereiste. In deze situaties moet dan de toch al vigerende norm van de Europese Nitraatrichtlijn (50 mg/l NO_3^-) worden aangehouden, een waarde die vrijwel overeenkomt met het gemiddelde van deze verarmde klasse.

Voor 'matig' en 'goed' kwalificerende habitats voldoet deze norm dus niet. Dergelijke situaties komen alleen voor bij nitraatconcentraties lager dan 28 mg/l NO_3^-. Hogere nitraatconcentraties zouden op die locaties leiden tot een afname van de kwaliteit, door achteruitgang en mogelijk verdwijnen van kritische soorten. Bij een dominantie van Gewoon diknerfmos verdwijnen immers de kwaliteit indicerende mossen. Is de doelstelling voor 'verarmde' locaties 'Verbetering van de habitatkwaliteit', dan zal de grenswaarde van 28 mg/l NO_3^- moeten worden aangehouden om de vestiging van meer kritische soorten mogelijk te maken.

Gebruik van de grenswaarde voor nitraat bij verschillende doelstellingen en habitatkwaliteit

Natuurlijke referentie	≤ 18 mg/l NO_3^-	
Matig / Goed ontwikkeld	Behoud: 28 mg/l NO_3^-	Verbetering: 18 mg/l NO_3^-
Verarmd habitat	Behoud: 50 mg/l NO_3^-*	Verbetering: 28 mg/l NO_3^-

*= Vereiste overeenkomend met de Europese Nitraatrichtlijn

Content
Inhoudsopgave

1 General introduction

Travertine-forming springs are also called ***petrifying springs*** (petrify: to become like stone) due to the encrustation of twigs, mosses, leaves etc., which over time can either become replaced with calcite, retaining physical structure, or be preserved in a casing of calcite.

The travertine (tufa) formations are found in a variety of environments, like spring forests, peatlands or in open countryside, both in the lowlands as well as in the alpine regions of Europe. The spring complexes are generally quite small (point or linear structure) and often dominated by bryophytes. However, these complexes can also result in large tufa deposits and terraces (Pentecost 2005).

The '*Cratoneurion commutati*', the scientific name given to the bryophyte vegetation of a classic travertine-forming spring, refers to the moss species *Cratoneuron commutatum* (now named *Palustriella commutata*) that, along with only a few other species, is usually abundant at, although not exclusive to, travertine-forming springs (Heery 2007). This type of springs is quite rare and endangered in Europe. Therefore 7220 Petrifying springs with travertine formation (*Cratoneurion*) are now not only a protected habitat type but a sense of urgency has also been assigned to this type (priority) under the European Natura 2000 Habitat Directive. The conservation status of this habitat type is labelled as unfavourable throughout Europe (*Interpretation Manual of European Union Habitats, version EUR 28, 2013*).

In The Netherlands N2000 habitat type 7220 is very rare and only listed for three Natura reserves, all located in the most southern part of the Province of Limburg (Figure 1.1):

NL2003012 Bunder- en Elslooërbos [Bunde & Elsloo Forest]
NL2003033 Noorbeemden & Hoogbos [Noor valley & High Forest]
NL9801041 Geuldal [Geul valley]

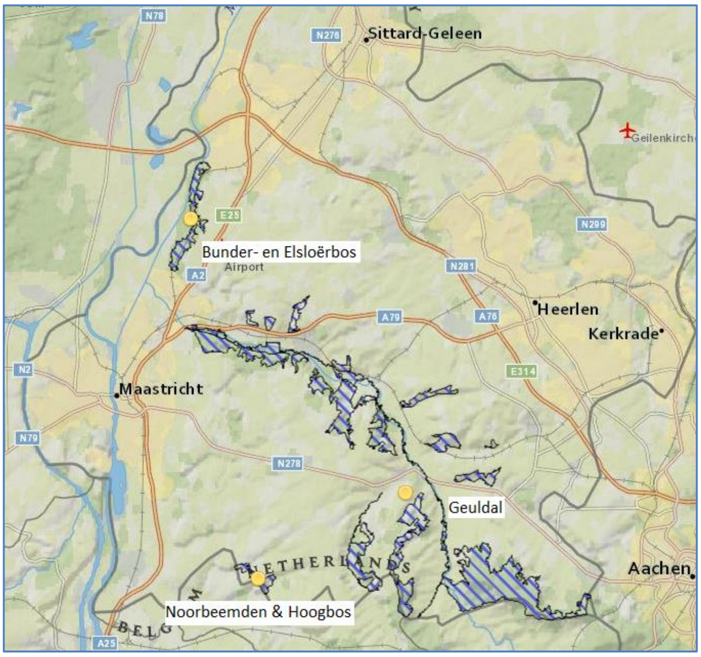


Figure 1.1: Locations of N2000-areas in South-Limburg designated for habitat type 7220
Figuur 1.1: Ligging van N2000 gebieden in Zuid-Limburg, aangewezen voor H7220

http://natura2000.eea.europa.eu/#

Although it is not listed, there are also some petrifying springs locally present in the catchment area of the Geleenbeek, between Heerlen and Sittard.

For more than 30 years the nitrogen pollution of the phreatic groundwater in this southern part of Limburg is severe (Broers et al. 2004; De Mars et al. 2015). Nitrate concentrations in phreatic groundwater and springs up to 200 mg/l are no exception. Furthermore in The Netherlands the habitat type 7220 is thought to be sensitive to nitrogen. This means, among other things, that specific measures need to be taken in order to preserve the present state of conservation. Additional measures will be needed to improve the present state of conservation. Although the European Nitrates Directive urges the Member States to reduce the nitrate levels in groundwater below 50 mg/l, a scientifically based maximum nitrogen load for groundwater feeding the Dutch petrifying springs has not yet been determined. Until now only a so called milestone-value of 25 mg/l (400 µmol/l) is used (De Mars & Vercoutere 2010). Therefore it remains unclear whether specific measures based on either the milestone-value or the European Nitrates Directive will be effective.

Table 1.1 Conservation objectives for petrifying springs (7220) for the designated Dutch N2000-areas.
Tabel 1.1 Instandhoudingsdoelen Kalktufbronnen (H7220) in de daarvoor aangewezen Nederlandse N2000-gebieden.

N2000-area	***Target surface area***	***Target habitat quality***
Bunde & Elsloo Forest	Preservation	Improvement
Noorbeemden & High Forest	Preservation	Improvement
Geul valley	Preservation	Preservation

In recent years it appears that little information is available on water quality in relation to bryophyte vegetation in petrifying springs abroad. Mostly the information concerns diatom flora (Arp et al. 2010; Denys & Oosterlynck 2015). However the diatom flora is not suitable to designate or to evaluate the conservation status of this habitat type. Recently only the UK Technical Advisory Group delimited a threshold value for nitrate in petrifying springs (20 mg/l [320 µmol/l]: UKTAG 2012; Farr et al. 2014). Although part of the elaborated sites show considerable landscape ecological differences compared to the locations in Limburg and surroundings, the given threshold value is useful as a guideline.

Aim
The aim of this study is:

- To establish a threshold value for nitrate in groundwater feeding petrifying springs in the European lowland <500 m above sea level. This threshold value is the value above which adverse effects on the conservation state of this type of springs will occur, or no longer can be excluded.

The present research is limited to nitrogen components in ground water. If appropriate we will indicate other factors in the groundwater (e.g. high concentrations of phosphate or sulphate) that could be a hindrance too.

This special OBN-project was financed by the Dutch Province of Limburg (2015/68374) and supervised by the VBNE. Because of her responsibility for the drafting of the N2000-management plans and the implementation of PAS-measures the Province requested the knowledge network OBN[3] to resolve the knowledge gap with respect to an acceptable nutrient load of petrifying springs.

[3] For further information on the OBN network see http://dt.natuurkennis.nl/uploads/OBN_English_Brochure_2016.pdf

Etymology

In German, French and English scientific papers and reports a lot of different names circulate referring to travertine and also for petrifying springs (Table 1.2).

In this study we follow Pentecost (2005) who proposed to use ***travertine*** for all forms of calcite precipitation over *tufa*. The latter can be confusing because *tufa* is also used for a range of soft, porous rocks for instance pyroclastic (volcanic) deposits and pumice.

Table 1.2: Commonly used names for travertine and petrifying springs in different languages

Tabel 1.2: Veel gebruikte namen voor kalktuf en kalktufbronnen in verschillende talen.

spring	English	***petrifying spring***			
	Dutch	kalktufbron			
	French	source petrifiante	source tufeuse	source incrustante	
	German	(kalk)tuffquelle	kalksinterquelle		
deposit	English	***travertine***	(calcareous) tufa	calc sinter	
	Dutch	(kalk)tuf	travertijn	sinter(kalk)	bronnenkalk
	French	travertin	tuf (calcaire)	tout	
	German	(Kalk)sinter(kalk)	Kalktuff	Quellkalk	Susswasserkalk

2 An introduction to Petrifying springs

Active travertine forming springs occur throughout Europe where the annual mean air temperature is > 5 degrees Celsius. Pentecost (1995) has briefly reviewed 320 published travertine sites in Europe, 156 of which are still active in some form. The remaining ones are inactive - fossil travertines - and range in area from 650 km^2 to just a few square metres and in thickness from 300m to a few cm. Fossil travertines are often quarried.

Still, petrifying springs are a rare phenomenon throughout the world, but very rare in The Netherlands. These petrifying springs have fascinated people for a long time. In the Netherlands the first account on this phenomenon, which also includes an attempt to explain the petrifying process, is probably found in an old folk tale from a small village in the N2000 reserve Bunde & Elsloo Forest, north of Maastricht. The origin of this folk tale seems to date back to the arrival of Christianity in the region around 900-1000 AD (De Mars 2010). The beginning of a real understanding of carbonate chemistry related to travertine formation can be placed at the end of the 19th and beginning of the 20th century (Pentecost 2005). It is for that reason that in 1923 the origin of the travertine formation in the Elsloo Forest is discussed in a few scientific meetings of the Natural History Society of Limburg. The debate was even supported by some chemical research in a few petrifying springs (Beckers 1923; Kurris 1923). Nowadays there is a good scientific understanding about the conditions concerning travertine formations.

2.1 Petrifying processes in short

Petrifying springs derive their name from their petrifying nature, as they are known to turn objects into stone. In literal sense these objects are not petrified, but rather laminated with a layer of calcite ($CaCO_3$). This calcite is called travertine or tufa, covering all kinds of objects in petrifying springs.

In principle there are three drivers stimulating travertine formation in springs:

- Inorganic driver
    - morphological co-driver
- Biogenic drivers

2.1.1 Inorganic driver

The main driver is based on oversaturation and starts when relatively acid water, with a high concentration of carbon dioxide (CO_2), infiltrates and passes a calcareous rich soil layer. While passing this layer, large quantities of calcium (Ca^{2+}) and carbonate (CO_3^{2-}) become dissolved in groundwater, so much that it becomes oversaturated with these components. When this oversaturated groundwater comes to the surface, CO_2 starts to degas into the atmosphere. As a result, the water gets oversaturated with $CaCO_3$ which begins to precipitate as travertine (Pentecost 2005). This process occurs according to the following reaction:

$$Ca^{2+} + 2(HCO_3^-) \leftrightarrow CaCO_3 + CO_2\uparrow + H_2O$$

The rate at which travertine precipitates depends on several factors like Ca^{2+} and CO_3^{2-} concentrations, the amount of CO_2 degassing and water temperature. These factors can differ greatly between the two major groups of travertine formations either from thermogene or from meteogene origin. The differentiation is based on the origin of the carrier CO_2, which in case of thermogene formation is thermally generated with volcanic or tectonic activity (Ford & Pedley 1996; Pentecost 2005). This results in high CO_2 concentrations capable of dissolving high amounts of Ca^{2+} and CO_3^{2-}.

These high concentrations in combination with high temperatures cause high precipitation rates and can result in enormous travertine formations as seen in Mammoth Hot Springs (USA) and Pamukkale (Turkey, Figure 2.1).

Figure 2.1: Travertine formation at Pamukkale, Turkey
Figuur 2.1: Tufcomplex van Pamukkale Turkije.
http://www.thousandwonders.net/Pamukkale

Meteogene travertine formations are generally less elaborate than thermogenic travertines, because of the different origin of the carrier CO_2. In this case the CO_2 originates mainly from soil processes, after being dissolved in percolating rainwater. This result in lower CO_2 concentrations with concomitantly lower amounts of Ca^{2+} and CO_3^{2-} dissolved. Although meteogene travertine can feature high temperatures as well, precipitation rates are often not as high as in thermogenic systems (Pentecost 2005). Thermogene travertines do not occur in the Netherlands and will therefore not be discussed in this report any further.

2.1.2 Stream morphology as co-driver

Landscape and stream morphology can have a great impact on travertine deposition, because they relate directly to several hydrological factors involved in the outgassing of CO_2. These factors are stream discharge, gradient, width-to-depth ratio of the stream bed and residence time, and are all interrelated.

The dimensions of a stream are important for the travertine forming capacity, and stream length alone can tell something about total travertine forming potential. Width and depth, however, are best assessed in relation to each other as the width-to-depth ratio. This ratio provides information on the amount of water at the surface in which CO_2 outgassing can take place in relation to water volume (Chen et al. 2004). Therefore, the amount of travertine precipitation is higher in a wide and superficial stream, compared to a narrow and deep stream (Drysdale et al. 2002).

Residence time, the time a volume of water needs to travel downstream, decreases when discharge increases. By reducing the residence time, the capacity for CO_2 outgassing is also reduced since the water is capable of outgassing for a shorter time. As a result, streams with higher discharge were found to have less travertine deposition (Drysdale et al. 2002).

Different aspects of landscape morphology can affect stream morphology. Most important is how the slope is responsible for the stream gradient. Gradient, in turn, can affect stream turbulence and residence time, and is thus also a factor determining travertine precipitation. A steeper gradient will lead to a shorter residence time and therefore theoretically also to less CO_2 outgassing. However, a steeper gradient will also lead to more turbulence with concomitantly more CO_2 outgassing (Jacobson & Usdowski 1975). The latter effect will presumably be of more significance since streams with steeper gradients were found to show higher travertine deposition (Drysdale et al. 2002). This is especially true when the stream water spreads all over the slope. This supports an increase of turbulence in residence time and in interaction with (bryophyte) vegetation, which may act as a biotic driver to travertine precipitation (see below). In addition, significant travertine forming structures like cascades and waterfalls (Zhang et al. 2001; Chen et al. 2004; Vázquez-Urbez et al. 2010) inherently occur at streams with a considerable gradient.

2.1.3 Biogenic drivers

In addition to the inorganic driver of calcite precipitation, there is also a biotic component involved in travertine formation. Travertine formation is generally promoted in the presence of cyanobacteria (Pentecost 1978), algae (Freytet & Verrecchia 1998) and bryophytes (Parihar & Pant 1975).

Figure 2.2: Moss encrustation with travertine in a petrifying spring

Figuur 2.2: Verkalking van mossen in een kalktufbron

Since degassing of CO_2 is essential to calcite precipitation, travertine formation is long thought to be primarily facilitated by photosynthetic CO_2 consumption (Cohn 1864). Formation of meteogene travertine would even be unlikely without the presence of algae and bryophytes. Although Pentecost (1996) estimated the contribution of bryophytes to be only 6 -12%, they may not only remove carbon dioxide from the water during photosynthesis. Bryophytes also can act as an extensive framework providing an increased surface area enhancing the precipitation of travertine in other ways (Pentecost & Zhang 2000; Emeis et al. 1987; Figure 2.2).
Although some bryophytes are attracted to the petrifying spring’s alkaline and wet conditions, they may become petrified themselves. The growth rate of such bryophytes must be at least as high as the accumulation rate of the travertine in order to survive otherwise it becomes buried under a crust of travertine (Figure 2.2).

Until now it is difficult to say which of the above mentioned drivers prevail. This usually varies according to relative emphasis placed by the researchers. Since purely inorganic travertine deposits appear to be rare (Kempe & Emeis 1985) it is very likely that both inorganic and biogenic drivers are active. There may even be a shift in precipitation mechanism from dominantly inorganic at the emergence point to a more biogenic one further downstream (Ford & Pedley 1996).

2.2 Water quality of Petrifying springs

Groundwater supplying petrifying springs has an alkaline character with little variation in temperature, mineral composition and acidity.

Ca^{2+}, HCO_3^- and CO_2 are the principal chemical components in groundwater and responsible for the precipitation of $CaCO_3$ in travertine forming systems. The high concentration of CO_2 enables groundwater to dissolve Ca^{2+} and CO_3^{2-} while passing soil layers rich in lime, usually calcareous loam clay or limestone deposits.

Smieja & Smieja-Król (2007) showed that petrifying springs have relatively high concentrations of calcium, magnesium and bicarbonate compared to other spring types (Figure 2.3).

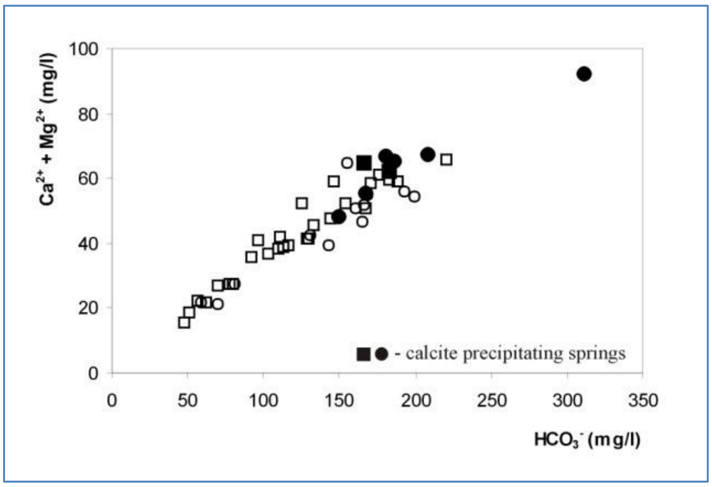


Figure 2.3: Summary of Ca, Mg and HCO_3 content of water from springs (Smieja & Smieja-Król 2007) which shows that petrifying springs in Poland have usually Ca + Mg content higher than 50 mg/l and HCO3 contents higher than 150 mg/l.

Figuur 2.3: Ca, Mg en HCO_3 concentratie in bronwater (Smieja & Smieja-Król, 2007) laat zien dat kalktufbronnen in Polen gewoonlijk minimaal een Ca+Mg gehalte hebben van meer dan 50mg/l en een HCO_3 gehalte hoger dan van 150 mg/l.

Hajek et al. (2002) studied (western) Carpathian spring fed vegetation. They found that in travertine forming fens (*Carici flavae-Cratoneuretum*) the minimum calcium concentration needed for occasional precipitation is about 90 mg/l (= 2250 µmol/l) although the mean calcium concentration was 231 mg/l (5775 µmol/l; n=26). Pietsch 1984, Boyer & Wheeler (1989) Pentecost (1992) and Arp et al. (2010) have reported lower calcium concentrations in *Palustriella commutata* springs with a maximum of 150 mg/l (3750 µmol/l). The lowest stable concentrations in a travertine forming fen was 80 mg/l (2000 µmol/l).

Columbu et al. (2013) reported travertine deposition at a minimum of approximately 100 mg/l (2500 µmol/l) in the summer. In some areas an increase in water temperature calcium concentration can rise from 40 to 150 mg/l (1000-3750 µmol/l). On the other hand values of 150-250 mg/l measured in summer do not always results in precipitation of travertine (Hajek et al. 2002). This shows that the supersaturation of the groundwater is decisive and not absolute concentrations. Most authors agree however that the minimum concentration for travertine formation is about 50 to 80 mg/l (1250-2000 µmol/l).

Travertine formation in *Cratoneurion*-springs occurs at a pH range of 6.9 to 9.0 with a mean of about pH 8 (Pentecost & Zhaohui 2002; Arp et al. 2010; Columbu et al. 2013). Farr et al. (2014) reported even a pH 12.2 for a location with travertine formation highly influenced by historic anthropogenic activities.

A characteristic feature of petrifying springs is the significant change in water chemistry as soon as the supersaturated water emerges up to a few hundred meters downstream (see also §2.1.1). Due to the outgassing of CO_2 alkalinity, pH and calcium concentrations show steady changes downstream (Coûteaux 1969; Arp et al. 2010; Farr et al. 2014: Figure 2.4). The outgassing of CO_2 results in an increase of the pH from about 7 up to and above 8-8.5 which favours the precipitation of travertine. As the outgassing takes some time usually the precipitation of travertine starts somewhat downstream of the spring. As a consequence calcium concentrations and alkalinity decrease steadily which is also indicated by the decrease of electrical conductivity. Only when the spring is also draining calcareous groundwater further downstream these latter effects may be less pronounced.

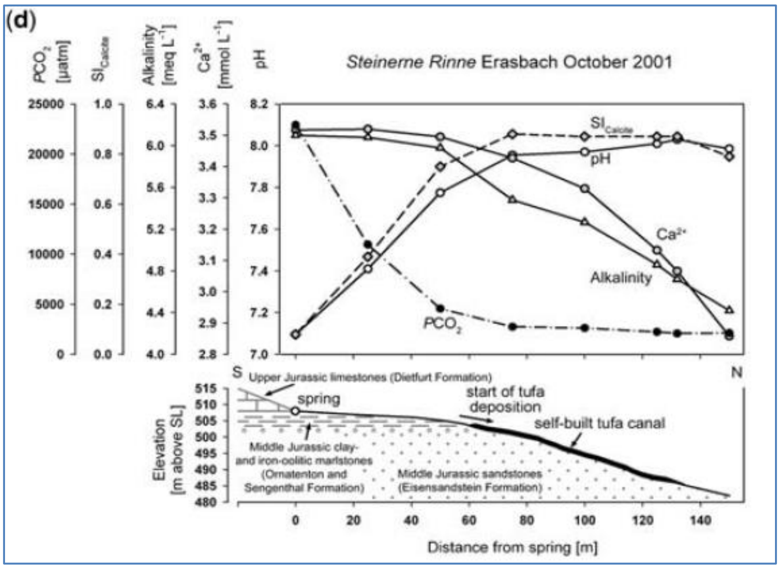


Figure 2.4: An example of the downstream changes in CO_2 pressure (pCO_2) calcite saturation ($SI_{calcite}$) Alkalinity, Calcium concentration and pH along a stream with travertine deposition (after Arp et al. 2010)

Figuur 2.4: Een typisch voorbeeld van het verloop van de CO_2-spanning, kalkverzadiging, alkaliniteit, calcium concentratie en pH in een kalktufbronbeek vanaf de bron (Arp et al. 2010)

2.3 Petrifying springs as a Natura 2000 habitat

In the Netherlands three species can be found which are specialised in growing in petrifying springs in the Netherlands (Ministerie van LNV 2008; Van Dort 2011). However Petrifying springs were not distinguished as an independent vegetation type until recently. Under the classification of the Vegetation of the Netherlands (Schaminée et al., 1995) the petrifying spring is 'hidden' in the *Cardamino-Montion* more particular in the sub-association of *Pellio epiphyllae-Chrysosplenietum cratoneuretosum*. However, the species composition found in these springs revers at a European level without doubt to the *Cratoneurion commutati.*

According to Ministerie van LNV (2008) the habitat 7220 is among others[4] described by the presence three bryophyte species:

- *Palustriella commutata*	(Geveerd diknerfmos)	Ch + *Co*
- *Cratoneuron filicinum*	(Gewoon diknerfmos)	*Co*
- *Brachythecium rivulare*	(Beekdikkopmos)	*Co*

Ch = Characteristic species. *Co* = Indicator species of good a-biotic conditions;

Other indicators of a well-developed habitat:
- *Permanent springs and seepage areas*;
- *Active travertine formation*;
- *Low stream velocity (superficial flowing)*;

[4] *Apart from Palustriella commutata another characteristic species of the Dutch petrifying springs 7220 is the caddis-fly Plectrocnemia brevis, whereas the flatworms Crenobia alpine, Dugesia gonocephala and Polycelis felina are listed as indicators of good conditions (Ministerie van LNV 2008)*

For a location to qualify as 7220 an active travertine formation has to occur with a surface area of more than $10m^2$ and at least one of the three moss species mentioned above must be present. Usually the habitat type is found in a mosaic with spring forest (91E0-c; Alluvial forests).
There are no typical vascular plants for petrifying springs. There are some species commonly present in spring (forest) habitats that prefer calcareous spring habitats. Therefore these species may also indicate good abiotic conditions for petrifying springs. These plant species are *Cardamine amara* (Large Bittercress), *Chrysoplenium oppositifolium* (Opposite-leaved Golden Saxifrage), *Chrysoplenium alternifolium* (Alternate-leaved Golden Saxifrage) and *Equisetum telmateia* (Great Horsetail) (Van Dort et al. 2012).

Farr et al. (2014) presented a list of species associated with active travertine formation (i.e. leaves and stems becoming petrified). Among others they mention *Bryum pseudotriquetrum*, *Campylium stellatum*, *Chara vulgaris*, *Eucladium verticillatum*, *Palustriella commutata*, *P. falcata*, *Philonotis calcarea* and *Scorpidium cossonii*.

They recorded species like *Ctenidium molloscum, Fissidens taxifolius*, *Pellia endiviifolia*, *Preissia quadrata*, *Conocephalum species* but also *Chrysosplenium species*, *Asplenium scolopendrium* and *Geranium robertianum* from (temporarily) non-active or eroded travertine formations within active petrifying springs.
Cratoneuron filicinum however does not belong to either of these groups. Apparently it is not very sensitive with regard to habitat conditions. According to Pentecost (2005), this species is even the third most common species in the United Kingdom.

In the Netherlands the presence of petrifying springs in alkaline fens (7230: *Caricion davallianae*) is nowadays unknown. However in Eastern Europe this is not the case. Besides the alluvial alder woods (91E0) petrifying springs here are also frequently found in a mosaic with alkaline fens (7230), chalk mires (7210) and related *Molinion* meadows (6410). From a landscape ecological point of view petrifying springs here are often an integral part of basiphilous mires or degraded forms of such systems (see also Appendix 2). Basiphilous spring mires may or may not deposit travertine on the surface but in time these mires may shift regularly from travertine (tufa) depositing systems into only peat forming systems (Wołejko et al. 2005, see also Appendix 2). Also Verbüchelen et al. (1995) recognises that the *Cratoneurion commutati* may evolve in time into spring forest (alluvial alder wood).

Box 2.1 Typical mosses of Petrifying springs in this study (see also photo plate 3)

Palustriella commutata (Curled Hook-moss) is the rarest of the three species listed for the habitat in the Netherlands and is only found at few sites in the Netherlands (Van Gennip & Weeda 2007). It is also the species with the most specific environmental preference for perpetually wet and calcareous sites. It is the only one of the three species that (almost) exclusively occurs at petrifying springs. It therefore derives the status of 'characteristic species' for this habitat (Ministerie van LNV 2008). *P. commutata* is therefore an indicator of 7220 habitats of a good quality.

Farr et al. (2014) consider this species as well as the closely related *P. falcata* as one of the typical species from active travertine formation often becoming encrusted with travertine. It may form extensive mats around springs and is kept moist by seepages and capillarity rather than fast flowing water but appeared to be tolerant to a wide range of environmental and hydrological conditions (Pentacost & Zhaohui 2002; 2006).

Cratoneuron filicinum (Fern-leaved Hook-moss) often occurs at petrifying springs but is not restricted to these specific spring sites. It also occurs at less calcareous sites or next to anthropogenic dolomite walk roads (Oosterlynck & Van Landuyt 2012). In springs it often grows on travertine deposits but also epiphytically on fallen branches or trees. Although it does not bear the 'specific species' status, it is only labelled as a 'constant species' (Ministerie van LNV 2008).

Brachythecium rivulare (River Feather-moss) is also often, but not exclusively, found at petrifying springs. This species is common in spring and brook habitats, present at slightly acidic as well as calcareous conditions. Due to this indifference towards certain environmental conditions, the status as characteristic species is being questioned (Oosterlynck & Van Landuyt 2012). The resemblance to the ordinary moss *Brachythecium rutabulum* does not add to its value as characteristic species either (Van Dort 2011). Nevertheless, it is still listed as a 'constant species' (Ministerie van LNV 2008).

In countries other than the Netherlands, a fourth moss is included in the list of characteristic mosses for 7220. ***Eucladium verticillatum*** (Whorled Tufa-moss) is even named after its occurrence in travertine forming systems and is common in petrifying springs around the world. In the Netherlands, however, it does not live up to its name. It was until recently not known from petrifying systems but only sparsely at dry marlstone (NDFF 2015). It is therefore not recognized as a characteristic moss for petrifying springs in the Netherlands. However, it will be treated as a characteristic species during this study, due to its importance in petrifying springs abroad. Farr et al (2014) consider this species as one of the typical species from, active travertine formations often becoming encrusted with travertine.

Another bryophyte often mentioned in relation to petrifying springs is the liverwort ***Pellia endiviifolia*** (Endive Pellia). Due to its high occurrence in Flemish petrifying springs, Oosterlynck & Van Landuyt (2012) granted it the status of 'constant species'. Although, this is not incorporated in the Dutch profile of habitat type 7220, *P. endiviifolia* will be treated as such during this research. This species is generally not associated with travertine formation, though it is often found to grow on travertine substrate. Also Farr et al. (2014) consider this species as one of the typical species from non-active or eroded travertine formations.

3 Approach of the present study

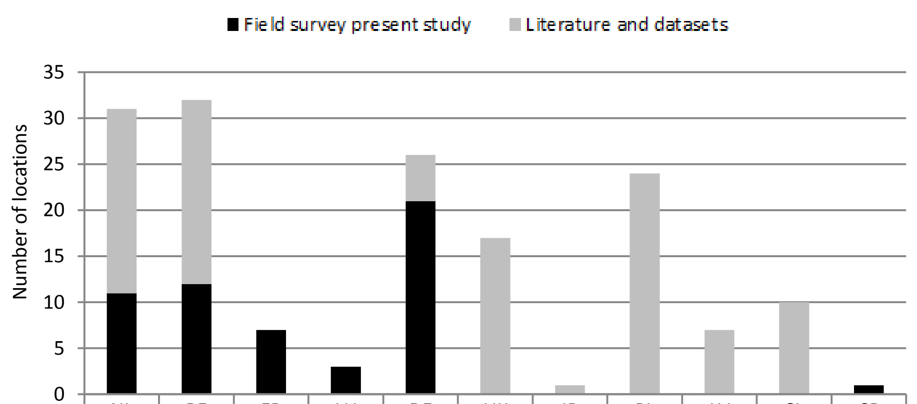
In this study both a literature review and a data survey are combined with additional field sampling of petrifying springs in the Netherlands and reference locations in surrounding countries. Furthermore a review of travertine forming systems studied in Poland and Slovakia is included (see Appendix 2).

3.1 Literature review and data survey

A literature review was carried out on both scientific articles and professional reports regarding petrifying springs and travertine formation in general with a focus on surface water composition and occurring moss vegetation. Additional to studies described in the literature it was possible to contact researchers abroad and use entire datasets for a series of petrifying springs. For example two larger datasets used are from the Belgian Institute for Nature- and Forest Research (INBO) (Oosterlynck & De Bie 2000) and a dataset from Wales UK (Farr et al. 2014).

Additional to (reference) data from surrounding countries data from geographical areas with lower nitrogen pollution (for example Central and Eastern Europe) were missing. Therefore extra effort was given to collect reference data for this region (Poland, Latvia and Slovakia).

The literature and data survey delivered in total 104 suitable data records from locations in Europe of which 20 are located in the Netherlands, 20 in Belgium, 5 in Germany, 17 in the United Kingdom, 24 in Poland, 7 in Latvia, 10 in Slovakia and 1 in Ireland (Figure 3.1). However, of each record not all the water chemistry parameters are available or detailed information on bryophyte composition was not present. In the Netherlands the available separate datasets on moss vegetation and of the water chemistry of petrifying springs proved to be impossible to combine unambiguously.



	NL	BE	FR	LU	DE	UK	IR	PL	LV	SL	CR
■ (grey)	20	20			5	17	1	24	7	10	
■ (black)	11	12	7	3	21						1

Country

NL: The Netherlands; BE: Belgium; Fr: France; LU: Luxembourg; DE: Germany; UK: United Kingdom; IR= Ireland; PL: Poland; LV: Latvia; SL: Slovakia; CR: Croatia;

Figure 3.1: The number of locations used in the present study.
Black column: the number of locations sampled during the field survey
Grey column: the number of locations obtained from collected datasets and found in literature.

Figuur 3.1 Het totale aantal monsterpunten zoals gebruikt in deze studie.
Zwarte kolom: het aantal aanvullend bemonsterde locaties:
Grijze kolom: het aantal monsters uit datasets en uit literatuurbronnen.

3.2 Field survey

3.2.1 Locations

The first analysis of the data collected via literature and datasets highlighted the absence of sufficient data on both water quality and bryophyte composition and reference material for petrifying springs in the Netherlands. Therefore a series of additional petrifying spring areas was selected in Belgium, France, Luxembourg and Germany based on literature, tourist information and information from local experts and from local governments. With respect to South Limburg these areas are the nearest spring complexes in the calcareous parts of Europe which have also comparable landscape ecological conditions, hydrological processes, habitats and species. They mainly differ in land use intensity. The selection of the sampling sites in these areas occurred randomly. Not only seemingly well developed, undisturbed locations were sampled, also clearly disturbed situations if available (see also photo plate 4).

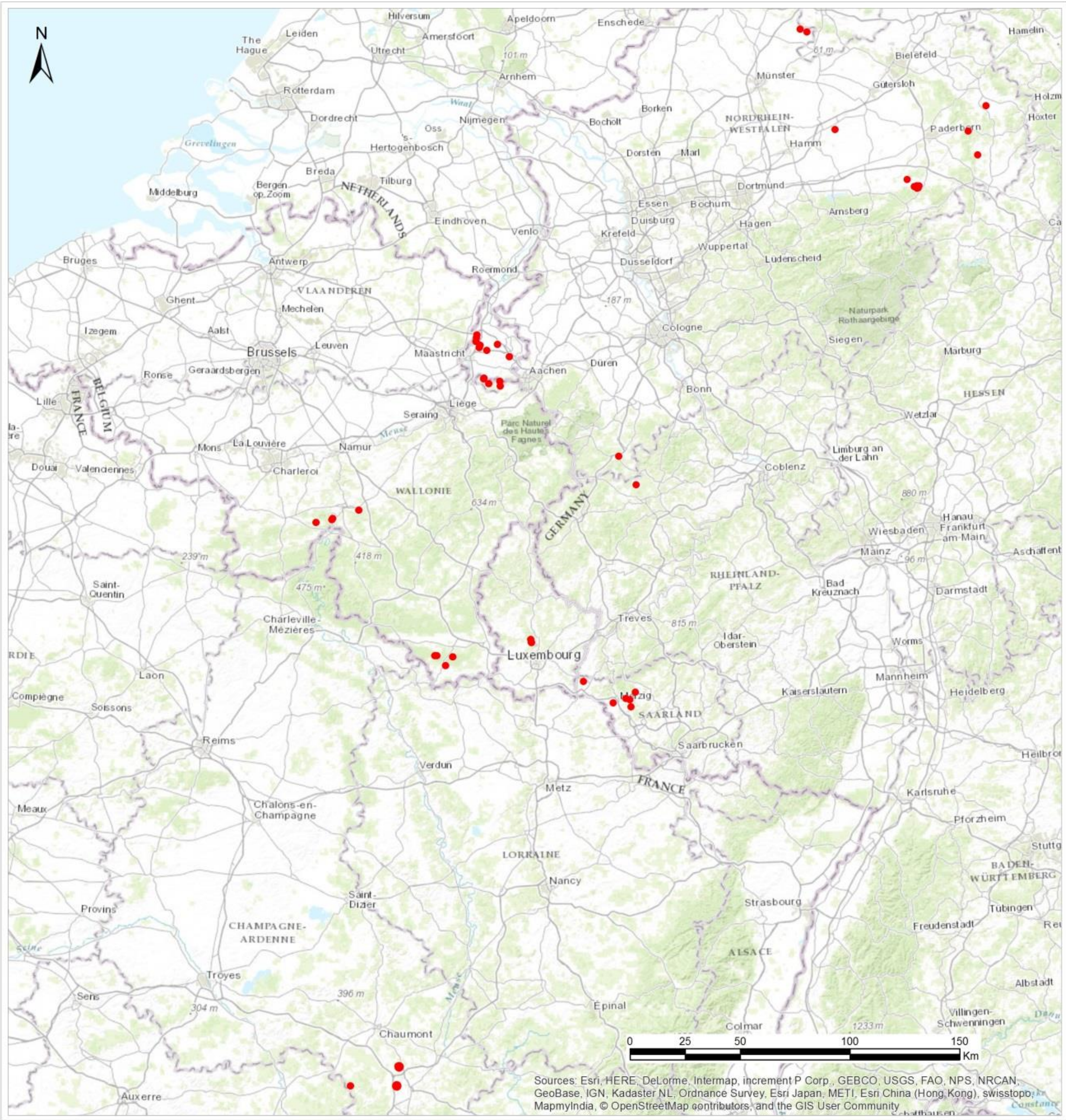


Figure 3.2: Map of the locations studied in South Limburg, Belgium, Germany, France and Luxembourg.

Figuur 3.2: Globale ligging van de aanvullend bemonsterde locaties in Zuid-Limburg, België, Duitsland, Frankrijk en Luxemburg.

In the spring of 2016 (February-March-April) this additional set of locations was sampled (water chemistry and bryophyte composition). Together with one location sampled in the summer of 2015 this dataset contains 51 locations, of which 11 in the Netherlands, 12 in Belgium, 20 in Germany, 5 in France and 3 in Luxembourg (see Figure 3.1 and 3.2). At three locations a second water sample was taken, downstream from the main petrifying zone. At the end of January 2016 a water sample of the Plitvice Falls in Croatia was also obtained. In total in the field survey 54 water samples were collected (Appendix 3).

The coordinates (WGS84) of the investigated locations were determined using GPS. With exception of the Plitvice location all sampled locations are situated between 47,8749 and 51,75299 latitude and 4,72491 and 9,12667 longitude (Figure 3.2).

All locations are easy to access by public footpaths, forest roads open to the public or sometimes even located in roadside verges or at picnic spots.

3.2.2 Location characteristics

On arrival, the site was surveyed globally to comprehend the complete system and its functioning. The geographical location, landscape ecological setting and other striking landscape features or anthropogenic influences (like drinking water springs or historical constructions,) were noted. Also signs of stress were identified (e.g. littering, drought, digging, pollution) as was the visible impact of it. The dominant soil type was determined and the amount of dead organic matter (e.g. mud, leaves and branches) was estimated. Next, the amount of shading from the canopy was estimated in percentage (100%: maximal shading; 0%: no shading). The cardinal direction of the slope was also determined, to get a better picture of the exposure to sunlight.

Furthermore, the degree of travertine formation, stream discharge, (bryophyte) vegetation cover and species composition were described (see below). All information was brought together in a checklist (Appendix 1)

3.2.3 Classification of Travertine (tufa) formation

The travertine formation of each petrifying spring system was classified based on the presence of different forms of travertine precipitation like fluvial crust, cascade, waterfall and/or barrage systems (Figure 3.3). Note that a petrifying spring system can be composed of a combination of different forms of travertine deposits. The amount of travertine was described and classified in five classes:

- 1: travertine formation absent
- 2: some travertine formation
- 3: considerable travertine formation
- 4: abundant travertine formation
- 5: extremely high travertine formation.

Class 1: Travertine formation absent

Although the characteristic mosses of petrifying springs are abundant this class includes locations with no visible travertine formation at the sampled site. Travertine formation usually occurs somewhat further downstream.

Class 2: Some travertine formation

This class represents marginal examples of travertine formation. Petrification is limited to the presence of some fluvial crust on twigs and pebbles only to be found locally. Therefore, the presence of travertine is sometimes not easy to detect.

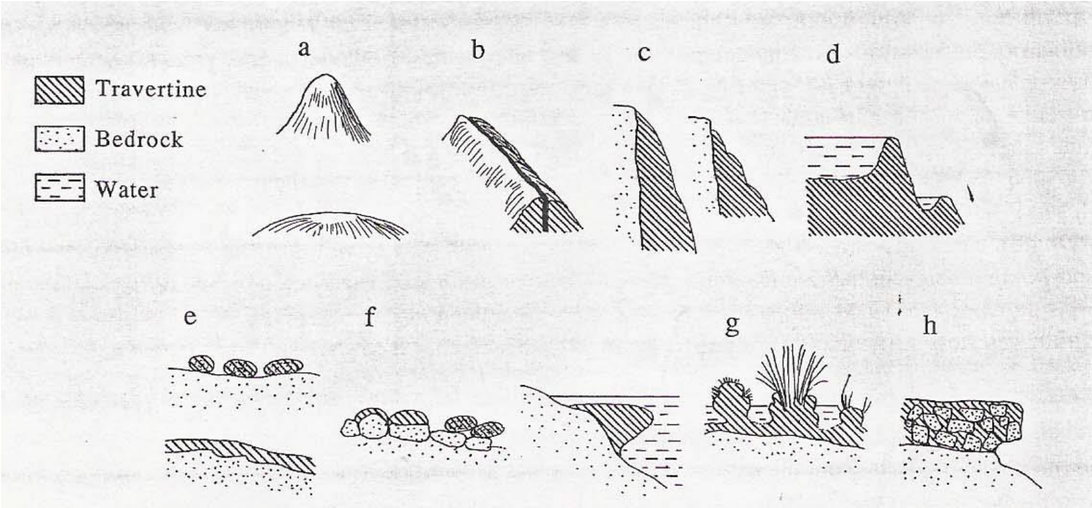


Figure 3.3: Different types of travertine formation (after Pentecost 1995)**.**
(a) spring mounds (cupola); (b) fissure ridge; (c) cascades/ 'crons'; (d) (mini) dams; (e) fluvial crust; (f) lake crusts;
(g) paludal deposits; (h) cemented rudite (not on scale).

Figuur 3.3: Verschillende verschijningsvormen van kalktufneerslag. (naar Pentecost1995)
(a) travertijn koepels; (b) spleet afzettingen; (c) cascades / crons / kalktufkegels; (d) (mini) dams; (e) fluviatiele korst;
(f) meer afzettingen (g) moerastuf; (h) kalkverkitting en -pleistering (niet op schaal).

Class 3: Considerable travertine formation

In springs and brooks of this class travertine is easy to find. There are many places with petrified deposits on twigs, stones and sometimes at the base of mosses. Locally a part of the gravel may be petrified. The petrified sediment has not (yet) a thick fixed layer, although sometimes petrified mini-dams and cemented small ridges may be present.

Class 4: Abundant travertine formation

In runnels and brooks of this class the alluvial bed is largely covered by petrified deposits over long distances. Mini-dams are also a frequent component in these systems but even solid petrified banks are locally present particularly on steep edges. Mosses can also be incrusted by travertine.

Class 5: Extreme travertine-formation

This class is characterized by a dominance of cemented petrified alluvial beds, cascade-like slopes (often with small pools) or waterfalls over loosely structured petrified deposits. The latter is usually to be found at the bottom of petrified slopes. Mosses are incrusted by travertine.

3.2.4 Measuring stream discharge

Generally stream discharge (base flow) provides a good indication of the size of the catchment area. In order to calculate the infiltration area of a spring, the discharge of the stream was measured preferable using a portable Thomson measuring weir (henceforth referred to as measuring weir). This portable weir is especially developed for measuring in vulnerable springs habitats (De Mars et al. 2014; Figure 3.4) The weir consist of a sharp-crested metal plate with a V-shaped opening (angle: 90°) and a ruler to read the height of impoundment (Figure 3.4). A plastic sheet attached to the plate made it watertight as the weight of the impounded water pressed it against the stream's bed and banks. The water needs to make a free fall of at least 5 cm (from the bottom of the V-shape to the water level) and must stand vertically and horizontally straight. When it is watertight, the height of impoundment can be determined after a short while using the ruler. Subsequently, the discharge (Φ) can be calculated using the following formula:

$$\Phi = (1.38 * hs^{2.48}) \times 1000 \; l/s$$

In which *hs* is the measured height of impoundment in meters and discharge is given in litres/second (Naudin-Ten Cate et al. 2000).

Figure 3.4: Small version of the portable sharp-crested weir (right) and from above (left) with plastic cloth

Figuur 3.4: Kleine versie van het mobiele meetschot (rechts) en van bovenaf (rechts)

The measuring weir could not always be used, e.g. in streams with a flat slope in which the minimum free fall of 5 cm could not be reached or the alluvial (braided) beds were too wide or when discharge is more than 14.5 l/s.
For a part of the springs an alternative approach was used by measuring the average dimensions of the stream profile (m^2) multiplied with the average flow rate (m/s). The average flow rate was acquired by timing leaves to travel downstream over a known length, and then dividing the length (m) by the time (s).

All measurements took place in a relatively dry period. It is therefore assumed that most springs approximately showed their base flow. So the surface area of the catchment area can be calculated roughly using the calculated discharge of the spring (during the moment of sampling) and mean annual groundwater recharge, which varies in the different research areas between 120 and 400 mm/y.

3.2.5 Bryophyte cover and vegetation composition

For all sampled locations the species composition was described. Both mosses and vascular plants directly in and along the petrifying spring were listed i.e. directly growing in the stream bed or on rocks, fallen branches or other debris in contact with spring water and at the spray zone on the lower banks. The upper banks were thus excluded, as were overhanging branches or trees not in contact with the water. In addition to the actual vegetation composition, the dominant tree species and overall forest type (when present) were determined separately.

The focus was on mosses. Although large travertine formations were not accessed because of their vulnerability nevertheless a fairly good impression of the mosses could be obtained from alongside (binoculars). The field survey period in early spring is less optimal for vascular plants. So the enlisted species and their coverage only present an indication. Nevertheless it gives a fairly good idea about species composition directly around the springs, including also the presence of indicators of good and of poor abiotic conditions.

Moss cover

The percentage of the potentially suitable area for plant growth in the petrifying springs was set as 100%. In many springs a relatively large area is permanently covered by flowing water. In such situations total cover may be fairly low, though plant cover is abundant. For instance, in springs with 60% open water bryophyte cover cannot be much higher than 40% but if all suitable open spaces are maximally covered the relative cover is 100%. In a situation with only 10% open water a bryophyte cover of 40% is seen than as low (relative cover =44%).

The relevees were made over a length of 20 - 50 m along a more or less homogeneous part of the alluvial bed of the runnels or brooks. The width of the relevee was determined by the width of the alluvial bed, varying from less than 1 m up to 20 m. In case of petrified slopes (crons) sometimes even more.

Bryophyte cover was estimated at each site by eye. Abundancy was noted in Braun-Blanquet scale and as percentage of coverage (%). Percentage of coverage was later translated to numerical abundancies (Table 3.1) for further statistical analysis.

From each site a number of photographs were taken. If necessary small vouchers of specimens were collected for further examination. Most samples collected were also examined by the bryophyte specialist Jurgen Nieuwkoop. Nomenclature follows Hill et al. (2006) and Van Dort et al. (2010) for bryophytes and Van der Meijden (2005) for vascular plants.

Table 3.1: Translation table from percentage cover to numerical abundancies.
Tabel 3.1: Omzettingstabel van procentuele bedekking naar numerieke bedekkingsgraad

Percentage cover	Numerical abundancies
<1 %	1
±1 %	2
2-4 %	3
±5 %	4
6-15 %	5
16-25 %	6
26-50 %	7
51-75 %	8
76-100 %	9

3.2.6 Water chemistry: sampling and analysis

Sampling en field measurements

To determine the chemical content of the spring water in each system, a sample was taken at each site. A water sample of 200 ml collected in small PE bottles filled to the brim was taken, preferably directly above the main petrifying zone, which in some cases resulted in sampling water from the spring itself. In a few cases the preferred sampling location was inaccessible, so the (flowing) water was sampled close by in the system. The effect on water chemistry is limited and may only affect the Ca, pH and HCO_3 concentrations due to outgassing of CO_2 (see Ch. 2.4). The effect on nutrients is negligible.

Each sample was kept cool immediately after sampling and stored in dark conditions until analysis at the laboratory of B-WARE research centre Radboud University (Nijmegen).

At each sampling point, Electrical Conductivity (EC, in µS/cm) and temperature (°C) were measured using a hand held conductivity meter WTW Cond3110, with a TetraCon® 325 electrode.

Additional 50 ml water samples were taken to determine alkalinity and pH within 16 hours after sampling. Prior to analysis these samples were kept cool as well. Alkalinity was determined using a titrimetric MColortest™ Alkalinity Test (Merck Millipore). The pH was measured using a hand held WTW pH96 meter with a SenTix21 electrode

Laboratory analysis
Prior to elemental analyses, 10 ml of each sample was stored at 4°C until analysis with 0.1 ml (65%) HNO_3^- to prevent metal precipitation. For the analyses of phosphorus, calcium, magnesium, iron, sulphur and aluminium inductively coupled plasma spectrophotometry (ICP-Optical Emission Spectrometer, Thermo Scientific iCAP 6000 Series ICP) was used. To determine nitrate (Kamphake et al., 1967), ammonium (Grasshoff & Johanssen, 1972), ortho-phosphate[5] (Henriksen, 1965), sodium and chloride concentrations, 20 ml of each sample was stored at -20°C and analyzed colorimetrically with an Auto Analyzer 3 system (Bran+Luebbe). Sodium and potassium were determined with a Technicon Flame Photometer IV Control (Technicon Corporation).

3.3 Statistics

Statistics were performed using the statistical program R (R Core Team 2016) and SPSS (IBM statistics, version 21). Next to the base package of R, the vegan package (Oksanen et al. 2016) was used for most statistics. A standard boxplot was used to depict the variation in water chemistry. Correlations between bryophytes and environmental parameters were tested using a linear model for regression.

Classification of the bryophyte composition was carried out using WinTWIN (Twinspan for windows, version 2.3), for which the species cover was converted from actual percentage of cover to a series of classes (Table 3.1). Data ordination was used to visualise the variance between the different sites. However, the data had to be transformed first, because the presence of null-abundancies distorts ordination based on Euclidean distances (Legendre & Gallagher 2001). To check which transformation suited the data the best, correlation was calculated between the actual Euclidean distances and the transformed Euclidean distances (Legendre & Gallagher 2001). The chord distance transformation (Orloci 1967) proved to be the most suitable for the data.

Redundancy Analysis (RDA) was chosen as ordination method to visualise the variance in occurring bryophyte composition between the different sites. This method allows for sites to be displayed according to their (dis)similarities regarding both bryophyte species composition and water chemistry. In such ordination graphs, sites close to each other represent a higher degree of resemblance than sites far from each other. Bryophyte species explaining variance between sites are graphically displayed using their abbreviated names in the direction in which they explain variance. The chemical parameters explaining variance are displayed as arrows pointing in the direction in which they explain variance. The first axis (x-axis, RDA1) is always the axis on which most of the variance in the data is explained. The second axis (y-axis, RDA2) explains the second most variance in the data.

[5] Attention: *all figures on ortho-phosphate in this report are presented as ortho-P0$_4^{3-}$* *<u>not as ortho-P</u>*.

4 Petrifying spring systems in the study area

4.1 Regional setting of the sampled locations

The locations studied show a range of geological and landscape settings, though eco-hydrologically they have in many ways comparable features except land use.

4.1.1 Geohydrological setting

The water discharging at the petrifying springs in the North western part of South-Limburg has passed a Pleistocene sandy aquifer underlain by calcareous clay of tertiary origin. However the calcareous nature of groundwater is derived from the calcareous rich loess layer covering the Pleistocene aquifer (Smolders et al. 2014; Goossens 2007). Roughly the same geological conditions apply to the Flemish sites of the Haspengouw though more to the west also some outcrops of iron sand stones and limestone are present. In the South eastern part of South-Limburg and the adjoining Belgian Voerstreek water has past the leached residual clay with flints (limestone eluvium) and loamy aquifers of late cretaceous origin (Rooijen 1989). The other Belgian sites, in Wallonia, differ in aquifer from the middle and upper Devonian deposits for sites on both sides of the Meuse valley to eroded calcareous (Jurassic) Luxembourg sandstone deposits in the cuesta landscape of the southernmost sites (Yans et al. 2009). They are underlain by a relatively impervious calcareous layer, which crops out only a few kilometres further to the north. Likely this layer is an important source for calcareous water.

The Luxembourgish springs find their origin also at the impervious base of the early Jurassic deposits of Luxembourg sandstone and the Triassic Keuper mudstones (Geol. Karte BRD 1983; Dabkowski et al. 2015). The French sites have also an aquifer of Jurassic (limestone) deposits covered by residual clay (limestone eluvium).

The petrifying springs in North-Rhein Westphalia near Lienen (Osnabruck) in the north and Leiberg in the south are located in the fringes of the so-called Munsterland Kreide Becken. The springs at Lienen emerge from the Cretaceous limestone on the border of the loamy calcareous morainic material (Saale ice age) in front of it.
In the south near Leiberg the springs emerge from the sandstone and limestone deposits of Cretaceous origin on the boundary with the underlying Carbonic mudstone (slate) deposits (Geol. Karte BRD 1983/2014).

The springs east of Paderborn find their origin in the Triassic limestone and mudstone (Keuper- and Muschelchalk) deposited over underlying low impervious sandstones (Bunter). The calcareous deposits are partly of a dolomitic nature and may contain locally some gypsum. To the north, near Nieheim (202-De-Beb) also some relics of Jurassic limestone are found while also a substantial coverage of loess is present here.

The springs in Saarland find their origin in (dolomitic) limestone deposits (Trias) which are underlain by either the impervious base of the limestone and mudstone (Middle Muschelkalk) and/or low pervious sandstone deposits (Bunter) of early Triassic origin. The limestone deposits are overlain by leached residual clay (limestone eluvium) (Geol. Karte BRD 1983/2014):

4.1.2 Stream discharge and catchment area

All petrifying springs in this study have a perched water table: the spring water emerges on hillsides from an aquifer underlain by an impervious layer. In South-Limburg and abroad usually the aquifer is either covered by a thick calcareous loess layer or by residual clays which makes it a semi confined aquifer.

Stream discharge on the studied sites ranged from 0.03 to 50 l/s. These great differences in stream discharge make clear that the petrifying springs will differ largely in the size of their catchment areas and therefore their potential vulnerability to anthropogenic influences i.e.

agricultural land use. Although all locations are imbedded in forests or forest edges their vulnerability will increase as a result of a lower percentage of natural habitat within their catchment area.
The potential catchment areas of the Dutch and Belgian-Flemish springs consist mainly of intensively used agricultural area. Although the majority of the German and French petrifying springs studied are located in large forests their potential catchment area does often contain a substantial percentage of agricultural land. This is especially the case when stream discharges are high as for instance Tufière de Rolampont (403-Fr-Rol; approx. 50 l/s). The presumed catchment areas of the Belgian-Walloon sites near Virton are dominated by forests, although some springs with high discharge are expected to include some agricultural land as well. The catchments of the springs near the Meuse valley and in Luxemburg include large agricultural areas.

High stream discharge usually contributes to significant travertine precipitation and may even result in large ‘crons’ (Figure 4.2) such as the Dreimühlen fall (219-De-Dmf), Tuffstein bei Buren (217-De-Bur), Cron de Montauban (308-Be-Mon) and Tufière de Rolampont (403-Fr-Rol). Although discharge may be very high with respect to other petrifying springs a substantial part of the spring water is divided widely over the large travertine body. Although some runnels may still have a relatively high discharge a lot of water is dripping and seeping through, stimulating both moss growth and travertine precipitation. This process is much more important because it guarantees the moss cover to remain wet or damp. Basically this is not very different to other springs with a far lower discharge. Thus absolute discharge in itself is not important, but the capacity to maintain the distribution of spring water all over the travertine formation. When seeping of water is redirected or reduced, for whatever reason, a part of the moss cover may dry out whereas in other parts the travertine formation is stimulated again. Such situations were encountered at the crons near Lahage (307 & 308-Be-Lah). However, a significant drop in discharge has a deteriorating effect. It may put a hold to (a part of the) active travertine precipitation.

4.1.3 Altitude and exposition

Site altitude of the investigated sites was about 45-180 m in The Netherlands in the other countries between 100-380 m.

Petrifying springs seem to have a preference for locations with expositions to the south eastern to western sky (59%) over locations with an orientation towards the opposite part of the sky. Nevertheless 41% of the locations did so (Figure 4.1).

Besides, one must keep in mind that locations with large travertine complexes can have multiple orientations. For instance the Dreimühlen fall (219-De-Dmf) is located on the steep west flank of the Ahbach valley (i.e. eastern exposition). The fall is like a petrified wall stretching out in the valley (Figure 4.2). Apart from east facing parts also south and north facing parts are present all with luxuriant growth of mosses. Apparently exposition is not a significant habitat factor.

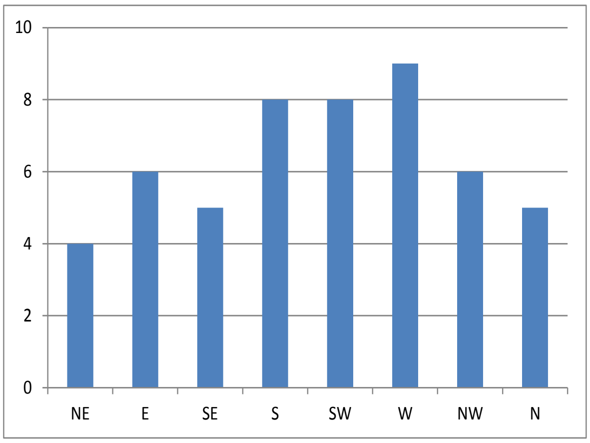


Figure 4.1: General orientation of the petrifying springs (n=51).
Figuur 4.1: Globale expositie van de bemonsterde kalktufbronnen (n=51)

Figure 4.2: Overview of the Dreimühlen fall with its multii facing orientation
Figuur 4.2: Overzicht van de Dreimühlen waterval met zijn meerzijdige exposities.
Foto: © Superbass / CC-BY-SA-4.0 (via Wikimedia Commons)

4.1.4 Shading
All investigated sites are characterized by some degree of shading by tree canopy, since nearly all sites were situated in open deciduous forest or in forest edges. The degree of shading in summer may range between 0% and 90%. Average shading was about 58% but the median value is 70%. Locations with no shading were found near Hillbringen in Germany (Saarland region: 211-De-Hill) and near Blankenheim (Eifel region: 214-De-Bin). Lowest degree in shading in the Netherlands was registered at Putberg (110-NL-Put: 5%). Some locations appeared to have been cleared from shrubs and trees in recent years, like Cron de Montauban (305-Be-Mon) and the Dreimühlen fall (219-De-Dmf).

Further analysis showed no significant relation between relative bryophyte coverage and tree canopy shading. However changes in tree canopy shading may have an effect. Some observations suggest that removing the canopy may affect moisture conditions of the existing bryophyte layer. When water supply is limited as on damp parts a sudden exposure to the sunlight may cause dehydration (see also §4.1.2). On the other hand in nutrient enriched conditions after removal of the tree canopy ruderalisation of the habitat is a serious threat (dominance of nettles) and may supress the bryophyte cover.

4.2 Hydrological types of petrifying springs

In petrifying springs, different forms of travertine precipitation can often be found adjacent to each other in a distinct pattern, depending on the geomorphological and hydrological conditions at the site. As a consequence there is also a distinct vegetation pattern in these petrifying springs that include not only the *Cratoneurion*. Based on both hydro-morphological and ecological characteristics we can distinguish four main types of petrifying systems (PS-Type) in our study area. They are based on the site descriptions of more than 40 sampled locations. Two specific terms we use in the typology below (mini-dams, tufa delta) are explained.

Mini dams

'Mini-dams' can be caused by small tree trunks and branches that have fallen in the alluvial bed, which get calcified in time. This can result in a partly irregular terraced appearance of the alluvial bed.

Tufa delta
In the descriptions we use the term *tufa-delta* frequently. Under a '*tufa-delta*' we understand a travertine sedimentation pattern, containing loosely structured calcified debris (gravel, small twigs etc.) usually coming from upstream parts of the system, although travertine precipitation can still be active here. In the upstream parts usually there is only limited accumulation of organic matter on the tufa-delta. Further downstream (less slope) the organic matter content usually increases and may even dominate in the end.
These deposits are sometimes referred to as (*litho*)*clastic deposits* (Pentecost 2005). However, we also include more paludified parts with a high percentage of organic material to the tufa delta.

PS-Type I: Mostly acrocrene/ rheocrene springs usually imbedded in <u>broad leaf forests</u>
Runnels and brooks (< 1 - 6) l/s) fed from spring(s) emerging on higher grounds with locally moderate to rather strong travertine formation (fluvial crust), sometimes with mini-dams. On small steep ridge(s) active mini-crons or travertine plastered water falls (height <1.5m) can also be present. In the upstream part the alluvial bed is mostly of an erosive nature.

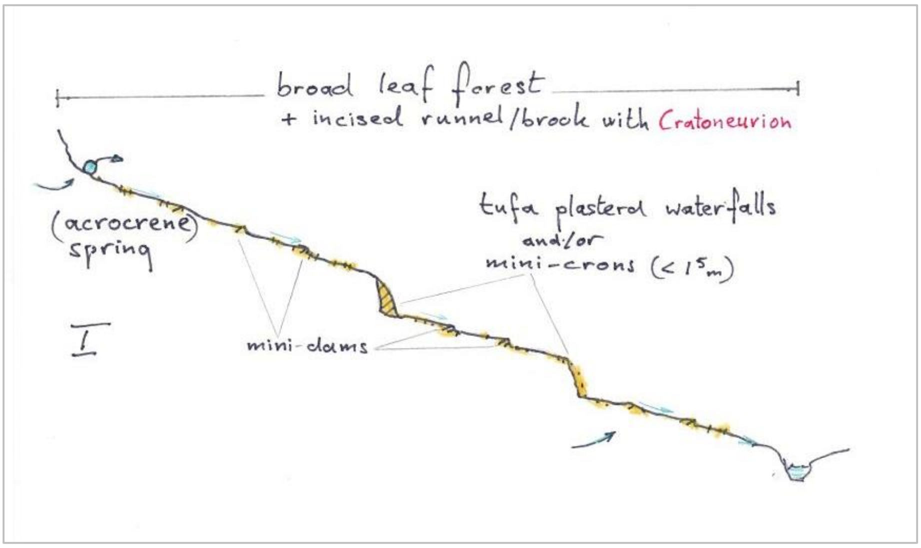


Figure 4.1: Petrifying spring type I (mostly acrocrene springs)
Figuur 4.1: Kalktufbron type I (vooral acrocrene bronnen)

PS-Type II: Helocrene springs *imbedded in <u>spring forests</u> (high org. matter content / peaty)*
Springs runnels and brooks (<1- 9 l/s) with moderate to locally strong travertine formation (*fluvial crust*). A slightly incised erosive bed is followed downstream by a tufa-delta often with mini dams (cascades). Strong erosion is hampered by travertine-plastering of steep ridges (*waterfall*). The alluvial bed has a braided character, mostly with little accumulation of organic matter. However on gentle slopes travertine deposits often alternate with shallow layers with high organic matter content. In the end sedimentation may fill up the alluvial bed to surface level (transition to alluvial forest / spring mire).

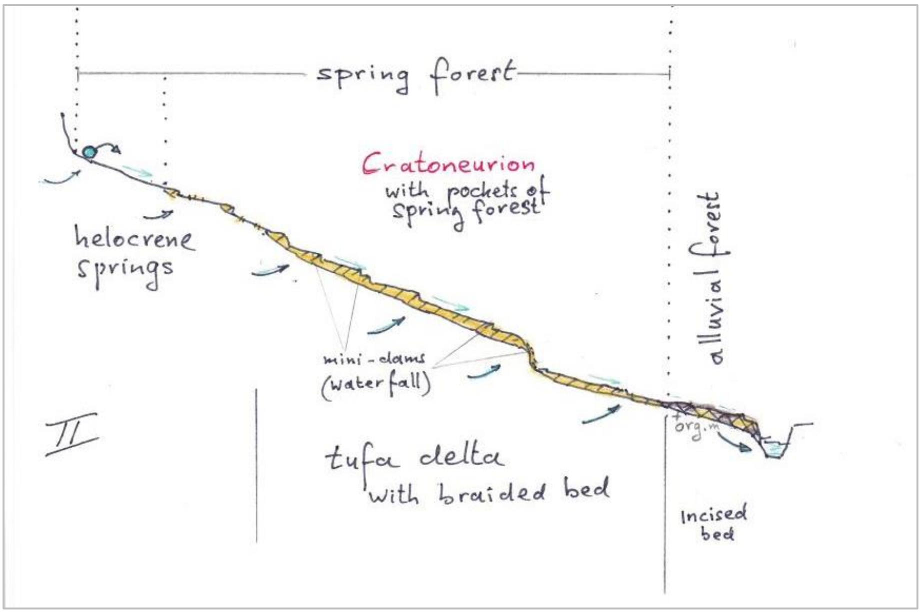


Figure 4.2: Petrifying spring type II (helocrene springs)
Figuur 4.2: Kalktufbron type II (helocrene bronnen)

PS-Type III: Springs with Cron-development

Mostly large springs and brooks (2 - 50 l/s) flowing over a faintly sloping terrace with limited travertine formation, followed by petrified steep slopes (height > 2.5 m), usually with mini-dams and pools (cascade). In optimal form on gentle fringes transitions to alkaline fen, followed by a tufa-delta whether or not overgrown. The lower parts evolve into alluvial forest or spring mire (high org. matter content/ peat). Sometimes even a large part of the cron may reflect close affinity to alkaline fens, like Cron de Montauban 308-Be-Mon (Parant 1973)
In some crons part of the overflowing water infiltrates on its way down the slope.

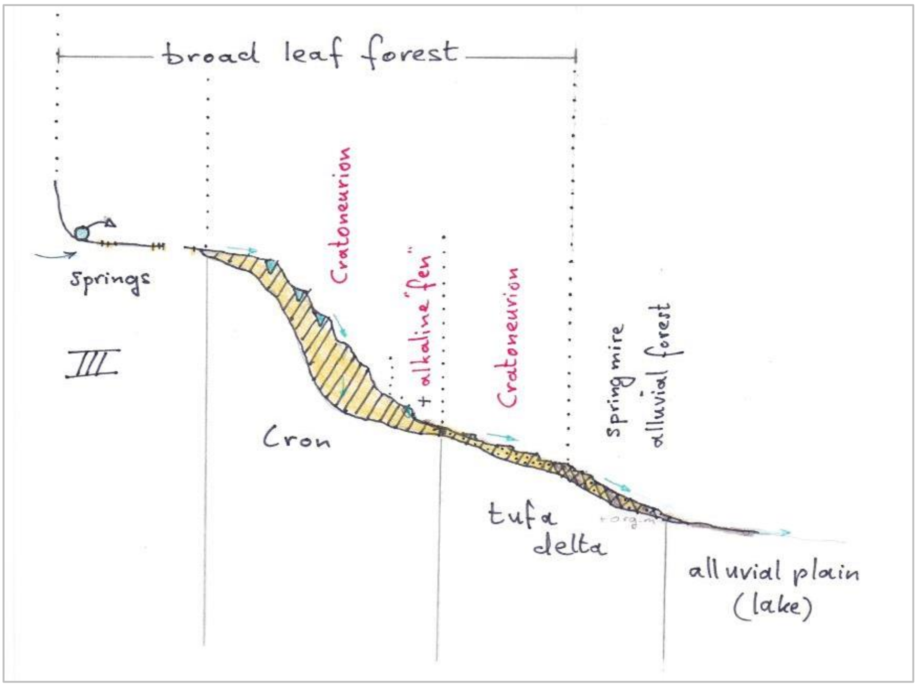


Figure 4.3: Petrifying spring type III (cron development)
Figuur 4.3: Kalktufbron type III (met kalktufkegel ontwikkeling)

PS-Type IV: Calcareous percolating fens and mires:
Mainly large-scale gently sloping mire systems fed by calcareous seepage water. Travertine precipitation occurs in seepages local springs and runnels. The mires often consist of alternating peat and travertine deposits. In places with a large seepage pressure (artesian) travertine / peat domes can arise: so called 'cupola's' *(spring mounds).*
In the initial stages of mire development a large area may be shallowly inundated and fed by a superficially flow of water.

Nowadays this PS-type IV is very rare in Western Europe. In the lowlands it is near to extinct due to drainage and land reclamation. For instance the petrifying springs and runnels near Terhagen (N2000-Bunde and Elsloo Forest) are part of seriously deteriorated calcareous spring mire. The runnels are the relics of the former drainage system (De Mars et al., 2016 ip).

Only in less intensively used parts of the continent, far better examples can be found such as in mountainous areas. Manneville et al., (1999) schematically describe these pristine spring complexes for the Alps (>1000m). During this research project one example of petrifying springs in a small spring mire system was encountered in the Eifel near Blankenheim (214-De-Bin).

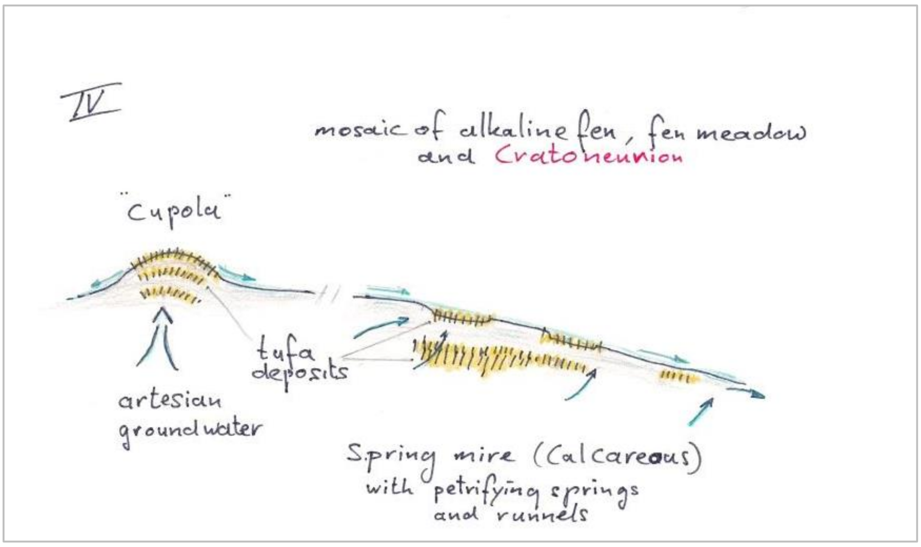


Figure 4.4: Petrifying spring type IV (spring mires)
Figuur 4.4: Kalktufbron type IV (bronvenen)

Probably one of the few examples left in the North-western lowlands of Europe is the well documented spring mire complex of Cors Erddreiniog in Wales. Although slightly drained, the spring mire has kept its high ecological value quite well. This mire is situated in front of a steep ridge of Carboniferous limestone. At the foot of this limestone ridge various active petrifying springs and seepages occur, whereas adjacent in the mire peat alternates with travertine layers (Farr et al. 2014). The alkaline spring mire Torfbroek (Belgium) is another example although travertine formation is only found locally in some runnels and seepages.

Palaeo-ecological research has revealed that this type of spring mire with travertine formation used to be present in other parts of the European lowlands as well. For instance, it was found not far from Maastricht just over the Belgian border in one of the headwater valleys of the river Dijle near the small village of Zammelen. Nowadays, travertine springs are still present here (Diriken 1982; Dreesen & Janssen 1997). Another example of travertine formation in a former mire system was found in the eastern part of South-Limburg near Voerendaal (Janssen 1960).

Thus information on this special type of petrifying springs seems to be very limited. However in Eastern Europe there are still different examples of petrifying springs embedded in spring mire complexes also varying in their degree of disturbance. In Appendix 2, more detailed descriptions are presented on different petrifying systems in Poland and Slovakia both near natural, fairly undisturbed systems as well as more deteriorated systems.

4.3 Bryophyte communities in this study

At all sampling sites the vegetation, with special focus to bryophytes, was described (see 3.2.2) comprising 51 relevees (see also Appendix 6). These relevees were used for further analyses of the moss species composition.

In total 45 moss species were found, of which the five species were frequently recorded also listed for the habitat type in literature; *Palustriella commutata*, *Cratoneuron filicinum*, *Brachythecium rivulare*, *Eucladium verticillatum* and *Pellia endiviifolia (see also Ch. 2.3; Box 2.1)*.

Based on the total moss species composition a cluster analyses (TWINSPAN) was carried out to reveal the variability in bryophyte communities in petrifying springs and to classify the sampled locations. In Figure 4.5 the tree-diagram is presented of bryophyte communities including the differential species.

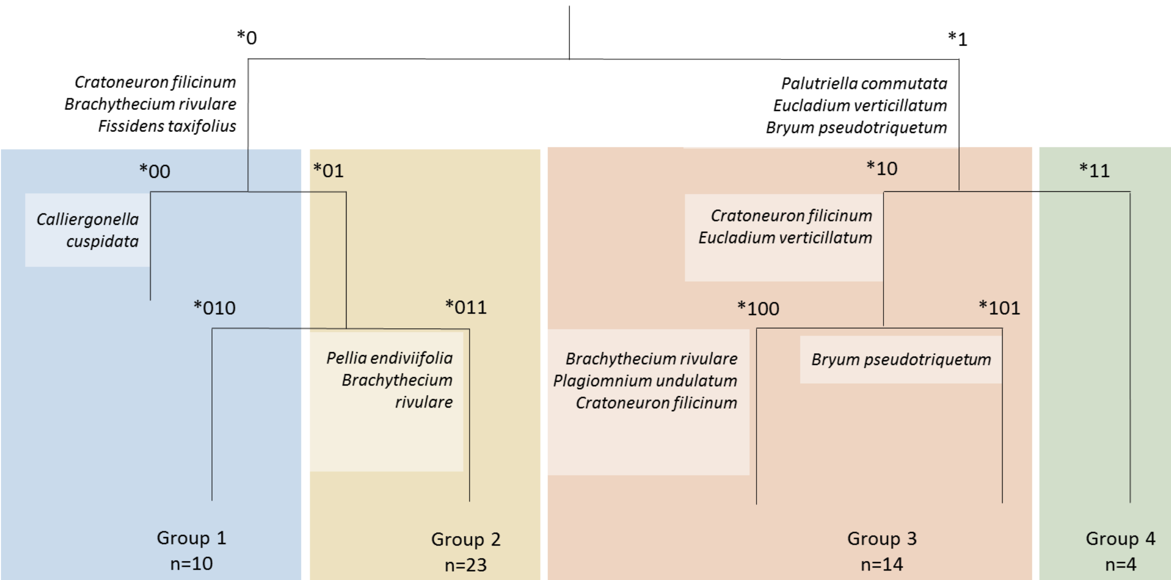


Figure 4.5: Tree diagram of the four distinguished bryophyte communities including their differential species.

Figuur 4.5: Boomdiagram voor de vier onderscheiden mos-typen in kalktufbronnen inclusief differentiërende soorten.

Based on the cluster analyses all sampled locations were classified into four different groups (Group 1 to 4). The TWINSPAN results show a differentiation in *Cratoneuron filicinum* springs (Group 1 and 2) and *Palustriella* springs (Group 3 and 4). The TWINSPAN table is presented in Appendix 6 including the list of locations per group.

- ***Group 1*** is characterised by a high cover of *C. filicinum,* often in combination with *Fissidens taxifolius* and *Brachythecium rivulare,* species like *P. commutata* and *E. verticillatum* are absent or present with a low cover.
- ***Group 2*** is characterised by high cover of *C. filicinum*, often in combination with *B. rivulare* and *P. endiviifolia*. In group 2, species like *P. commutata* and *E. verticillatum* are also absent or present with a low cover.
- ***Group 3*** is characterised by the presence of *P. commutata* and often *E. verticillatum.* In this group *C. filicinum* and *B. rivulare* are sometimes present although with lower cover.

Other moss species like *Palustriella falcata* and *Bryum pseudotriquetrum* are often present on these locations too.

- ***Group 4*** is characterised by a high cover of *P. commutata* and the absence of *C. filicinum* and *E. verticillatum*.

The members of Group 1 and 2 are in view of the bryophyte composition often rather impoverished forms of the habitat type 7220 as the characteristic species like *Palustriella commutata* and *Eucladium verticillatum* are frequently absent.

Group 1 is rather species poor and, apart from *Cratoneuron filicinum*, not particularly characterised by the presence of other characteristic mosses of petrifying springs. Nevertheless, all locations belonging to this group show travertine precipitation. In general, the other groups usually feature the characteristic species of petrifying springs.

It should be noted that the species diversity of some larger travertine complexes was not thoroughly inspected because of the vulnerability of these environments. So some species may be overlooked or may be underestimated there. It is assumed that this had negligible effect on the clustering of results as these species are only likely to occur with a low coverage and/or presence.

5 Water chemistry of petrifying springs

5.1 pH and base cations content

Petrifying springs are described as rather specific habitats fed by calcareous groundwater. However the present study shows a wide diversity in spring water chemistry. Including all detailed information available (i.e. including North West European scientific papers) we see a relatively high pH ranging from 7-8.5 as was expected. However, the differentiation in mineral content of the springs is remarkable. Electrical conductivity varies widely between 375 to over 1000 µS/cm (Figure 5.1a) and is related with the high base cation concentrations (Ca+Mg: 1500 - 6250 µmol/l; Figure 5.1b). Nevertheless all selected springs contain fresh water and derive their water only from calcareous rich deposits. None of these springs are from thermogene origin (volcanic). Highest base cation concentrations are found in The Netherlands (South-Limburg) and to a lesser extend at the Flemish locations. Surprisingly most springs here do not derive their water from limestone aquifers but only from partly calcareous sandy and loamy Pleistocene deposits.

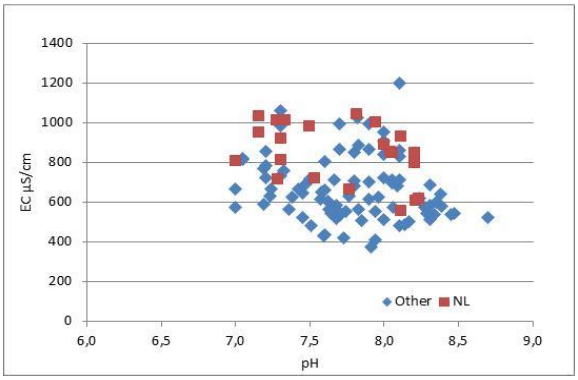


Figure 5.1a: The relationship between conductivity (µS/cm) and pH in spring water of petrifying springs in The Netherlands (NL) and in other parts of North West Europe (n=109)

Figuur 5.1a: Geleibaarheid (µS/cm) in relatie tot de pH van kalktufbronnen in Nederland (NL) en andere delen van Noordwest Europa (n=109)

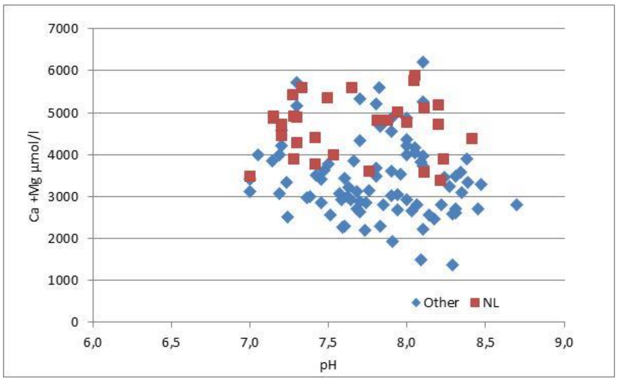


Figure 5.1b: The relationship between Ca + Mg (µmol/l) and pH in spring water of petrifying springs in The Netherlands (NL) and in other parts of North West Europe (n = 117)

Figuur 5.1b: De relatie tussen Ca+Mg (µmol/l) en pH in kalktufbronwater in Nederland (NL) en ander delen van Noordwest Europa (n=117)

5.2 Nutrients in spring water

Further inspection of the dataset on nitrate concentrations (figure 5.2a) revealed that almost all Dutch petrifying springs and to a lesser extend the Flemish locations contain much higher nitrate concentrations in comparison to petrifying springs in other European countries. The data presented below on nitrate concentration in water of petrifying springs are a combination of data from literature and our own field measurements (n=98).

The average nitrate concentration in Dutch petrifying springs is 85 mg/l (1360 µmol/l), versus an average nitrate concentration of about 15-30 mg/l (250-450 µmol/l) in surrounding countries (Figure 5.2). In springs in Belgium, the regions Flanders (Be.Fl) and Wallonia (Be.Wa) are presented separately due to the significant difference in nitrate concentrations. Nitrate concentrations in Wallonia are comparable to other petrifying springs in Germany (De) United Kingdom (UK) France (Fr) and Luxembourg (Lu). However the petrifying springs and seepages in nearly pristine spring mires in Latvia (LV), Slovakia (SL) and Poland (PL) show even lower nitrate concentrations.

A similar pattern appears when looking at the phosphate concentrations in spring water (Figure 5.2b). The data presented below on phosphate concentration in water of petrifying springs are also a combination of data from literature and our own field measurements (n=74). Once again the highest concentrations are found in the petrifying springs in South- Limburg. Only in Germany there appear to be some springs with elevated phosphate concentration.

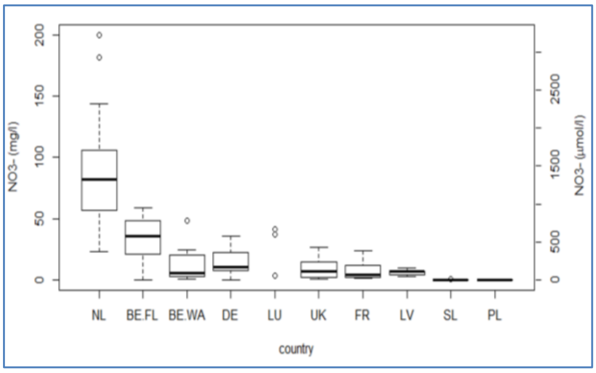


Figure 5.2a: The nitrate concentration in petrifying spring water presented in boxplots per county (n=98).
Number of locations/country: NL=31, BE=32 (BE-FL=20 and BE-WA=12), DE=23, LU=3, UK=12, FR=5, LV=7, SL=10, PL=24.

Figuur 5.2a: Boxplots van het nitraatgehalte in het water van kalktufbronnen per deelgebied/land (n=98)
Aantal locaties per land: NL=31, BE=32 (BE-FL=20 en BE-WA=12), DE=23, LU=3, UK=12, FR=5, LV=7, SL=10, PL=24.

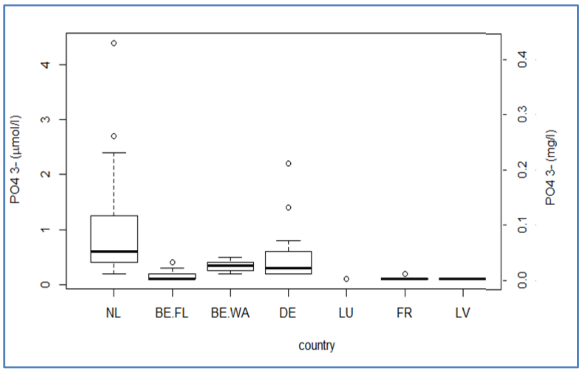


Figure 5.2b: The ortho-phosphate concentration in spring water presented in boxplots per county (n=74)
Number of locations/country: NL=31, BE=32 (of which BE-FL=20 and BE-WA=12), DE=23, LU=3, UK=12, FR=5, LV=7.

Figuur 5.2b. Boxplots van het ortho-fosfaatgehalte in het water van kalktufbronnen(per deelgebied/land (n=74).
Aantal locaties per land: NL=31, BE=32 (waarvan BE-FL=20 en BE-WA=12), DE=23, LU=3, UK=12, FR=5, LV=7

5.3 Base cation concentration in relation to nutrients

If we compare both nutrients with base cation content of spring water, a trend can be observed that petrifying springs in South-Limburg and to a lesser extent Belgium (Flanders) in general have higher calcium + magnesium *and* nitrate concentrations compared to petrifying springs in other European countries. A comparable pattern is found for phosphate. Thus the petrifying springs of South-Limburg (the Netherlands) are not only the most strongly enriched with base-cations but also the strongest nutrient contaminated springs by far compared to springs in other parts of Northwest and Eastern Europe (Figure 5.3a, b).

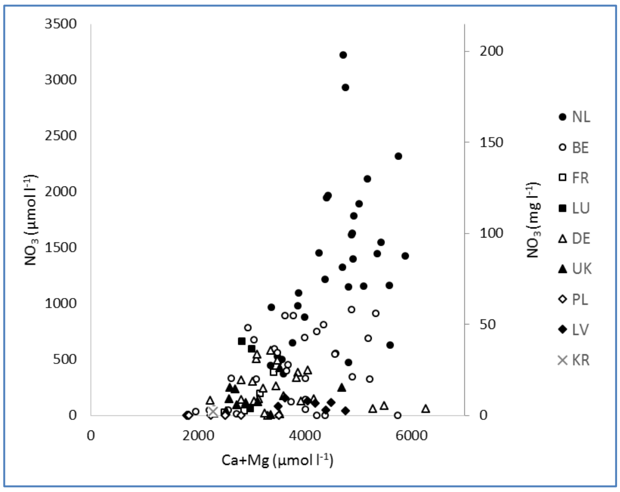


Figure 5.3a: The nitrate (NO_3) concentration against Ca+Mg concentration in water from petrifying springs.

Figuur 5.3a: Nitraatgehalte (NO_3) in relatie tot het Ca+Mg gehalte in bronwater van kalktufbronnen.

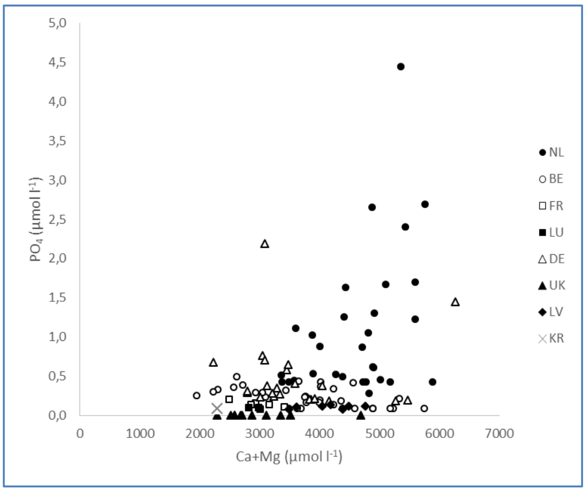


Figure 5.3b: The ortho-phosphate concentration against Ca+Mg concentration in water from petrifying springs.

Figuur 5.3b: Ortho-fosfaat gehalte in relatie tot het Ca+Mg gehalte in bronwater van kalktufbronnen.

5.4 Chemical surface water composition and the occurrence of bryophytes

To study if the chemical composition of the surface water influences the bryophyte composition a Redundancy analysis (RDA) was carried out including both bryophyte composition and the water chemistry of spring water. In Figure 5.4 the result of the redundancy analyses is presented. This was only done for the sampled sites (n=51). Only for these locations there are sufficient data (water quality parameters) matching with vegetation (moss) data and all sampled in a uniform way. The five most frequently represented typical mosses for petrifying springs with tufa formation in the data set (Ch. 4.3) were used for this RDA analysis.

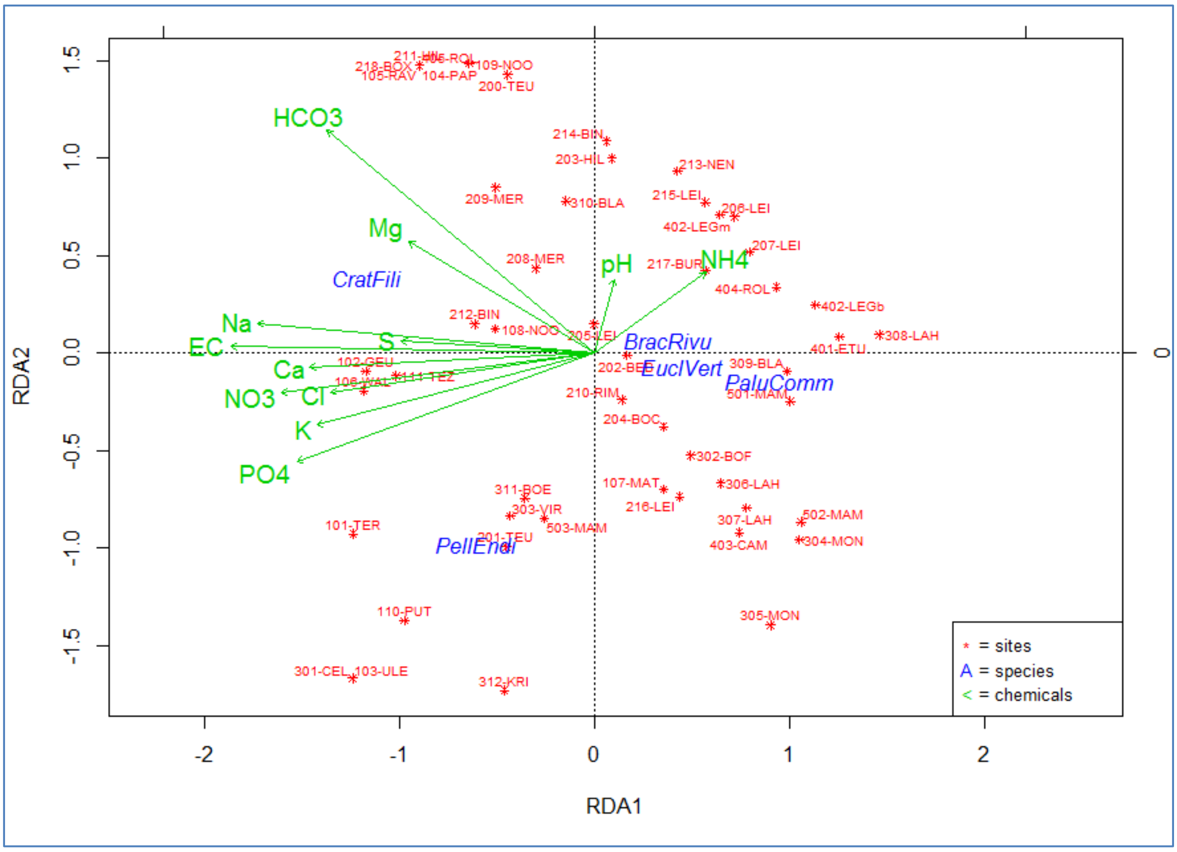


Figure 5.4: RDA analyses of all petrifying springs sampled during this study.
Locations are presented in red with a location code, the five petrifying moss species are presented in blue and chemical parameters are presented in green. The length of the green arrow indicated the amount of the variance in bryophyte composition what the chemical parameter explains.

Figuur 5.4: RDA analyse van alle tijdens deze studie bemonsterde kalktufbronnen.
Locaties in rood; mossoorten in blauw, chemische parameters in groen. De lengte van de pijlen indiceren de mate van variantie in mos samenstelling die wordt verklaard door de waterkwaliteitsparameters.

The first axis explains 28% and the second axis explains 14% for the variation in spring water composition (total 42%). For the variation in bryophyte composition the first axis explains 19% and the second axis explains 7%.

There appears to be a correlation between the chemical parameters calcium, sodium, chloride nitrate phosphate and potassium (Figure 5.4). This bundle of parameters is directed to the negative side of the first axis (left side of the diagram). The length of the arrows indicates joint high concentrations for these parameters at locations plotted on this side of the diagram, whereas lower concentrations are found at locations on the opposite (right) side of the diagram. Except calcium these parameters are all typical pollutants in groundwater. Magnesium and bicarbonate show a somewhat different pattern but indicate also relatively high concentrations on locations in that particular section of the diagram.

The five typical bryophytes used in this analysis show different trends to spring water quality. The presence of *Cratoneuron filicinum* is favoured by high nutrient and (base) cation concentrations. Also *Pellia endiviifolia* seems to be favoured by somewhat more enriched conditions. However *Palustriella commutata* and to a lesser extent *Eucladium verticillatum* and *Bryum rivulare* show the opposite and tend to occur at lower nutrient and base cation concentrations.

A further statistical analysis revealed that the abundancy of *Cratoneuron filicinum* shows a significant positive trend with higher nutrient concentrations, while *Palustriella commutata* shows a significant trend with lower nutrient concentrations (Table 5.1). Under higher nutrient levels this species is only present with a low cover or absent.

Table 5.1: Linear correlation results of the correlation between spring water nitrate concentration and ortho-phosphate concentration and the cover of the five bryophyte species typical for petrifying springs

Tabel 5.1 Toetsingsresultaten van de correlatie tussen nitraat en ortho-fosfaatgehalte in het bronwater en de bedekkingsgraad van vijf typische mossoorten van kalktufbronnen

	NO_3^-		**0rtho-PO_4^{3-}**	
	R^2	**P**	**R^2**	**P**
Cratoneuron filicinum	0.168	**0.003**	0.106	0.02
Palustriella. commutata	-0.166	**0.003**	-0.121	0.012
Bryum rivulare	-0.064	0.073	-0.045	0.135
Eucladium verticillatum	-0.039	0.162	-0.038	0.172
Pellia endiviifolia	0.062	0.079	0.095	0.028

Roughly summarized the majority of the Dutch petrifying springs and some springs in Belgium and Germany are plotted at the left side of the RDA diagram corresponding to *Cratoneuron filicinum* dominated springs related to nutrients enriched conditions and relatively high base cations concentrations (Figure 5.4). At the lower left corner a series of Belgian locations is found and some Dutch springs which correlate with the presence of *Pellia endiviifolia.* On the right side of the diagram however the majority of the *Palustriella commutata* dominated locations in France Luxembourg and a series of German and Belgian (Wallonia) springs can be found related to relatively low concentrations of nutrients and base cations (Figure 5.4).

6 Discussion and Conclusions

6.1: Water chemistry under Nitrate enriched conditions

6.1.1 Nitrate and Ca+ Mg hardness

Part of the samples shows a strong correlation between Ca+Mg *and nitrate* (Ch. 5.2). Most samples from The Netherlands (South Limburg) belong to this group. In fact the petrifying springs in The Netherlands contain the highest nitrate and base-cations concentrations compared to the other springs studied in North Western Europe (Oosterlynck & de Bie 2000; Pentecost & Zahaohui 2002; Pentecost 2005; Arp et al. 2010, Far et al., 2012) The correlation between base cations and nitrate is no coincidence.

Generally there is a correlation found between Ca + Mg and bicarbonate which confirm that calcite ($CaCO_3$) and dolomite ($MgCO_3$) weathering that contributes to Ca, Mg and bicarbonate concentrations in the ground water (box 6.1).

Box 6.1: Dissolution of calcium

$Ca(Mg)CO_{3(s)} + CO_2 + H_2O \rightarrow Ca^{2+}_{(aq)}\ (+\ Mg^{2+}_{(aq)}) + 2HCO_3^-{}_{(aq)}$

The dissolution of calcium carbonate is directly proportional to the partial pressure of CO_2. Normal air contains 300 ppm of CO_2 or in other words, 3×10^{-4} atmospheres of partial pressure. The solution constant for carbon dioxide in equilibrium with air is: $(CO_{2aq})/CO_{2air}$ = 0.034. This results in an CO_2 concentration in rain water of $0.034 \times 3 \times 10^{-4} = 1{,}2 * 10^{-5}$ M = 12 µmol L^{-1}.

In carbonate rich subsurface soils, the water in semi confined aquifers is under a greater pressure and an abundant source of carbon dioxide is readily at hand - as calcium carbonate. As the water is free to pick up carbon dioxide until the water is saturated with CO_2 at a much greater partial pressure, the water can hold much more CO_2 and can also dissolve much more calcium carbonate.

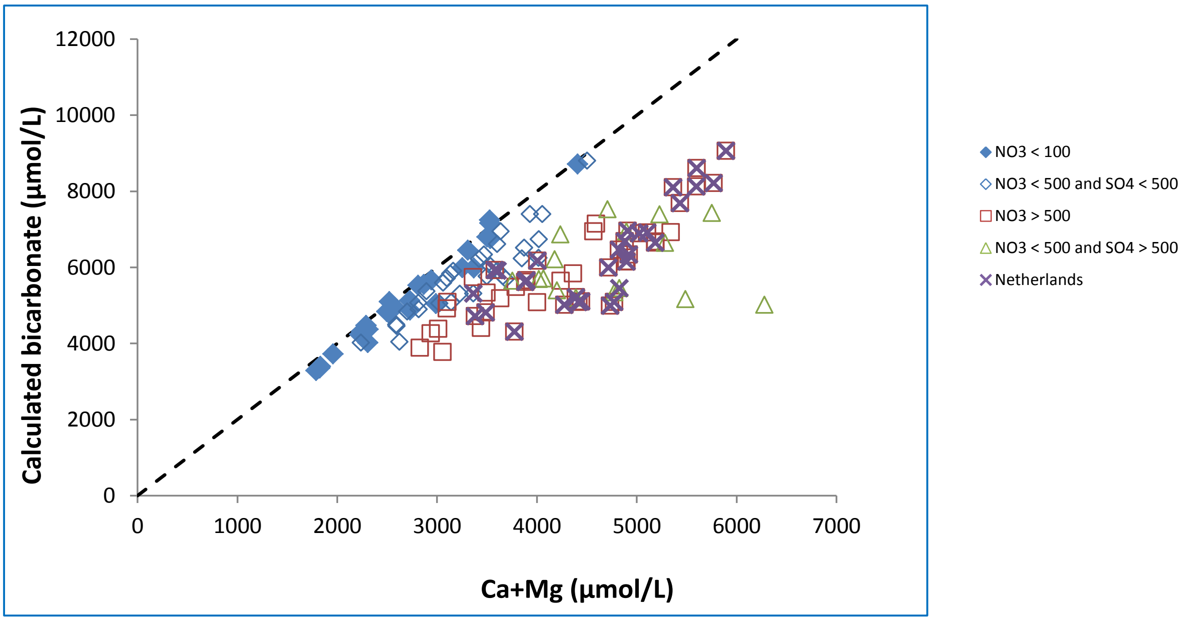


Figure 6.1: Relation between Ca+Mg and bicarbonate concentration for the petrifying springs sampled in this study.

Figuur 6.1: Relatie tussen Ca+Mg en bicarbonaatgehalte in de voor deze studie bemonsterde kalktufbronnen.

However in Figure 6.1 we can see that only in a part of the samples Ca+Mg and HCO_3 show an exact 1:2 ratio which means that for these waters calcium (magnesium) carbonate dissolution in the (sub)soil is probably the main process determining Ca+Mg and HCO_3 concentrations in the samples.

In a large part of the samples, however, the ratio between HCO_3 and Ca+Mg is much lower than 2 indicating that other processes are also responsible for the dissolution of Ca and Mg. For most of these samples nitrate and/or sulphate are present in considerable amounts. Most of these samples originate from South-Limburg (The Netherlands).

In the past century the intensification of agricultural activities and the application of artificial fertilizers have caused a severely disturbed nitrogen balance in agricultural soils. The input of nitrogen exceeds the yield in these systems (e.g. Goodchild 1998; Iversen et al. 1998; Kirchmann et al. 2002). Next, forests which intercept atmospheric nitrogen deposition, may also contribute to increased groundwater nitrate concentrations (e.g. Rothe & Mellert, 2004; Gundersen et al., 2006). Under aerobic soil conditions ammonia and ammonium ions are microbially transformed (nitrified) to nitrate.

$$NH_4^+ + 2\,O_2 \rightarrow NO_3^- + H_2O + 2\,H^+$$

This process generates protons which result in an acidification of the soil. Buffering can be provided by the consumption of alkalinity

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

Dissolution of carbonates such as calcite (or dolomite)

$$CaCO_{3(s)} + H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + HCO^-_{3\,(aq)}$$

or cation exchange reactions

$$]\text{-}Ca^{2+} + 2H^+_{(aq)} \rightarrow\ ]\text{-}2H^+ + Ca^{2+}_{(aq)}$$
$$]\text{-}Mg^{2+} + 2H^+_{(aq)} \rightarrow\ ]\text{-}2H^+ + Mg^{2+}_{(aq)}$$

Eventually all buffering reactions result in the release of Ca+Mg and bicarbonate which explains why Ca+Mg also show a correlation with nitrate in waters which are affected by leakage of nitrate. In poorly reductive aquifers high nitrate and base cation leaching result in nitrate rich groundwater and high base cations concentrations, as is the case for most of the Dutch springs and some of the Belgian-Flemish springs too.

Fertilisers

Apart from the processes mentioned above calcium magnesium and nitrate (also indirectly via ammonium oxidation) are also provided by the application of artificial fertilizers such as $Ca(NO_3)_2$ or $CaNH_4NO_3$. The latter Calcium Ammonium Nitrate (CAN) is the most commonly used N-fertiliser in the European Union, especially North-Western Europe (Sutton et al. 2011). To counteract acidification of the soil and to replenish the soil, Mg is sometimes also added to CAN fertilisers. The excessive amounts of NO_3^- then provide a negative counter charge which promotes concurrent leaching of these cations (Di & Cameron 2004). After leaching through the soil, they will end up in the groundwater (and subsequently in springs) where it thus indicates heavy use of artificial fertilisers. The influence of Mg-fertilisers is also expressed in the proxy value Mg:Ca. In an unpolluted environment without dolomite limestone this proxy value is very low (<<0.25) (Pentecost 2005). Especially the springs in the north western part of South Limburg (around the so called Central Plateau) show increased values of >0.2 pointing to Mg leaching compared to the other springs (Appendix 3).

6.1.2 Sulphate and Iron interactions

In general the reduction capacity of the aquifer soils will determine the extent to which reduction of nitrate may take place which is determined by the availability of sedimentary organic matter (SOM). SOM is a relevant electron donor in anaerobic aquifers controlling the denitrification of nitrate. As a result nitrate concentrations decrease while bicarbonate concentrations increase.

$$4\ NO_3^- + 5\ C_{Organic} \rightarrow 2\ N_2 + 4\ HCO_3^- + H_2CO_3 + 2\ H_2O$$

However this cannot explain why compared to 'clean springs', without nitrate and/or sulphate, the Dutch springs show such high nitrate concentrations (up to max. 3200 μmol/l) which also coincides with a relatively low increase of sulphate (arrow 1 in Figure 6.2). An intermediate group shows nitrate concentrations up to 950 μmol/l concomitant but with a steeper increase of sulphate concentrations (arrow 2 in Figure 6.2).

Iron sulphides (such as pyrite) but also ferrous iron (Straub et al. 1996) and ferrous iron bearing carbonates (such as siderite) turn out to be important electron donors for denitrification in aquifer soils where reactive organic matter is absent (Postma et al. 1991; Aravena & Robertson 1998; Pauwels et al. 1998; Moncaster et al. 2000; Lucassen et al. 2004; Haaijer et al. 2006; Haaijer et al. 2007; Burgin & Hamilton, 2008).

Ferrous iron present in iron carbonate (siderite) may be microbially oxidized by nitrate (Straub et al. 1996; Senn & Hemond 2002). This process results in a decrease of nitrate and an increase of bicarbonate concentrations but not of sulphate.

$$2\ NO_3^- + 10\ FeCO_3 + 14\ H_2O \rightarrow N_2 + 10\ FeOOH + 8\ H_2CO_3 + 2\ HCO_3^-$$

So the geological iron-sulphides and pyrite are important sources of sulphates in (polluted) groundwater. The chemical-lithotrophic oxidation of iron sulphides by nitrate, will lead to a concomitant increase of sulphate and a decrease of nitrate concentrations (Postma et al. 1991; Aravena and Robertson 1998; Pauwels et al. 1998; Moncaster et al. 2000; Broers & Van der Grift 2004; Broers et al. 2004; Van Beek et al. 2006).

$$14\ NO_3^- + 5\ FeS_2 + 4\ H^+ \rightarrow 10\ SO_4^{2-} + 5\ Fe^{2+} + 7\ N_2 + 2\ H_2O$$

$$2\ NO_3^- + 10\ Fe^{2+} + 24\ H_2O \rightarrow 10\ Fe(OH)_3 + N_2 + 18\ H^+$$

Moreover, protons are released which will result in an increase of Ca, Mg and bicarbonate following the acid buffering reactions given above (see §6.1.1).

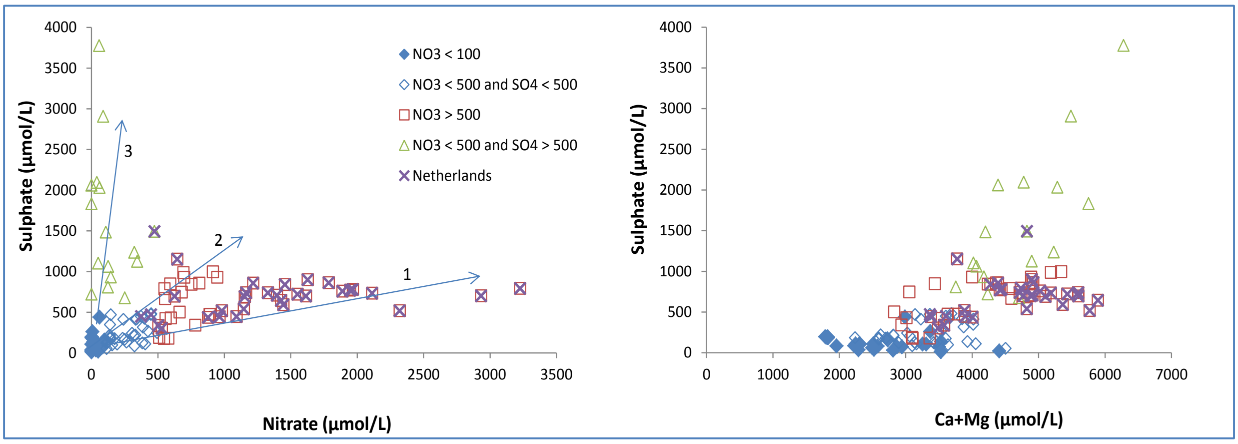


Figure 6.2: Sulphate (µmol/l) in spring water (n=51) in relation to (left) nitrate concentration and (right) Ca+Mg concentration

Figuur 6.2: Sulfaatgehalte (µmol/l) in bronwater (n-51) in relatie tot(links) het nitraatgehalte en (rechts) het Ca+Mg gehalte.

Apparently the availability of iron sulphides or ferrous iron is higher in the second group (along arrow 2) than at the locations along arrow 1. In this second group, to which many of the Flemish samples belong, oxidation of iron sulphides by nitrate in the subsoil might play a more important role than in the petrifying springs in South Limburg (arrow 1).

However, there is still a third group which is characterized by low nitrate concentration and high sulphate concentrations (arrow 3 in Figure 6.2). For this group oxidation of iron sulphides in the subsoil might play a very important role preventing the accumulation of nitrate or, alternatively, these locations are not especially affected by nitrate but by dissolution of gypsum and/or a high leakage of sulphate. Dissolution of gypsum ($CaSO_4$) in the (sub)-soil also results in the release of calcium.

$$CaSO_{4(s)} \rightarrow Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Although in some regions gypsum is a natural constituent of the soil it is usually the result of the application of $(NH_4)_2SO_4$ fertilizers which are especially used on alkaline soils. So nowadays this can result to an increased leakage of sulphate everywhere.

6.1.3 Synthesis

The foregoing described effects of nitrate on ground water chemistry are perfectly displayed by the RDA-graph showing the strong correlation between Ca, Mg, K and PO_4^{3-} concentrations and NO_3^- and S concentrations (Figure 5.4). The main trigger to all this is the high N input due to excessive use of fertilisers (and atmospheric deposition) in the catchment areas. The observed differences in nitrate and sulphate loads can be explained in geological differences especially the presence of iron sandstones or gypsum rich sediments (i.e. dolomite limestones). In the catchment areas of most petrifying springs in South-Limburg pyrite oxidation does not play such an important role in the reduction of the nitrate load in groundwater while natural gypsum deposits are absent here.

A synthesis of the processes described earlier which determine groundwater quality of petrifying springs under N-enriched conditions is presented in Figure 6.3.

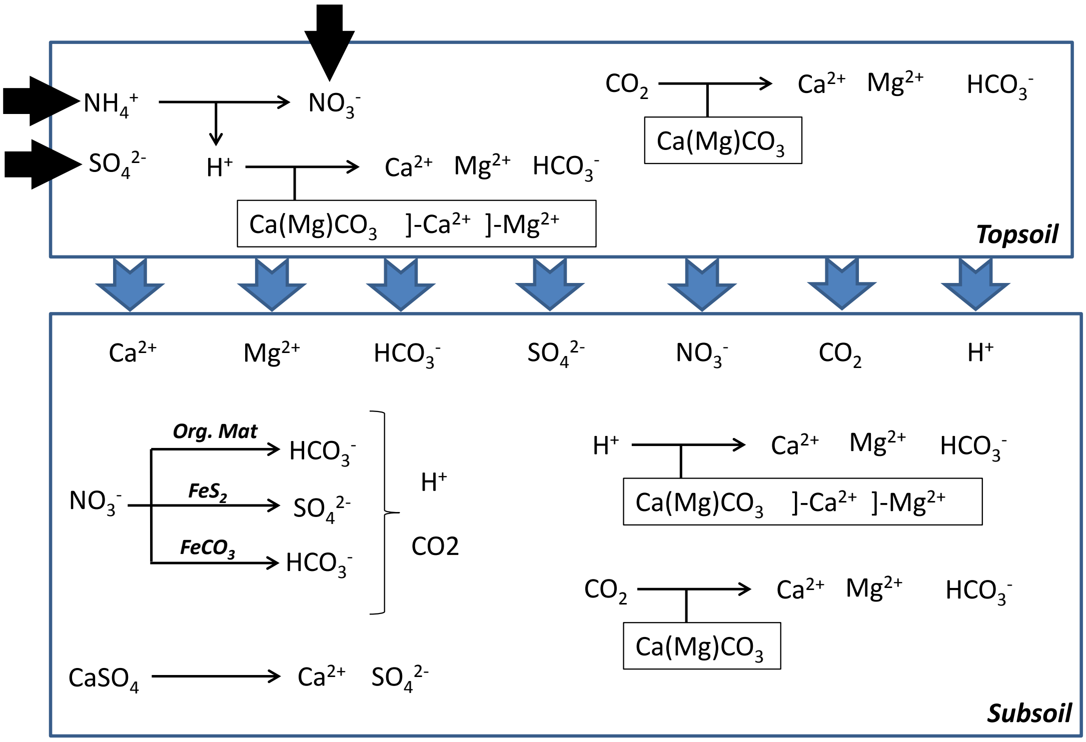


Figure 6.3: Processes determining the water quality of petrifying springs
Figuur 6.3: Bodemchemische processen die de waterkwaliteit voor kalktufbronnen bepalen

6.2 Towards a critical concentration for nutrients in groundwater

6.2.1 Introduction

Defining habitat quality
The role of nitrate as a major pollutant also results into significant changes in water chemistry, among others the strongly increased base cations concentrations.

To determine a critical concentration for nitrate all locations studied and sampled within the present study were classified based on the presence of critical mosses and their cover. Three species were selected to define three different categories based on:

- Typical or characteristic bryophyte species from petrifying springs
- Sensitive species for high nutrient concentrations

Based on the trends between spring water nutrient concentrations and the presence and cover of typical moss species (Ch. 5.4; Figure 5.4, see also §3.2.5) *Palustriella commutata*, *Eucladium verticillatum* and *Brachythecium rivulare* were selected as being most sensitive for high nutrient concentrations in this study.
Based on the criteria listed in Table 6.1 all locations were classified into three categories, poor (impoverished) quality, moderate quality and good quality (see also Appendix 6).

Table 6.1: Criteria for the classification of the quality of petrifying springs, based on critical bryophyte species typical of petrifying springs.

Tabel 6.1: Criteria voor de classificatie van de mosvegetaties in kalktufbronnen op basis van de drie kritische mossen.

Quality class	*Criteria*
Poor	*Absence of the three selected critical moss species*
Moderate	*Presence of one to three of the selected moss species: coverage < 50 %*
Good (reference)	*Presence of one to three of the selected critical moss species: coverage > 50 %*

Threshold values
To define a threshold value from this classification we follow the proven approach from the UK Technical Advisory Group on the Water Frame work Directive (UKTAG, 2012):

- The threshold value must lie below the mean and preferably below the 25^{th} percentile for sites in poor condition.
- The threshold value must lie above the mean and preferably above the 75^{th} percentile for sites in good condition.
- The threshold value must reflect available knowledge from literature and knowledge from within the site research.

6.2.2 Threshold value for Nitrate

The three quality classes are plotted in boxplots for groundwater nitrate concentrations (Figure 6.4). The distribution of the nutrient concentrations within the three quality classes can be used to determine the critical threshold values following the UKTAG method.

Figure 6.4 shows that locations with a poor (impoverished) quality occur over a broad range of nitrate concentrations. The majority of these locations occur under a high nitrate concentration 30-95 mg/l NO_3^-.

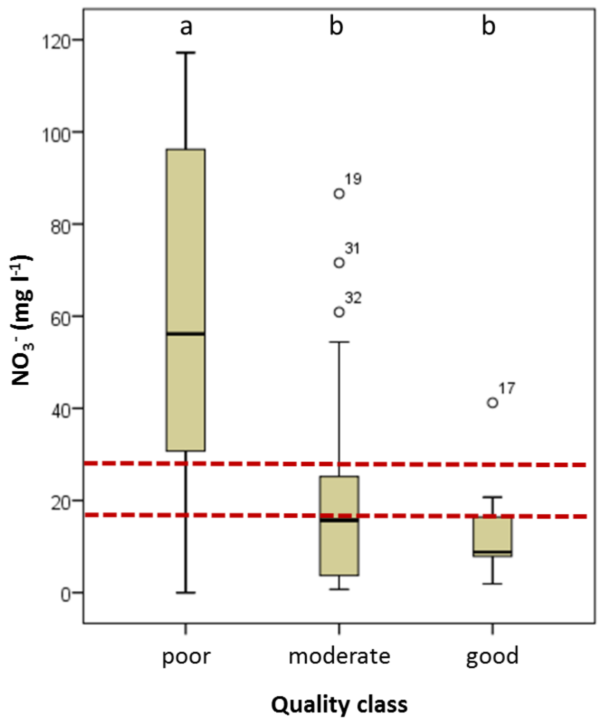


Figure 6.4: Boxplots of the surface water nitrate concentrations for the three quality classes of petrifying springs.

In red the two critical concentrations values are presented. With letters to significant differences between the classes are indicated.

Figuur 6.4: Box plots van het nitraatgehalte in bronwater voor de drie kwaliteitsklassen

In rood zijn de twee kritische concentraties weergeven (zie tekst). Met de letters bovenaan zijn de significante verschillen tussen de klassen aangeven.

Both the locations of moderate quality and of good quality occur under much lower nitrate concentrations. They even significantly differ as classes from the poor group ($P < 0.005$). The mean nitrate concentrations in the groups moderate and good do, however, not differ significantly from one another. However, the moderate group is very likely accounting for a group of petrifying springs already under stress. The 95th percentile of the moderate group is much higher than in the good group. Besides we see some remarkable outliers. While the coverage of the critical species is relatively low.

Following the UKTAG method the threshold (reference) value for nitrate is found at 18 mg/l (288 µmol/l NO_3^-), the lower red line in Figure 6.4. The defined threshold value is quite similar to the threshold value determined by UKTAG (2012) for lowland petrifying springs in the United Kingdom (20 mg/l = 320 µmol/l NO_3^-).

Would we assume that the moderate group could still be categorized as locations with a sufficient habitat quality the threshold value needs to be depicted above the 75th percentile of the moderate class. In that case the threshold value for nitrate could be set at 28 mg/l (450 µmol/l NO_3^-).

6.2.3 Threshold value for Phosphate
As was shown in earlier paragraphs, a correlation was also found between spring water phosphate concentrations and the presence and cover of specific bryophyte species of petrifying springs. Therefore, using the same method critical surface water phosphate concentrations were selected.

Here again significantly higher ortho-phosphate concentrations were found in the poor quality group ($P < 0.005$). Ortho-phosphate concentrations in the quality classes 'moderate' and 'good' do not differ significantly from one another as the ortho-phosphate concentrations in the moderate and good quality group show to a large extend an overlap for both critical concentrations (Figure 6.5).

The critical ortho-phosphate concentration for a good (reference) bryophyte quality is set at 0.04 mg/l (0.42 µmol/l ortho-PO_4^{3-}).

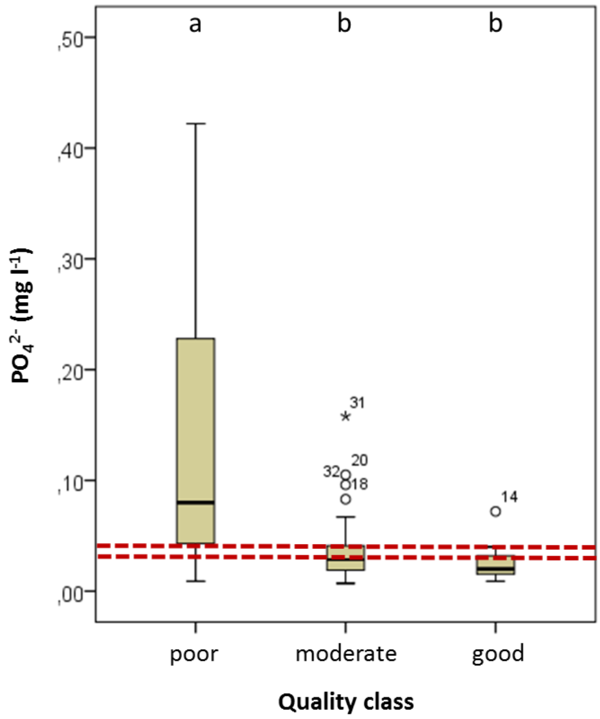


Figure 6.5: Boxplots of the spring water ortho-phosphate (o-PO_4^{3-}) concentrations for the three quality classes of petrifying springs.
In red the two critical concentrations values are presented (see text). With letters the significant differences between the classes are indicated.

Figuur 6.5: Box plots van het ortho-fosfaat gehalte in bronwater voor de drie kwaliteitsklassen
In rood zijn de twee kritische concentraties weergeven (zie tekst). Met de letters bovenaan zijn de significante verschillen tussen de klassen aangeven.

Assuming that the moderate group could still be categorized as locations with a sufficient habitat quality the threshold value of ortho-phosphate must be depicted above the 75th percentile of the moderate group but also below the 25th percentile of the poor group. In that case the threshold value is determined at 0.05 mg/l (0.53 µmol/l ortho-PO_4^{3-}).

6.3 Which threshold value to be used?

From the preceding analysis different threshold values can be deduced. What value should we handle, also with respect to the European Nitrates Directive and the N2000 objectives?

The 'moderate' and ' good' group, are in terms of the nitrate and phosphate levels not significantly different (Figure 6.4 & 6.5). They only differ in their moss coverage, but they significantly differ from the impoverished ‘poor’ group. The 'moderate' and ' good' group must be regarded as the habitat type 7220, bearing in mind the presence of critical mosses of petrifying springs in both groups. This means that the following threshold values for this habitat type can be assigned:
- Ortho-phosphate: **0.05 mg/l** (0.53 µmol/l ortho-PO_4^{3-})
- Nitrate: **28 mg/l** (450 µmol/l NO_3^-).

With regard to nitrate only a few petrifying springs in South Limburg, near Epen, meet this nitrate standard at the moment. The other South Limburg petrifying springs are often a factor of two to four above!

In case locations of the moderate group suffer from high nitrate levels measures should be taken to reduce these levels below 28 mg/l NO_3^- to maintain habitat quality. However, if the objective is to improve habitat quality of this group, the reference value should be aimed at (18 mg/l NO_3^-).

The impoverished group ('poor') is missing the critical moss species. Within this group may *Cratoneuron filicinum* still be present. As previously shown, this species is even stimulated by increasing nitrate levels. Therefor *Cartoneuron* can be considered as negative quality indicator for this habitat type. Because of this negative trend the upper limit of this impoverished group, about 95 mg/l NO_3^-, is not useful. It cannot guarantee the conservation of these already impoverished situations, let alone improve the quality. When it comes to 'conservation' a lower value is a required. In these situations should by aimed at the current standard of the European Nitrates Directive (50 mg/l NO_3^-), a value that also closely matches the average value of this impoverished group.

For the 'moderate' and 'good' qualifying habitats this European standard is not appropriate. As previously argued such situations only occur when nitrate concentrations are lower than 28 mg/l NO_3^-. High nitrate concentrations in these habitats would lead to a decrease in habitat quality, by decline and possible disappearance of critical species, and may result in a dominance of *Cratoneuron filicinum*.

If the target for impoverished locations is the 'improving habitat quality' the threshold value of 28 mg/l NO_3^- is to be aimed at in order to promote the establishment of the more critical moss species.

Table 6.2 Threshold values for nitrate at different N2000-targets (1st instalment) and habitat quality

Natural reference 7220	*18 mg/l* NO_3^-	
Moderate / Good habitat	Preservation: 28 mg/l NO_3^-	Improvement: 18 mg/l NO_3^-
Impoverished (Poor) habitat	Preservation: 50 mg/l NO_3^-*	Improvement: 28 mg/l NO_3^-

*= Requirement European Nitrates Directive

6.4 Conclusions

In North-West Europe the petrifying springs of the Netherlands (South-Limburg) are the most polluted with nitrate and phosphate. Due to nitrate pollution the springs are also significantly enriched with base cations (Ca+Mg). The total hardness of the polluted spring water is higher compared to relatively undisturbed petrifying springs in Europe, even in the limestone areas.

The bryophyte species *Cratoneuron filicinum* is significantly favoured by nitrate eutrophication and base cation enrichment of spring water over *Palustriella commutata*. Also *Brachythecium rivulare* and *Eucladium verticillatum* show a preference to nutrient poor conditions and relatively low base cation content. Although undoubtly a species common to petrifying springs *Cratoneuron filicinum* cannot be considered to be an indicator of good habitat quality. If it is the only characteristic species present it is an indicator of a stressed habitat.

Threshold value for the habitat type 7220 was delimited at 28 mg/l (450 µmol/l NO_3^-) and for phosphate at 0.05 mg/l (0.53 µmol/l ortho-PO_4^{3-}). Above these concentrations the presence of critical mosses of petrifying springs are not likely to be sustainable. The use of this threshold values also depend on the conservation objectives of the different N2000- areas. In case of strongly impoverished situations the nitrate standard of the European Nitrate Directive (50 mg/l NO_3^-) must be achieved at least to prevent further degradation.

One should always keep in mind that the reference value for petrifying springs for nitrate is 18 mg/l NO_3^- and ortho phosphate 0.04 mg/l (0.42 µmol/l ortho-PO_4^{3-}).

The delimited threshold values for nitrate are close to the threshold value of 20 mg/l NO_3^- determined by UKTAG (2012) for the United Kingdom.

Nowadays in the Netherlands the average nitrate concentration in spring water is 85 mg/l (1360 µmol/l NO_3^-) exceeding the nitrate threshold value by far. The least contaminated springs in South-Limburg are found at the Terzieter Springs and the Fröschebron near Epen.

Nitrate pollution may stimulate petrification processes in springs. However the resulting habitat conditions do not support the critical demands of the typical mosses (nutrient poor, low base cation hardness). Reducing intensive fertilisation in South Limburg will not only reduce the nitrate contamination of the ground water but also reduce the leaching of base cations. This will favour mosses in petrifying springs.

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Photo plate 1: Different manifestations of travertine deposits
(photos: H.de Mars)

Fotoplaat 1: Verschillende verschijningsvormen van kalktuf (alle foto's: H. de Mars)

Photo 1a: Fossil travertine (Rolampont, Fr)
Foto 1a: Fossiele kalktuf (Rolampont, Fr)

Photo 1b: Porous structure of fossil travertine in detail.
Foto 1b: Poreuze structuur van fossiel kalktuf in detail

Photo 1c: Fresh travertine deposits on fallen leafs
Foto 1c: Eerste kalktufvorming op afgevallen bladeren

Photo 1d: Encrustation of twigs and Alder fruit
Foto 1d: Verkalkte taken en elzenkatje

Photo 1e: Iron-rich encrustation of mosses
Foto 1e: Verkalkte mossen met ijzerneerslag

Photo 1f: Travertine deposits with purple bacteria on a pebble (Terzieter Springs, Nl).
Foto 1f: Kalktuf afzetting met purper bacteriën op grind

Photo plate 2: Different manifestations of petrifying spring systems
Fotoplaat 2: Verschillende kalktuf vormende bronsystemen

Photo 2a: Cascade with pools (Tufière de Rolampont, Fr)
Foto 2a: Kalktuf-cascade (Tufière de Rolampont, Fr)

Photo 2b: Cascade: (Cron de la Bonne Fontaine, Be)
Foto 2b: Kalktuf-cascade (Cron de la Bonne Fontaine, Be)

Photo 2c: Fluvial crust (Leiberg, D) (Photo Bas v.d. Weijden)
Foto 2c: Fluvatiele korst (Leiberg, D).

Photo 2d: Detail of fluvial crust and a mini dam (Elsloo forest, Nl)
Foto 2d: Detail van fluviatiele korst en een mini-dam (Elslooërbos)

Photo 2e: Detail of a tufa delta (clastic deposits)
Foto 2e: Detail van een *kalktuf-delta*

Photo 2f: Tufa delta in transition to spring fed mire (Fontaine Légère, Fr)
Foto 2f: Overgang van kalktuf-delta naar bronveen

Photo plate 3: Characteristic (bryophyte) species of petrifying springs
Fotoplaat 3: Karakteristieke (mos)soorten van kalktufbronnen

Photo 3a: Palustriella commutata (*Photo Bas v.d. Weijden*)
Foto 3a: Geveerd diknerfmos

Photo 3b: Cratoneuron filicinum *(Photo H. de Mars*)
Foto 3b: Gewoon diknerfmos

Photo 3c: Brachythecium rivulare *(Photo G. van Dijk)*
Foto 3c: Beekdikkopmos

Photo 3d: Eucladium verticilatum *(Photo G. van Dijk)***.**
Foto 3d: Tufmos

Photo 3e: Fissidens taxifolius *(Photo G. van Dijk)*
Foto 3e Kleivedermos

Photo 3f Pellia endiviifolia *(Photo H. de Mars)*
Foto 3f Gekroesde pellia

Photo 3g: Chrysosplenium oppositifolium
Foto 3g: Paarbladig goudveil (Photo G. van Dijk)

Photo plate 4: Some examples of anthropogenic induced encrustations
Fotoplaat 4: Voorbeelden van kalktufvorming onder antropogene invloed

Photo 4a: Travertine deposits on a bottle cap and a chicken bone (Fontaine Légère, Fr) Photo H.de Mars
Foto 4a: Kalktuf op een flessendop en een kippenbotje (Fontaine Légère, Fr Foto H.de Mars

Photo 4b-1: The village water well 'Kaanjel' (Ulestraten, Nl) early 20th century (Erkenbosch 2012 / WRO)
Foto 4b-1: De Kaanjel in Ulestraten begin 20e eeuw
(Erkenbosch, 2012 / WRO)

Photo 4b-2: Present day travertine deposits on the former the village water well 'Kaanjel' (Ulestraten, Nl)
Photo H.de Mars
Foto 4b-2: Kalktuf afzettingen op de voormalige putplaats van Ulestraten (Kaanjel)
Foto: H. de Mars

Photo 4c: Artificial discharge with travertine deposit fed by drip water (Mamertal, Lux): Photo H.de Mars
Foto 4c: Kunstmatige bron met travertijn vorming door spatwater (Mamertal, Lux:) Foto H.de Mars

Photo 4d: Petrifying bath tub, a former water hole for cattle (Merzig-Saarland, Germany). *Photo: G. van Dijk*
Foto 4d: Verkalkende badkuip. een voormalige drinkplaats (Merzig-Saarland, Germany): *Foto: G. van Dijk*

Appendix 1: An example of the checklists for petrifying springs

Voorbeeld van het opnameformulier voor kalktufbronnen

Dreimühlen wasserfall / Nohner wasserfall			***219 - De - DMF***
site code (+village): ***Nohn - Nohnermuhle***			
coordinates x;y	**N. 50.19.28.74 E 6.46.8.05**		
date, time	***20-7-2015***	**EC (µS/cm)**	***628***
temperature (°C)	***8,7***	**alkalinity**	***5,9 meq/l***
flow rate (l/s)	***est. 3 l/s***	**pH**	***7,38***
exposure (N,E,S,W)	***East***	**shade %**	***5%***
tufa forming (1-5)	***5***	**tufa type**	***cron***
distance to source	***?***	**soil**	***loam***
tufa forming length	*>50m*	**DOM**	*<1%*
forest/fen type	*vochtig hellingbos en kapvlakte met veel Moesdistel (Cirsium oleraceum).*		
(historical) land use	*aan voet van vm spoorweg, thans fietspad.*		
visible stress	*Betreding vnl aan de voet van de waterval, Omstreeks 1985/6 nog verstevigd, vanwege verzakking kalktufmassief. Zeer recent ontbost.*		
remarks	*Waterval circa 8m hoog bestaande uit twee kalktuftrappen; Beek komt uit bovengelegen moerasbos met kalktuf en kalkmoerassoorten*		
total cover (%)	95%	**total moss (%)**	95%
Palustriella commutata (geveerd diknerfmos)		*80%*	
Cratoneuron filicinum (gewoon diknerfmos)			
Brachythecium rivulare (beekdikkopmos)		*15%*	*(incl. Bryum pseudotriquetrum)*
Eucladium verticillatum (tufmos)			
Pellia endiviifolia (gekroesd plakkaatmos)		+	
Fissidens taxifolius (Kleivedermos)			
Chrysosplenium oppositifolium (paarbladig goudveil)			
Chrysosplenium alternifolium (verspreidbladig goudveil)			
Equisetum telmateia (reuzenpaardenstaart)			
Cardamine amara (bittere veldkers)			
Cardamine pratensis (pinksterbloem)			
Hedera helix (klimop)		*r*	
Urtica dioica (grote brandnetel)			
Poa trivialis (ruw beemdgras)		*r*	
Ranunculus repens (kruipende boterbloem)			
Rubus fruticosus (braam)			
Geranium robertianum (robertskruid)		+	
Eupatorium canabium (koninginnekruid)		*r*	
Berula erecta (kl watereppe)		+	*bovenaan waterval in de beek*
Aneura pinguis (vetmos)		+	
Lysimachia vulgaris (gewone wederik)		*1*	*tientallen plannten*
Mentha cf x rotundifolia (cf witte munt)		*1*	*flinke populatie bovenop kalktufrots/waterval*

Appendix 2: Petrifying springs in mires in Poland and Slovakia

Kalktufbronnen in Poolse en Slowaakse veenmoerassen

A2.1 Petrifying (travertine forming) springs in Poland

A.2.1.1 Introduction

Tufa-forming springs and spring mires fed mires probably had their optimal development in the 18th century in northern Poland. This was the period before massive drainage works were carried out and when the landscape was rather intensely used and large forests were not present. It is likely that in that period actively chalk depositing mires werecommon.

Human-induced change in hydrological conditions (water-level drop, change in direction and intensity of groundwater flow) in the recharge areas always affects the vegetation of groundwater fed mires. It is reflected in the encroachment of woody species, reduction of peat-forming abilities, and in the extreme cases in peat mineralization and invasion of nitrophilous species. In case of abandonment drained mires are rapidly overgrown by willows and trees.

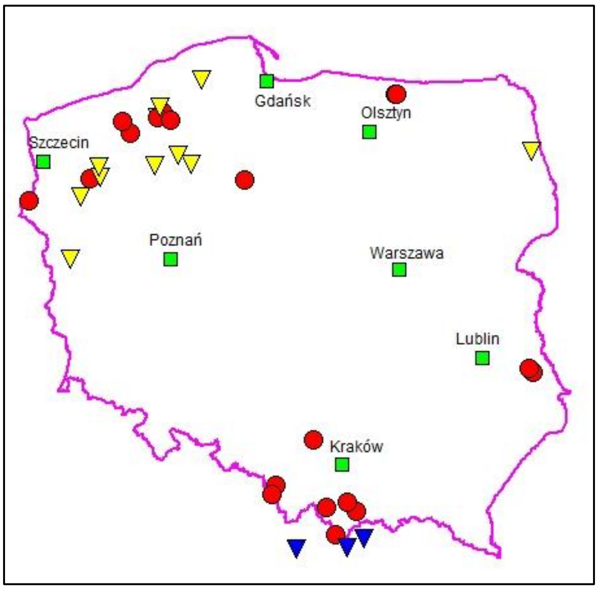


Figure A2.1: Locations of studied petrifying spring sites in Poland (yellow triangles), Slovakia (blue triangles) and sites referred to in literature (red circles). Main cities shown as green squares

Figuur A2.1: Ligging van de onderzochte kalktufbronnen in Polen (gele triangels), Slowakije (blauwe triangels) en locaties waarna in de literatuur wordt verwezen (rode cirkels). Belangrijke steden aangegeven met groene vierkantjes).

The occurrence of petrifying springs is associated with a combination of geologic, hydrogeologic, hydrochemical and geomorphological factors (Pentecost 2005). In the south of Poland the original source of calcium ions in the groundwater are solid carboniferous rocks, while in northern Poland these are the small pieces of rock debris, contained in young-glacial deposits (Wołejko 2004). The precipitation of travertines around groundwater outflows takes place in Europe in areas with an average yearly temperature exceeding 5^{o}C (Pentecost 1995) and is associated with physico-chemical and biochemical processes (Pazdur et al. 2002; Heery 2007).

In general, even in Poland petrifying springs are a very rare ecosystem. In a typical form they occur mainly in southern Poland (Figure A2.2). In the rest of the country they are scattered and usually constitute an element of some wider set of ecosystems, such as hanging mires, spring-mires, alkaline moss-fens, streams and erosion gullies in different types of post-glacial landscapes. Most of the studied areas in that region of Poland contain petrifying springs occurring only as small scale elements of larger ecosystems accumulative in the past, but which have turned to eroded systems in the course of time (Wołejko 2000).

Figure A2.2: In the top left photo a moss facies of *Palustriella commutata* (within the *Cratoneuretum falcati* community) can be seen in the Tatra National Park (photo; Agata Smieja). At the top right a moss dominated *Caricion davallianae* vegetation is shown with open patches, exposing the underlying travertine in the Polish Tatra Mountains (photo: Robert Stanko). Secondary habitats for spring bryophytes (*Preissia quadrata*) in the Diabli Skok nature reserve (lower left; photo A. Szafnagel-Wołejko). A mountain flush with *Eriophorum latifolium* in the Gorce Mountains (lower right; photo Alma Szafnagel-Wołejko.

*Figuur A2.2**:** Foto linksboven; moss facies van Palustriella commutata (onderdeel van de Cratoneuretum falcati community) in het Tatra Nationaal Park (photo; Agata Smieja). Foto rechtsboven; een mos gedomineerde Caricion davallianae vegetatie (kalkmoeras) met open plekken waarin het onderliggende travertijn is blootgelegd (Tatra gebergte, photo: Robert Stanko). Secundair habitat voor typische bronmossen (Preissia quadrata) in het natuurgebied Diabli Skok (foto linksonder; foto A. Szafnagel-Wołejko). Een bronbeek in het Gorce gebergte met Eriophorum latifolium (foto rechtsonder: foto Alma Szafnagel-Wołejko*.

A.2.1.2 Plant communities in Polish N2000 petrifying springs

Plant communities recognized in Poland as phytosociological indicators of petrifying springs *sensu stricte* represent the alliance *Cratoneurion commutati* (belonging to the class of springs' vegetation *Montio-Cardaminetea*) (Wołejko 2000; 2004; Matuszkiewicz 2008; Parusel 2010). The commonly distinguished plant communities include:

(i) *Cratoneuretum falcati* (=*Arabido-Cratoneuretum falcati*),
(ii) (ii) *Cratoneuro-Saxifragetum aizoidis*,
(iii) (iii) *Cratoneuro filicini-Lemnetum trisulcae*,
(iv) (iv) *Pellia endiviaefolia* (=*P. fabbroniana*) comm., and (v) *Cratoneuron commutatum* comm.

The first two of these communities are found only in the mountainous areas of southern Poland, while the other are reported also from the lowlands of northern Poland. In general, the scope and status of alkaline spring vegetation units in Poland is poorly recognized and is a subject of continuous discussion in the scientific literature (e.g. Ratyńska et al. 2010).

The plant communities described above are dominated by bryophyte species, with only a limited number of higher plants, usually originating from the adjacent ecosystems. The prevalence of bryophytes is responsible for the tendency of some authors to include the so-called independent bryophytic communities into this vegetation, such as *Preissia quadrata* sensu (Hübschmann 1986), which originally represents a vegetation class of streaming waters (class *Fontinaletea antipyreticae*).

From the point of view of the Natura 2000 habitat classification petrifying springs (code 7220) are most frequently found in complexes with alkaline fens (7230), chalk mires (7110), alluvial alder woods (91E0) and Molinion meadows (6410). From a system point of view petrifying springs often are an integral part of basiphilous mires or degraded forms of such systems. Basiphilous may or may not deposited tufa on the surface and in time basiphilous mires may shift regularly from tufa (travertine depositing systems into only peat forming systems. In this chapter we will use the term basiphilous mire to describe all ecosystems characterized by abundance of different forms of calcium carbonate and supplied with moving groundwater (Wołejko et al. 2005).

A2.1.3 Basiphilous mires

All basiphilous mires are sloping to some extent (some considerably so), and thus, in the case of concentrated surface flow, are prone to erosion.

Basiphilous fens in Poland occur in three landscape-related geomorphological forms: ***hanging mires*, (*cupola shaped*) *spring mires*** and ***percolating mires***.

Hanging mires

Hanging mires are found on relatively steep slopes in places, where only a shallow layer of peat can accumulate (usually only a layer of gleyey soil is formed). Therefore they are found almost exclusively in the mountainous and sub-mountainous parts of southern Poland. The transitional form between a spring and hanging mire are so called "mountain flushes". These are permanently wet places on mountain slopes, supplied with moving groundwater that reaches the ground surface in a form of non-concentrated seepage water.

The vegetation is usually rich in calcium as the underlying strata often contain limestone or flysh rocks. Impeded outflow of water results in paludification and enables accumulation of shallow peat layers or formation of peaty-gleyey soils (Pawłowski at al. 1960). These weakly peat-forming ecosystems are habitats of the large number of plant species listed among the rarest and most endangered elements of Polish flora (e.g. *Primula farinosa*, the only locality of which in the country is found on the mountain flush in the Beskid Sądecki Mts. (Zaboklicka 1964). Typical floristic elements of petrifying springs are often found in these mires in places of more concentrated outflow. Although considered originally natural ecosystems, mountain flushes expanded in size and numbers as a result of human influence – deforestation of the catchments and consequently increased groundwater supply (Stuchlokowa 1967; Piękoś-Mirkowa & Mirek 1996).

Cupola-shaped spring mires

Cupola-shaped spring mires are found in various topographical situations, where a long-lasting, continuous supply of groundwater occurs. The spring water reaching mire surface is sometimes under a considerable hydraulic pressure. Well-developed spring mires have a distinctive shape, usually resembling a regular cupola or an elongated hill. These structures originate through the alternating or simultaneous accumulation of peat and travertine. The latter is composed mainly of calcium carbonate, but admixtures of magnesium and iron are also commonly found. The largest of these mires – “Spurgle”, found in the north-eastern part of Poland, contains as much as 16 m of travertine dominated deposits (Jasnowski 1964; Łachacz 2000). In the north-western Poland the deepest series of spring deposits with domination of travertine with a depth of ca. 8 m were recorded in the Opatówek mire near Bobolice (Wołejko 2001; Pidek et al. 2012).

The presence of different types of peat, gyttia and travertine give clues to the estimation of the degree of naturalness. Wołejko (2001) studied c. 100 stratigraphic profiles in groundwater-fed mires in NE-Poland, situated in 13 small river valleys. The profiles provided information about the coexistence of so-called percolating mires and spring mires: percolating mires were relatively frequent in the past while typical, travertine-accumulating spring-mires have always been rarer. The most common development started with a spring alder wood, developed directly upon a paludified mineral ground or with a tall sedge communities in case of lake terrestrialization. Further successional stages commonly included the development of tall sedge and small sedge-moss communities, but the return of forest communities has also been observed. The continuous existence of mesotrophic sedge-moss communities to the present times has been found in only 2% of the studied profiles and point to the pronounced human impact on the investigated mires.

In the upland zone of central and southern Poland well developed basiphilous mires of this subtype have formed of extensive cupolas on the slopes of valleys. The discharging groundwater is always close to mire surface. Due to autogenic or human-induced processes in some places groundwater appears at the mire surface in form of springs or small pools, usually collected in cascade-like systems. In such places the most intense precipitation of calcium carbonate takes place, resulting in deposition of travertine layers in peat profile. The vegetation is mostly mesotrophic, but local drainage, both due to natural and anthropogenic reasons, in most cases has led to mineralization of peat and establishment of more eutrophic vegetation types (e.g. tall-sedge vegetation).

(Former) Percolating mires

Percolating mires are practically restricted to northern Poland and peat development usually started at the lower part of slopes of the ice-marginal valleys, river valleys and lake basins. In due time peat development fills virtually the entire valley.

The most prominent percolating mire systems in Poland are found in the Biebrza and Rospuda valleys in NE-Poland. Originally, large complexes of percolating mires filled the valleys of many smaller rivers of northern Poland. At present mires in the Biebrza valley belong to most extensive and the best preserved, not only for Polish standards, but also in the scale of whole central Europe (e.g. Jasnowski 1975, Pałczyński 1975, Herbich 1994, Wołejko 2000).

A2.2 Case studies: Travertine-forming mires in Slovakia and Poland

Between 2002 and 2010 various studies have been done in the framework of two PIN-Matra projects, in which Dutch, Polish and Slovakian Universities and NGO were participating (2002-2004 and 2006-2009). The case studies presented here originate from these two projects, from students report and also from a report which was published after the 10 days excursion of the IMCG in Slovakia and Poland in 2010 (Grootjans et al. 2010).

A2.2.1 Calcareous spring mires in Slovakia

Hajkova & Haject 2003 show that in the region of Machova the deposition of calcite was very much increased in the profile after the cutting of trees in the region this was later confirmed by Hájková et al. (2012) working in the region of Poprad (Belianski Luki; Figure A2.3).

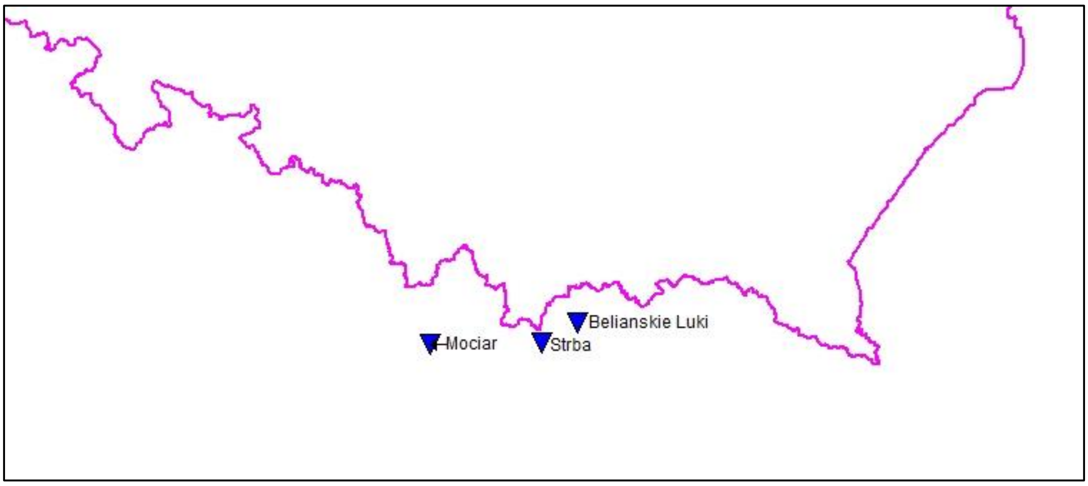


Figure A2.3. Petrifying spring sites studied in Slovakia.
Figuur A2.3. Onderzochte locaties met kalktufbronnen in Slowakije

The nature reserve Močiar

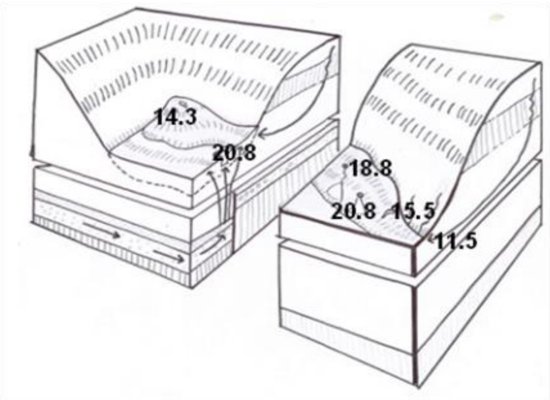
Močiar possesses a unique geological phenomenon, in the form of flat travertine formations (Box A2.1). Along a geological fault, mineralized, hydro-carbonate-sulphate, calcium-magnesium water springs out, in which calcium carbonate coatings are created by sedimentation. We can observe here flat, peaking calcium carbonate formations here, which is rather unique in the West Carpathians. The Močiar Nature Reserve represents the largest travertine spring fen reserve in Slovakia where still active precipitation of calcium carbonate and calcium sulphate takes place. The vegetation is very species-rich and a well-developed. The start of travertine sedimentation in the locality was dated to be more than 10 thousand years ago. The thickness of the sediment is 420 cm (Horsák et al. 2009).

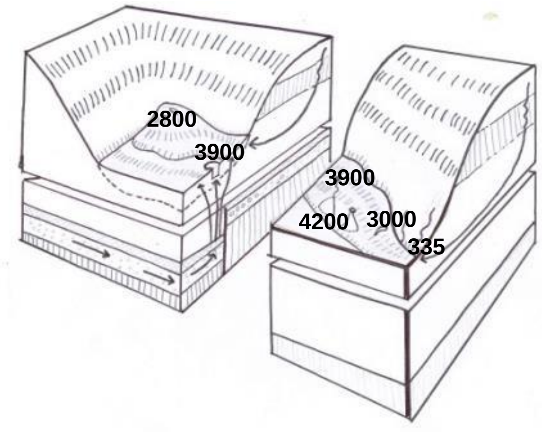
Box A2.1. The origin of the petrifying phenomena at Močiar

There are quite a number of springs in the Nature Reserve Močiar, but some of the discharging groundwater is intercepted and leaves the reserve through artificial bore holes. Travertine precipitates in the surroundings of springs and bore holes, thus creating 'shields' of travertine layering, which are flooding by discharging groundwater.

Measurements of temperature (in °C) and electrical conductivity (in µS/cm) depicted in a 3D conceptual ecohydrological model of the Nature Reserve Močiar. The concentrations of dissolved minerals from the springs are ten times higher than normal calcareous groundwater and the temperatures are more than ten degrees higher then groundwater from some ten of meters depths. These measurements suggest the presence of thermal springs in Močiar. Local groundwater from the mountain appears to discharge at the edges of the reserve as well, because temperatures and EC are much lower there.

Left: Iron pipes that bring groundwater to the surface





The vegetation types belong to the habitat types 'calcareous fens' (mainly *Caricion davallianae*). Because the discharging groundwater is very rich in dissolved minerals, in particular calcium, bicarbonate and sulphate, even a number of halophytic species are present in the vegetation. The areas with intensive travertine precipitation are associated with a vegetation type dominated by *Schoenus ferrugineus.* One of the two largest and most vital populations of this species in Slovakia can be found here. Along with it, a number of fen species grow here, such as *Blysmus compressus*, *Carex davalliana, C. dioica, C. distans, C. hostiana, Dactylorhiza incarnata, Eleocharis quinqueflora, Epipactis palustris, Eriophorum latifolium, Equisetum variegatum, Gymnadenia densiflora, Pedicularis palustris, Triglochin palustre* and *Tofieldia calyculata*. Typical fen moss species are *Bryum pseudotriquetrum, Campylium stellatum,* and *Drepanocladus cossonii*.

Štrba fen

The Štrba fen (official name Pastiersko 2) is a small dome shaped mire of approximately 2 hectares, which is fed by calcareous groundwater. It is positioned in the cadastral area of the village of Štrba between two brooklets, bordering the reserve and joining at the western end. Upstream, an agricultural field, used for haymaking, borders the reserve. The fen catchment is bordered by a watershed approximately 1 km upstream to the East.

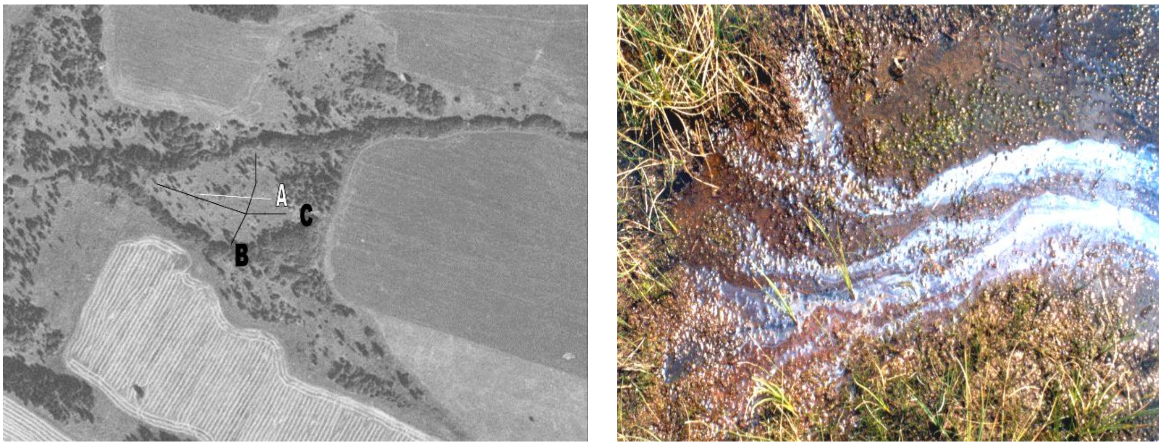


Figure A2.4: Position of transects A, B, C for hydrological observations at Štrba fen (photo left).
The right photo shows that iron rich seepage water is flowing through the small pools.

Figuur A2.4 Ligging van de ecohydrologische onderzoekstransecten A,B,C in het Štrba veen (foto links)
Rechter foto: ijzerhoudend kwelwater stroomt af via kleine geulen en poeltjes

Štrba fen was proposed to be established as the Nature reserve in the end of 70ties, together with two other fens, lying close to each other. The vegetation represents a very well preserved complex of fen communities, which is unique within the Slovak Republic. Many threatened species have been found here: *Dactylorhiza incarnata*, *D. lapponica, Gymnadenia densiflora, Pedicularis palustris, Menyanthes trifoliata*, and *Primula farinosa* (Dítě & Vlčko 2000).

Hydrological system of Strba fen

The hydrological system of Strba Fen has been described by Grootjans et al. (2006), using temperature measurement to indicate groundwater flow (Figure 2.5). The coldest groundwater (less than 10^{o}C) discharges at the top left and more so in the middle of the transect. Warmer water is present at the surface in between the two springs. In more detail we see that the systems of small pools attract groundwater at one side, then this surface water is warmed up and infiltrates again on the other side of the pools (Figure A2.4 and A2.5). In this way relatively warm water is present at the lower end of the system and also between the cold springs.

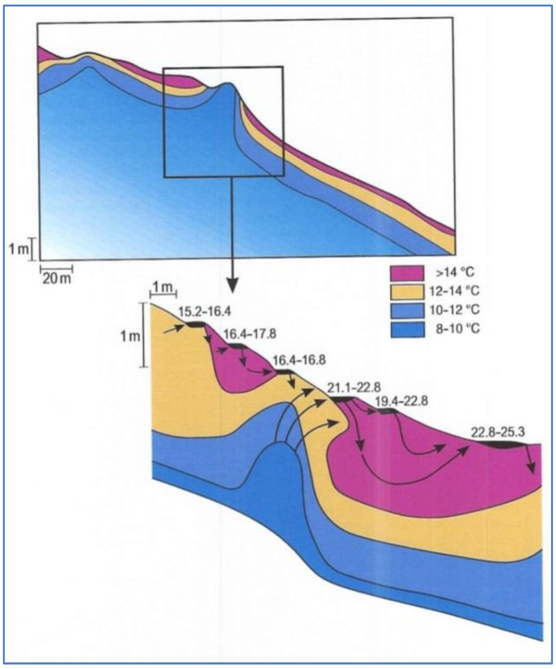


Figure A2.5 Hydrological system of Strba Spring Fen in Slovakia (after Grootjans et al 2006)

Figuur A2.5 Hydrologisch systeem van het Strba bronveen in Slowakije (naar Grootjans et al 2006)

Development of the fen
Based on both morphology and chemical properties of the profiles, we come to some basic conclusions on fen development and hypothesize possible reasons for observed features. Some essential information is missing in the data in particular dating of the horizons and more precise categorization of the origin of accumulated organic material –

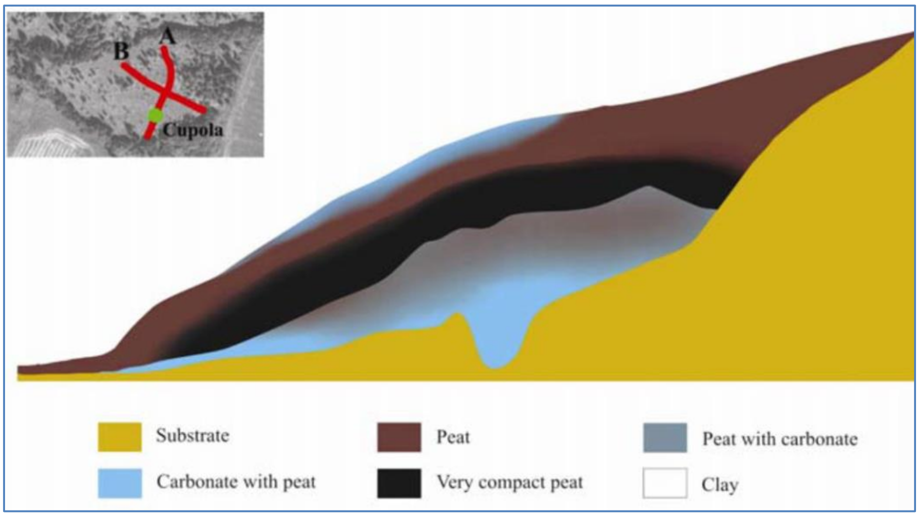


Figure A2.6: Relief of the soil surface and the thickness of the peat en travertine deposits (Maderas et al. 2012).

Figuur A2.6: Maaiveld verloop en dikte van het veen en travertijnafzettingen (Maderas et al. 2012).

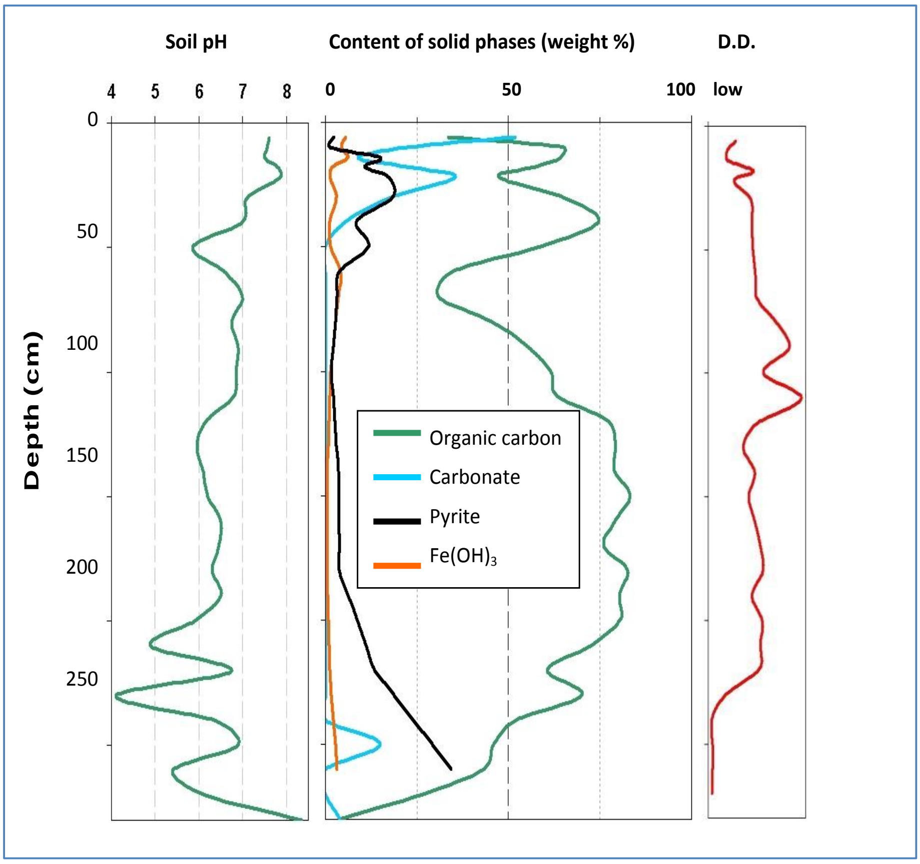


Figure.A2 7: Chemical characteristics of the peat profile C (from Madaras et al. 2012)
(D.D.= degree of organic matter decomposition)

Figuur A2.7: Chemische samenstelling van het veen profile C (Madaras et al. 2012)
(D.D.= decompositiegraad van de organische stof)

The basal parts of the deepest profiles are highly calcareous (Figure A2.6 - A2.7). Layers of almost pure chalk alternate with layers of pure peat. This spring system apparently was very dynamic. Some of the non-calcareous peat layers consisted of strongly decomposed organic matter. A possible explanation of such dynamic changes could be that the spring in the system may regularly change position as a result of hydrological or climate changes. Chalk-forming groundwater may then occasionally not reach the profile site and then peat formation is predominantly influenced by rain water. Further palynological research should prove if we are dealing with so called mixed mires, which are both influenced by ground and precipitation water.

Above the calcareous layered horizon, a very compacted and highly decomposed peat is present (Figure 2.8). The deepest layers were more decomposed then upper ones. The peat was, without exception, non-calcareous and contained remnant of wood, pointing to presence of forest vegetation. Even in the site of the spring cupola the chalk profile was interrupted by an organic layer with a thickness 30 cm. This change can only be explained by a decrease in groundwater pressure. Apparently the groundwater discharge was sufficient for accumulation of organic matter, but not for precipitation of $CaCO_3$.

Higher in the profile in this horizon, non-calcareous brown moss peat is increasingly found toward the surface, pointing to increased wetness and gradual retreat of trees. The presence of calcium carbonate in the top layer of the central parts of the mire, points to intensive activity of the springs. The presence of a compacted layer (forested phase) underneath the upper horizons may be important for the present groundwater movement in the fen, since it functions as an almost impermeable layer for water flow. Groundwater discharging in upper part of the fen is afterwards retained to the upper more permeable parts. This superficial water flow is easily warmed up, which stimulates sulphate reduction. The formation of pools in upper (flat) part of the dome probably also contributes to this heating. Seepage of water hampered by impermeable peat layer and restricted outflow in flat areas leads to very high water levels and long residence times in the soil profile. We hypothesize, that such conditions favour a low REDOX potential and stimulates sulphate reduction, while such a drop in REDOX potential would be not possible if the water flow through peat would be faster. If once – for any reason - small pools of open water have been formed, some – for now unknown – mechanism, leads to the persistence of the pool and its enlargement, preferably in direction perpendicular to the slope (and groundwater flow). Such a mechanism might include: (1) warming up during the summer, (2) precipitation of chalk, (3) anaerobic mineralization of organic matter at the bottom of the pool and (4) accumulation of travertine and organic matter at the sides of the pool. Nowadays, it appears that the activity of wild animals plays also some role in persistence of the pools.

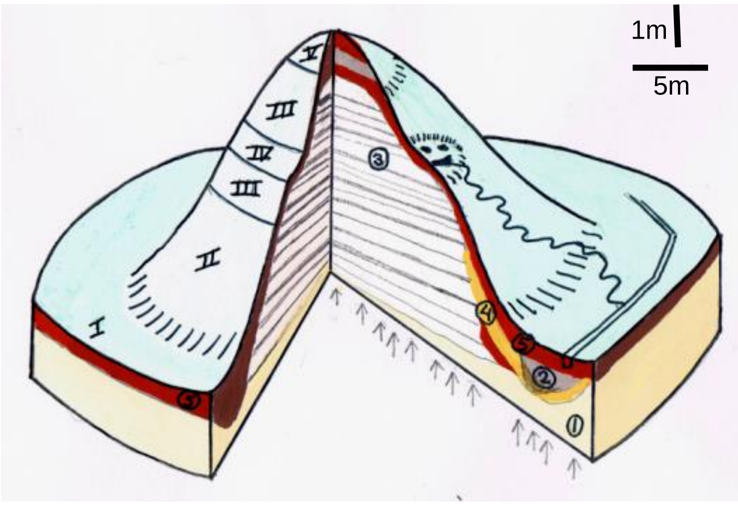
A2.3.2 Cupola-shaped spring mires in Poland

Near the village of Sidra in NE-Poland (Figure A2.8) a very rare type if travertine forming system is present. It is a c. 10 meter high tufa hill with very soft travertine, and with regular occurrence of peat layers. The spring ire is situated I the middle of the valley. It is likely that groundwater is reaching the valley via a geological fault. Drainage in the surrounding area has decreased the groundwater pressure, resulting in a dried out top layer. The groundwater does not leave the system via the top anymore, but escapes at the side of the dome.

A similar spring mound is present in Slovakia (in the region of Spiš (e.g. Sivá brada), near the High Tatra Mountains, but here the peat cover is lacking. Only a decomposed organic layer is covering the travertine hill.

Figure A2.8. Petrifying spring sites studied in northern Poland.
Figuur A2.8. Onderzochte locaties met kalktufbronnen in Noord Poland.

Sidra spring fen
The Sidra spring fen, situated in the upper basin of the Biebrza catchment, near the village of Makowlany, is considered to be the highest known spring fen cupola in Poland (Bitner, 1959, 1961). The cupola consists mainly of travertine (calcium carbonate) and reaches ca. 10 meters above the valley bottom (Figure A2.9). The spring mire complex is relatively small and covers ca. 4 hectares. The cupola hill is a very prominent feature in the local landscape. The thickness of spring fen deposits exceeds 7 meters, including calcium carbonate-rich peat near the surface and more than 4 meters of pure travertine below. The water discharging in the spring system is rich in calcium, magnesium and iron.



1 = sand, 2 = sedge peat, 3 = travertine with peat banding, 4 = brown moss peat, 5 = decomposed peat. The arrows indicate the position of the peat coring (from Grootjans et al. 2011).

Figure A2.9 Spring cupola of Sidra showing banded deposition of travertine ($CaCO_3$) and peat.
The travertine mound is covered by a thin layer of peat, which is degraded at the top of the hill due to escape of groundwater discharge to lower areas.
Figuur A2.9 Kalktuf-koepel van Sidra met zijn afwisselende afzettingen van kalktuf ($CaCO_3$) en veen.
De koepel is bedekt met een dunne veenlaag, die hogerop veraard is als gevolg door de constante afstroming van bronwater naar de lager gelegen delen.

The vegetation of the cupola forms four main zones (Figure A2.9). On top a small forest of *Alnus glutinosa* is present (zone V), which has established itself probably during the 1960ties, after intensive regional drainage. The second vegetation zone consists mainly of *Phragmites australis*, and grows on the upper, steep slopes (zone III). The lower part of the slope is covered by species-rich brown moss-sedge vegetation (zone II), *Carex rostrata* is the most prominent species. Mosses that dominate the vegetation are *Tomentypnum (Homalothecium) nitens* and *Aulacomnium palustre*. Rare species *are Epipactis palustris, Parnassia palustris, Carex dioica* and *Helodium blandowii*. The last zone (zone I) consists of the managed fen meadow with a nice aspect of Cirsium rivulare. Zone IV is part of the *Phragmites* zone, but here spring water is flowing out of the system. It is very wet and the vegetation is almost floating on the water.

Płonia valley
In Płonia valley (NW-Poland) (fossil) cupola-shaped spring mires were found with considerable travertine deposits at the valley flanks, where presently a man-made stream is flowing (Grootjans et al. 2007; Box A2.2). However some part of the peatland travertine was found at the top of the old cupula, indicating that travertine deposition had occurred quite recently. Nowadays the travertine formation has stopped because the mire has been drained and is used as a meadow. At some sites the top soils may contain over 70% $CaCO_3$.

Box A2.2. Travertine deposition in the upper course of Płonia Valley.

Near the small village of Zydowo remnants of fossil travertine forming spring mires and percolation mires have been found. We analyzed the past development of the peat and investigated if chalk deposition had occurred. In the transect shown here lake chalk deposition at the bottom was followed by peat formation in the centre and travertine formation occurred at one or both valley flanks during many centuries. In June 2005 the $CaCO_3$ contents in various depths was determined and it appeared that chalk deposition continued throughout the shift from lake to terrestrial peat. Only few peat samples were without chalk deposition. A very interesting phenomenon is that close to the valley flank travertine deposition increased in time. The highest values were found in the top layer at the right side of the transect. This shows that travertine deposition continued until very recent times.

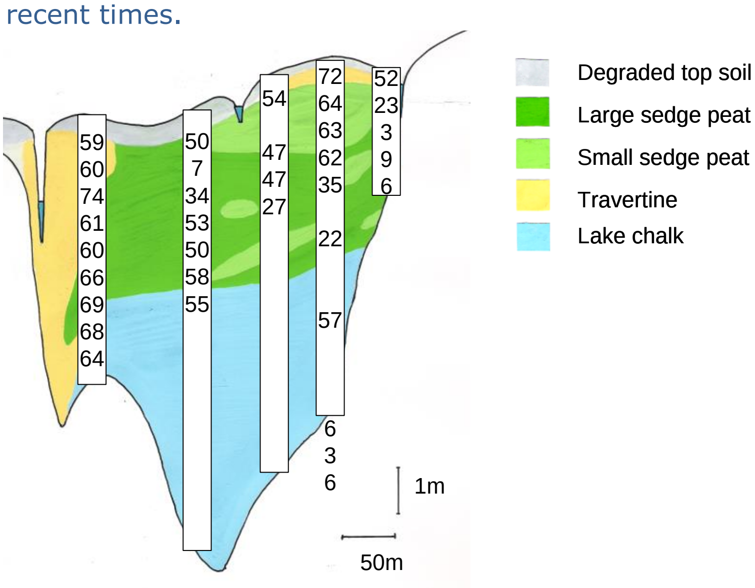


Figure A2.10: Stratigraphic transect from valley flanks to the River Płonia near Barlinek.
Figuur A2.10: Stratigrafisch transect vanaf de valleirand tot aan de Płonia.

The present Płonia River is clearly artificial here since it cuts through travertine deposits at the left hand side which have been present there for centuries (figure A2.10). Eco-hydrological research showed that the groundwater is still under much pressure and that the water is very rich in calcium and also supersaturated. It is certainly not unthinkable that travertine deposition may start again when the local ditches are closed and the (artificial) Płonia stream less deep (Grootjans et al. 2007).

Degraded cupola shaped spring mire in Topiel valley
In northern Poland near the village of Debrzynca, Osadowski et al. (2009) described an old peat system that consisted of a rather classic combination of a cupola-shaped spring mire at the valley flank which was bordered by a more flat percolation mire (Figure A2.11). The system had much in common with the typical example of a spring mire complex (Faulerort) described by Succow (1988).

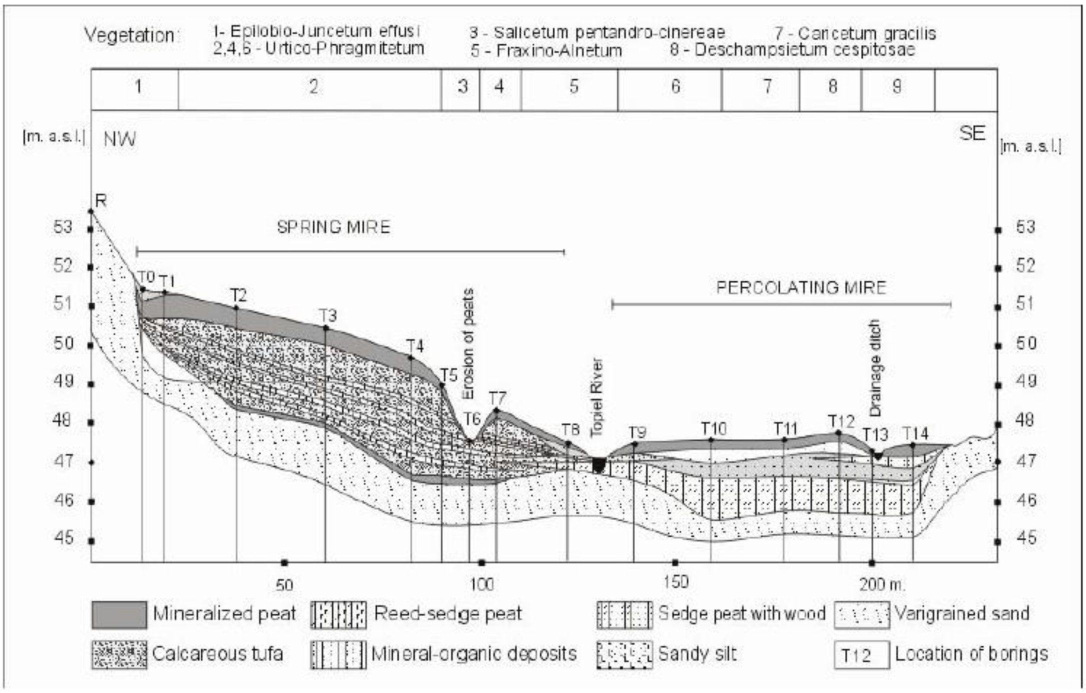


Figure A2.11.Cross-section through the spring mire in Topiel valley (Osadowski et al 2009).
Figuur A2.11: Dwarsdoorsnede van het bronveen in de Topiel vallei (Osadowski et al 2009)

The spring mire part showed numerous bands of travertine, interspaced by peats without travertine deposition, indicating regular changes in hydrology and/or climate conditions. At present the system is severely degraded by drainage channels.

A2.3 Synthesis: The degradation of Travertine-forming spring mires

In the NW-European lowlands the cupola-shaped spring mires have almost all been affected and severely degraded by changes in the hydrology. These systems are very sensitive for relatively local changes in the hydrological systems, such as lowering of water levels or deepening of draining runnels and rivulets. In Eastern Europe spring mires are still quite common as is the occurrence of layers of travertine in the peat. This indicates alternating phases in the formation of travertine and peat over time. These changes are likely related to subtle changes in hydrology under the influence of ever changing climatic conditions (wet and dry periods) over the past few thousand years. However, in historic times anthropogenic influences have resulted in a significant degradation of the mires which can even evolve into a spring complexes.

The possible degradation of spring mires in North Poland in to spring complexes is based on Wołejko (1980) and Grootjans et al. (1999).

The eco-hydrological development and degradation of the spring mire complex Mlanski Lasy in NW-Poland was derived from profile descriptions of the peat layers (Wołejko 1980). The spring mire had developed alongside a lake that was mostly filled with lake chalk. A sloping fen with well preserved (mesotrophic) peat had developed on the slopes and spring cupolas were present higher up at the slope. Here alternating layers of tufa and (degraded) peat were found. Nowadays the whole mire consists of eutrophic alder forest with various eroding spring rivulets. The erosion was probably triggered by lowering of water levels (lake) downstream in the past (Wołejko 1980).

Grootjans et al. (1999) presented even a similar but even more severe case of spring mire degradation. The investigated spring complex (Diably Skok, which means; *Devil's jump*) is situated within a 8 meter deep erosion gorge, where numerous springs are present within a system of cupola's that still develop due to erosion of the sandy hill by intensive discharge of relatively base-rich groundwater (Figure A2.12). Within the spring complex the remnants are present of a large spring mire which have been degraded by active spring rivulets. Parts of the peatland have also been drained in order to make hay meadows.

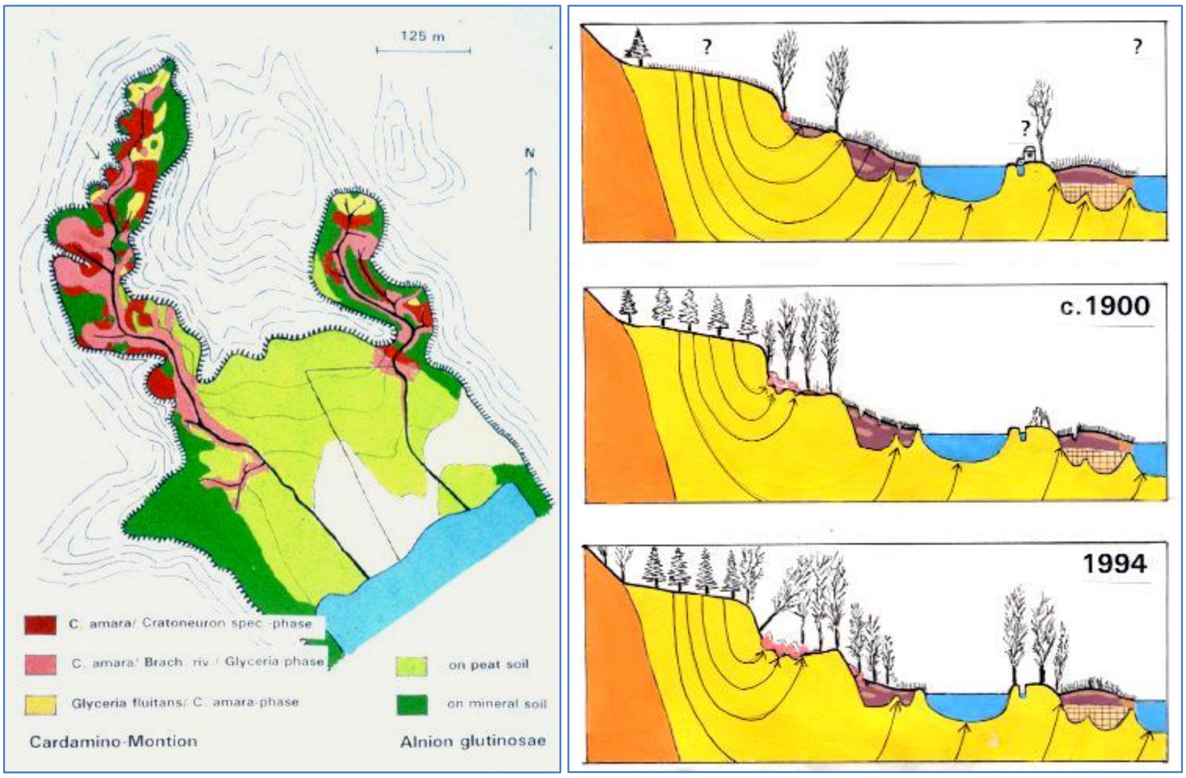


Figure A2.12 Extreme example of past erosion in spring systems is represented in the spring reserve Diably Skok in North Poland (Grootjans et al. 1999).
Lowered lake level has caused enormous erosion upstream of a spring mire that was drained by the eroding rivulets that a large (petrifying) spring complex without any peat.

Figuur A2.12 Een extreem voorbeeld van de aftakeling van een bronveensysteem in het natuurgebied Diably Skok in Noord Polen (Grootjans et al. 1999).
Verlaging van het waterpeil in het aangrenzende meer heeft gezorgd voor terugschrijdende erosie en daarop volgende verdroging van het bronveen, resulterend in een groot (kalktuf)bronnen complex.

Grootjans et al. (1999) presented a reconstruction of possible development of the spring system (Figure A2.12; Figure A2.13). It seems plausible that the erosive spring circuses upstream of the degraded spring mire are much younger than the mire and have most likely developed after an increase in the hydrological gradient, such as the digging of drainage ditches or the lowering of the lake level (which have both occurred). It is also possible that deforestation on the surrounding plateaus has increased groundwater discharge, which could also have contributed to a further destabilization of the spring mire.

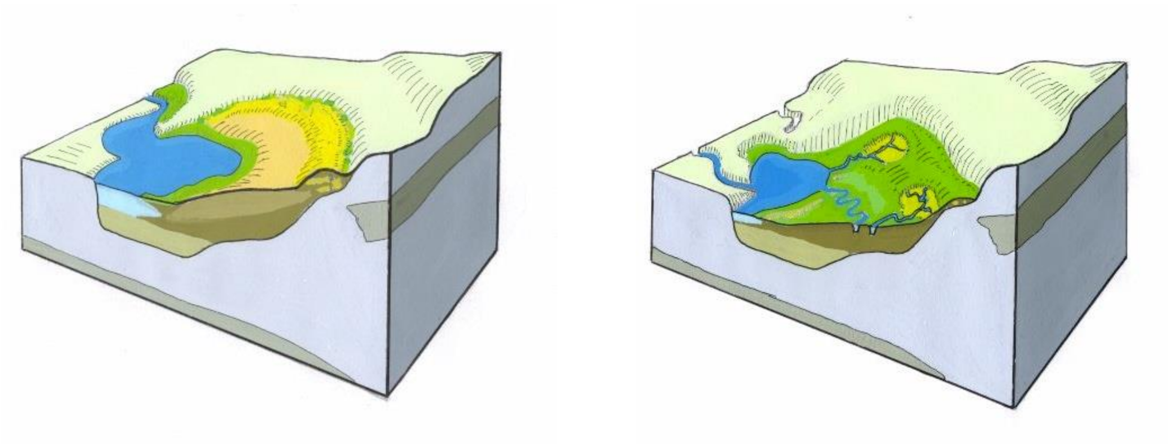


Figure A2.13. Conceptual model of mire development before (l) and after (r) lowering lake water levels in Eastern Europe.

In the lowlands of Eastern Europe lake levels have been lowered already in medieval times. This has led to a severe drop in lake levels (Grootjans et al. 1999). The steeper hydrological gradient cause erosion in the cupola-shaped spring mires (yellow) that had developed next to the lakes. The eroding spring rivulets caused peat degradation and establishment of eutrophic forest types (mainly alder).

Figuur A2.13. Schematisch model voor de bronveen ontwikkeling in het Oost-Europese laagland voor(l) en na (r) de verlaging van waterpeilen in meren in de middeleeuwen (Grootjans et al.1999). Het verlaagde waterpeil zorgde voor een steilere hydrologische gradiënt resulterend in erosie en verdroging van de aangrenzende bronveensystemen (geeloranje). De aftakeling leidde tot de ontwikkeling van eutrafente (bron)bossen.

A2.4 On the origin of some petrifying springs in the Netherlands

Especially in the Netherlands, petrifying springs are seen as local ecological systems. However, from a landscape ecological point of view, they are usually imbedded in a much larger ecohydrological system that usually also involve spring mires or spring forests (*petrifying springs type II*). Such combinations are quite rare in the Netherlands and mostly found in the Noor valley (N2000 Noorbeemden) and in Elsloo Forest (N2000 Bunder- & Elslooërbos). Near Terhagen petrifying springs are associated with relics of calcareous spring mire.

Another tantalizing combination is found in petrifying springs with cron development (type III). In these systems in Belgium (Wallonia), France and Germany, on several sites we found fragments of alkaline fens (*Caricion davallianae*) including various critical fen species such as *Carex flava*, *Carex flacca*, *Orchids* and *Blysmus rufus*.

Paleo-ecological research suggests that in fairly undisturbed environments, the ecological habitats mentioned above may alternate in time (A2.2; Janssen 1960; Diriken 1982; Farr et al. 2014). In some petrifying spring complexes (i.e. Noorbeemden [108 / 109-Nl-Noo], Papenbroek [103-Nl-Pap], Blaimont [308-Be-Bla], Fontaine Légère [402-Fr-Leg]) we noted that tufa-delta’s ceased to exist due to paludification and deposition of organic rich peaty muds whereas the vegetation changed into spring forest or in eutrophic spring mire with tall sedges. In case of the Dutch locations this paludification process is spontaneously and part of a natural restoration of formerly drained situations. The petrifying runnels are no more than former drainage ditches. The foregoing suggests that at least a part of the petrifying springs originate from former spring mires.

However much less is known about the degradation of spring mires in South-Limburg, since cultivation and drainage started already during the Middle Ages. Important information on this matter is found in Janssen (1960) and Diriken (1982) which deal with the late glacial and postglacial vegetation of Dutch and Belgian South Limburg.

Janssen (1960) sampled several peat deposits in the (calcareous) loess part of the Province and also some bogs in less calcareous regions (Leiffenderveen, Brunssummer-heide). He studied pollen profiles, but also described peat profiles. Most of the peatlands had shallow peat layers mostly less than 1 meter. A few had thicker peat deposits, such as the small peatlands near Brommelen (3m), Nuth (2.4 m), Rimburg (1.4 m) and Cortenbach/Voerendaal (ca 3m). Most peat deposits did not show deposition of travertine and they had developed after the large scale cutting of forest on the plateaus. Most of the peat consisted of sedge peat with remnants of alder wood. One peat profile near Cortenbach showed at more than 1 meter deep alternating layers of sedge peat and travertine. This sloping fen showed much resemblance with the spring mire complexes in Eastern Germany (Succow 1988), Poland (Osadowski et al. 2009) and Slovakia (Madaras et al. 2011) (see also Appendix 2). The mire was relatively open (indicating few trees), bordered a lake that had formed calcareous gyttja (= travertine). The mire was on the slopes and also had regular formation of travertine, which alternated with *Phragmites* and sedge peat.

Diriken (1982) and Deersen & Janssen (1997) describe the alluvial deposits in the Mombeek valley near Zammelen. They revealed comparable alternating layers of peatmuds, small sedge peat while travertine was formed during many centuries. A zone with active petrifying seepages is still present bordering the marshy (rewetted) valley floor. The mires alternated in time between alkaline fen (*Caricion davallianae*) into spring forest and eutrophic spring mire. Nowadays willow shrubbery and meso-eutrophic spring forest dominate this site.

Although the findings of Jansen (1960) suggest that travertine formation is quite rare all over South-Limburg we can still find small spring mire relics on the valley flanks which also contain active travertine like at Ravensbos Papenbroek and the earlier mentioned Terhagen. The peat layers here are only 0,5-1 m thick or less (De Mars et al. 2012; 2015; 2016ip). These small mire relics are drained by runnels supporting petrifying springs.

Based on the findings in this research and research on spring mire development in Eastern Germany, Poland and Slovakia we made a reconstruction of the possible spring mire and petrifying spring development and degradation in South-Limburg (Figure A2.14).

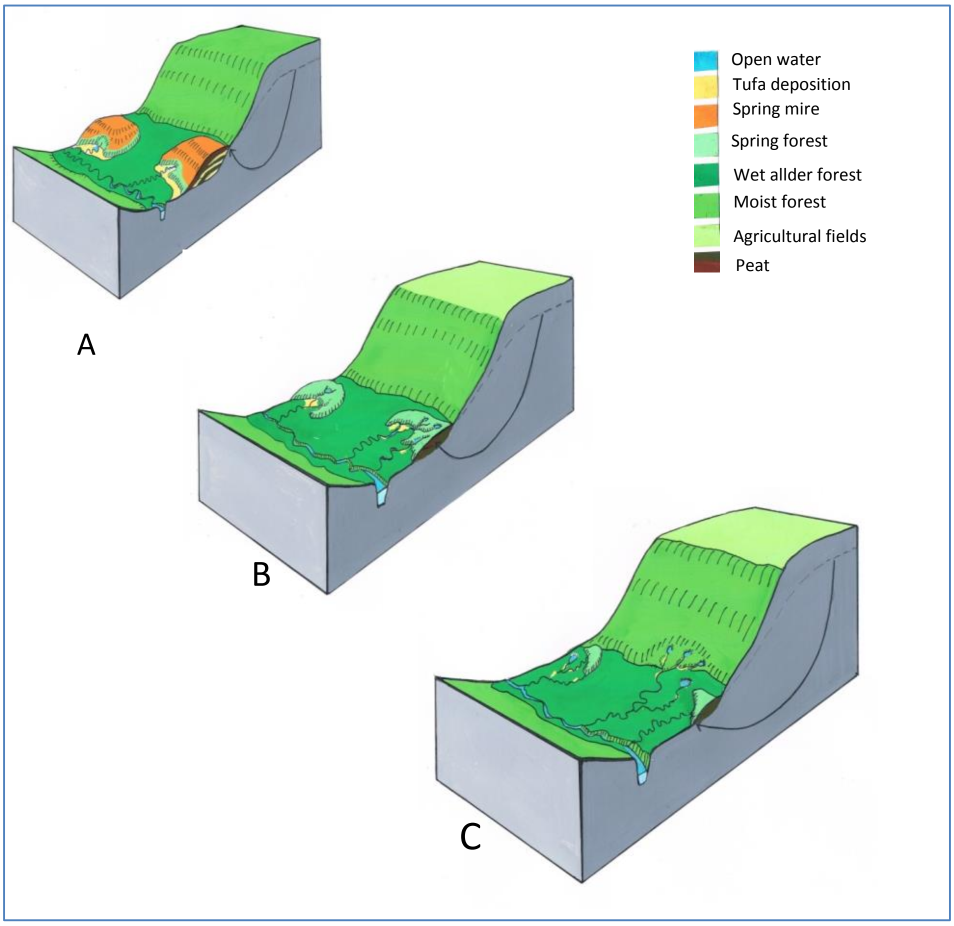


Figure A2.14: Possible reconstruction of the degradation of calcareous spring mires in South Limburg.

*(**a**): undisturbed situation - before cutting of forest on the plateaus with calcareous spring mire and travertine deposition.*
*(**b**): initial deteriorating phase induced by forest cutting, increased drainage and back ward erosion, development of spring forests and petrifying springs with tufa deltas (type2)*
*(**c**): deteriorated situation - strong backward erosion formed spring circuses at a higher position on the slopes and resulted in near disappearance of peat. Only petrifying runnels (type 1) may still be present.*

Figuur A2.14: Conceptueel model voor de aftakeling van kalkrijke bronvenen in Zuid-Limburg.
*(**a**): ongestoorde situatie voor dat bossen op het plateau warden gekapt*
*(**b**): begin stadium aftakeling veroorzaakt door boskap, toegenomen drainage en terugschrijdende erosie: ontwikkeling van kalktufbronnen met tuf delta's (type2)*
*(**c**): Afgetakeld situatie door sterke insnijding door terugschrijdende erosie, vorming van bron-erosienissen hogerop in de hellingen en het nagenoeg verdwijnen van veen. Alleen kalktufbronbeken (type 1) kunnen nog aanwezig zijn.*

Most groundwater fed mires in South-Limburg developed after extensive forest clearing on the plateaus (Janssen 1960). But the degradation of spring mires was also initiated by human interferences, when people changed local hydrology (Figure A2.14b) by digging drainage ditches and triggered erosion. The eroding streams stimulated the degradation of the spring mires and the mineral springs developed when due to backward erosion spring circuses were formed. Most of the spring mires became eroded and drained, leaving only relics of peat deposits (Figure A2.14b-c). Nowadays most spring systems do not have much peat anymore (Figure A2.14c). Springs are more common than in the past and travertine is mostly deposited in runnels and brooks that are fed by the springs. The described Petrifying spring type II (Ch. 4.2) embedded in organic rich spring forests may well reflect this phase.

A2.5 Restoration former spring mires: a multiple challenge

Earlier we argued that petrifying springs of PS-type II are very likely relics of formerly alkaline, mesotrophic spring mires. Restoration of hydrological conditions is possible by reducing drainage. Sometimes this may occur spontaneously for a part due to paludification of former small drainage ditches as was seen for instance in the Noorbeemden spring forests and near Zammelen on a local scale. This is only a first step. Restoration of deeply incised backward erosion gullies is the first real challenge in restoration of the hydrological conditions. This is necessary to stop the slow deterioration process and to enlarge spring forests again. Eventually this will lead to the development of spring mires. The petrifying nature of these systems can be helpful, because of petrification and development of tufa-deltas thanks to damming and tree trunks. Cemented barrages and waterfalls may evolve from it and will reduce or protect against erosion. Examples of this can be seen for instance near Geulle (103-Nl-Geu) and near Virton (303-Be-Vir). Without the cemented waterfall the spring forest behind would not stand a chance.

However, to regenerate spring mires, the built up of a new peat layer is an essential but very delicate process. This is only possible in an environment where:

-sufficient groundwater is available (all year round)
-groundwater quality is good, at least calcareous and nutrient poor.

The threshold values for petrifying springs for nitrate and phosphate cannot be used for peaty/organic rich spring fed habitats like spring forests let alone spring mires. The basic problem is the interaction between nitrate and organic matter. Reduction of nitrate in presence of organic matter results in denitrification of nitrate but at cost of organic material. Under nitrate rich conditions organic matter will be inevitably lost. So under the present conditions peat development is hardly possible. For sustainable restoration of spring mire, the nitrate concentration in groundwater must even be much lower than the earlier determined threshold values. In (fairly) undisturbed alkaline spring mires nitrate concentrations are only 1-5 mg/l NO_3^- (Farr et al. 2014; Grootjans et al. 1999; 2015). Although approximately half of the petrifying springs we sampled (class: good) have nitrate concentrations below 18 mg/l NO_3^- (§ 6.2.2), none of these locations is located in The Netherlands at present. Apparently for regeneration of spring mires substantial lower nitrate concentrations are necessary to start peat development again.

Appendix 3: Water quality of sampled petrifying springs

Waterkwaliteit in de bemonsterde kalktufbronnen

Kalktufbronnen - (OBN 2015-75HE)

Data **:** 1 = own data; 2: data others /literature

C/M **:** 0 =only chemistry; 1 = chemistry & bryophytes available

					sampling	*WGS84*	*WGS84*	altitude	travertine	flow rate	catchment	main	shade	HCO3	**HCO3**	**EGV**	**temp**	**pH**	**Ca**	**Mg**	**Fe**	**Mn**	**Na**	**K**	**Cl**	**S**	**NO_3**	**NH_4**	*ortho* **PO_4**	Si	Al	Zn	***Ca+Mg***	*Mg/Ca*	
					date	*Lat.*	*Long.*	m	class	l/s	ha	exposition	%	mg/l	µmol/l	µS/cm	°C		µmol/l	µmol/l	µmol/l	µmol/l	µmol/l	µmol/l	µmol/l	µmol/l	µmol/l	µmol/l	µmol/l	µmol/l	µmol/l	µmol/l			
Data	*C/M*			*origin of data*							(approx)			(veld)	(veld)	(veld)	(veld)	(veld)																	
1	1	101-NL-TER	NL	OBN-*kalktufbronnen*	18-1-2016	50,94556	5,75692	45	4	0,03	0,4	W	80	390,5	6401,8	1035	10,9	7,15	3914,7	964,61	0,11	0,00	763,1	149,2	970,3	698,8	1615,53	0,78	2,65	247,5	0,0	< 0,01	4879,3	***0,25***	***+antropogenic***
1	1	102-NL-GEU	NL	OBN-*kalktufbronnen*	18-1-2016	50,91809	5,75131	85	4	0,6	7,6	W	80	396,6	6501,8	1047	8,3	7,81	3947,1	875,72	4,70	0,06	982,7	55,4	1991,2	539,8	1147,44	2,10	1,05	232,3	8,9	< 0,01	4822,8	***0,22***	***+antropogenic***
1	1	103-NL-ULE	NL	OBN-*kalktufbronnen*	18-1-2016	50,90307	5,7763	100	5	2	25,3	NW	20	402,7	6601,8	1017	10,5	7,27	4453,6	979,84	0,09	0,02	655,3	30,4	873,6	720,3	1551,15	1,07	2,40	241,5	5,6	< 0,01	5433,4	***0,22***	***+antropogenic***
1	1	104-NL-PAP	NL	OBN-*kalktufbronnen*	18-1-2016	50,90585	5,88975	85	3	0,1	1,3	SE	70	506,4	8302,3	1016	9,7	7,33	4585,8	1015,23	0,75	0,06	729,9	16,9	1321,9	696,9	626,04	0,91	1,23	252,0	0,0	< 0,01	5601,1	***0,22***	***+antropogenic***
1	1	105-NL-RAV	NL	OBN-*kalktufbronnen*	19-1-2016	50,88143	5,82051	120	4	0,12	1,5	NE	80	408,8	6701,8	1007	7,4	7,94	4261,5	762,55	5,21	0,10	971,7	16,3	734,4	757,4	1890,33	1,04	0,45	300,4	10,1	< 0,01	5024,0	***0,18***	***+antropogenic***
1	1	106-NL-WAL	NL	OBN-*kalktufbronnen*	19-1-2016	50,89267	5,77217	115	4	0,1	1,3	SE	90	445,4	7302,0	984	9,5	7,49	4421,2	943,21	0,31	0,00	709,3	13,7	720,2	591,8	1444,86	4,21	4,44	269,2	0,0	< 0,01	5364,4	***0,21***	***+antropogenic***
1	1	107-NL-MAT	NL	OBN-*kalktufbronnen*	20-1-2016	50,93381	5,75416	90	4	0,1	1,3	W	80	396,6	6501,8	934	6,5	8,11	4149,2	954,73	0,22	0,01	582,5	11,3	1344,5	692,5	1154,45	0,34	1,66	240,4	0,0	< 0,01	5103,9	***0,23***	***+antropogenic***
1	1	108-NL-NOO	NL	OBN-*kalktufbronnen*	18-2-2016	50,76571	5,79792	130	3	0,15	1,6	S	90	305,1	5001,4	721	9,0	7,28	3715,1	168,27	1,78	0,07	260,1	23,4	415,1	517,6	982,52	1,33	1,02	469,6	3,1	0,03	3883,3	*0,05*	
1	1	109-NL-NOO	NL	OBN-*kalktufbronnen*	18-2-2016	50,76876	5,80181	130	3	0,15	1,6	S	90	408,8	6701,8	726	9,6	7,53	3842,3	161,56	1,01	0,04	306,9	21,3	410,3	436,2	878,03	0,70	0,87	462,4	1,7	0,04	4003,9	*0,04*	
1	1	110-NL-PUT	NL	OBN-*kalktufbronnen*	5-4-2016	50,85545	5,96631	180	4	0,4	4,2	W	5	396,6	6501,8	954	10,4	7,15	4690,6	218,89	0,22	0,02	407,0	114,0	559,7	710,0	1396,61	2,17	0,61	457,1	0,3	0,02	4909,5	*0,05*	
1	1	111-NL-TEZ	NL	OBN-*kalktufbronnen*	5-4-2016	50,75484	5,90391	165	3	0,8	8,4	NW	80	329,5	5401,5	669	10,9	7,76	3503,0	100,49	0,28	0,01	187,4	18,0	229,9	448,4	373,67	0,74	1,11	453,9	0,8	0,02	3603,5	*0,03*	
1	1	200-DE-TEU	DE	OBN-*kalktufbronnen*	1-3-2016	52,1687	7,91695	131	2	5,3	55,8	S	80	366,1	6001,7	716	9,6	7,66	3752,5	119,75	0,31	0,02	472,3	15,5	692,2	316,2	389,04	1,21	0,20	91,6	0,1	0,02	3872,2	*0,03*	
1	1	201-DE-TEU	DE	OBN-*kalktufbronnen*	1-3-2016	52,15572	7,96273	127	5	47,7	502,1	S	75	353,9	5801,6	685	7,6	8,09	3755,0	93,54	0,44	0,22	338,1	10,5	638,6	416,9	340,68	1,18	0,20	106,1	0,7	0,01	3848,5	*0,02*	
1	1	202-DE-BEB	DE	OBN-*kalktufbronnen*	1-3-2016	51,82347	9,12667	174	4	2	21,1	WWS	60	347,8	5701,6	714	9,2	8,05	2158,9	2018,93	0,32	0,07	184,2	28,4	344,2	932,3	147,29	1,32	0,18	148,8	0,2	0,09	4177,9	***0,94***	***+antropogenic***
1	1	203-DE-HIL	DE	OBN-*kalktufbronnen*	2-3-2016	51,72307	9,00073	332	4	5	52,6	E	40	329,5	5401,5	864	6,4	8,10	4184,1	1100,00	1,01	0,15	416,4	24,1	236,8	2034,3	61,77	2,17	0,18	106,4	0,8	0,04	5284,1	***0,26***	***+antropogenic***
1	1	204-DE-BOC	DE	OBN-*kalktufbronnen*	2-3-2016	51,6238	9,05405	249	5	8,4	88,4	NNE	70	408,8	6701,8	642	8,3	8,38	3278,4	651,44	0,75	0,02	276,7	12,8	346,3	138,5	125,77	1,27	0,21	98,6	2,0	0,06	3929,9	*0,20*	
1	1	205-DE-LEI	DE	OBN-*kalktufbronnen*	2-3-2016	51,5096	8,66035	339	4	15,8	166,3	N/E	75	305,1	5001,4	582	7,1	8,39	3300,9	58,15	0,67	0,10	143,4	10,3	191,6	179,2	578,72	0,68	0,27	121,1	1,1	0,02	3359,0	*0,02*	
1	1	206-DE-LEI	DE	OBN-*kalktufbronnen*	2-3-2016	51,50193	8,65578	347	4	3,5	36,8	NW	50	292,9	4801,3	508	7,6	7,85	2762,0	52,96	0,25	0,05	156,4	15,5	160,8	212,7	319,30	0,76	0,29	116,7	0,2	0,01	2814,9	*0,02*	
1	1	207-DE-LEI	DE	OBN-*kalktufbronnen*	2-3-2016	51,49933	8,64825	333	3	2,5	26,3	W	80	292,9	4801,3	526	7,7	8,70	2762,0	52,06	0,38	0,02	190,6	12,3	194,3	215,8	139,42	0,82	0,30	119,7	0,4	< 0,01	2814,0	*0,02*	
1	1	208-DE-MER	DE	OBN-*kalktufbronnen*	9-3-2016	49,44675	6,7044	361	2	9,4	98,9	SW	40	414,9	6801,9	623	9,1	8,24	2567,4	903,29	0,54	0,05	86,0	22,8	184,2	132,6	264,42	1,69	0,58	102,2	0,5	0,02	3470,7	***0,35***	***dolomite***
1	1	209-DE-MER	DE	OBN-*kalktufbronnen*	9-3-2016	49,45097	6,68038	332	1	0,25	2,6	W	5	396,6	6501,8	539	7,6	8,34	2500,0	1102,47	12,80	3,08	77,5	13,8	155,8	175,2	175,35	1,72	0,40	114,1	18,5	0,09	3602,5	***0,44***	***dolomite***
1	1	210-DE-RIM	DE	OBN-*kalktufbronnen*	9-3-2016	49,47692	6,74047	325	5	41	431,6	WN	80	488,1	8002,2	701	8,3	8,05	2166,7	1888,48	1,55	0,22	152,1	30,4	267,4	110,7	406,62	1,90	0,37	99,0	3,9	< 0,01	4055,1	***0,87***	***+antropogenic***
1	1	211-DE-HIL	DE	OBN-*kalktufbronnen*	9-3-2016	49,43477	6,59925	289	1	0,08	0,8	N	0	414,9	6801,9	546	6,5	8,47	2207,6	1099,59	11,99	1,28	57,2	12,0	20,4	105,2	0,72	1,83	0,34	114,0	35,5	0,10	3307,2	***0,50***	***dolomite?***
1	1	212-DE-BIN	DE	OBN-*kalktufbronnen*	10-3-2016	49,41772	6,71028	291	3	13	136,8	S	20	439,3	7202,0	575	6,7	8,27	2377,7	876,95	0,73	0,19	152,7	10,7	457,7	104,1	17,57	1,84	0,24	87,4	1,3	0,01	3254,7	***0,37***	***dolomite?***
1	1	213-DE-NEN	DE	OBN-*kalktufbronnen*	10-3-2016	49,52455	6,41558	262	1	0,25	2,6	S	90	335,6	5501,5	585	6,2	7,68	1529,4	1611,93	5,60	0,50	462,2	21,8	595,0	469,9	147,51	2,06	0,37	158,5	8,4	0,15	3141,4	***1,05***	***dolomite?***
1	1	214-DE-BIN	DE	OBN-*kalktufbronnen*	10-3-2016	50,4424	6,66198	506	2	0,48	5,1	SW	0	384,4	6301,7	567	8,7	7,63	2976,5	250,00	20,75	5,48	214,8	31,0	327,8	411,3	241,62	1,36	0,28	113,5	19,7	0,20	3226,5	*0,08*	
1	1	215-DE-LEI	DE	OBN-*kalktufbronnen*	30-3-2016	51,50936	8,6444	299	4	4,7	49,5	E	70	311,2	5101,4	484	8,4	8,10	2171,9	65,84	0,56	0,02	138,0	4,2	89,2	185,6	136,19	1,04	0,68	104,4	0,8	< 0,01	2237,7	*0,03*	
1	1	216-DE-LEI	DE	OBN-*kalktufbronnen*	30-3-2016	51,50722	8,6291	324	4	1,07	11,3	W	85	372,2	6101,7	557	7,9	7,94	3001,5	58,11	0,35	0,02	165,6	7,8	157,2	204,6	129,75	0,36	0,76	110,4	0,5	< 0,01	3059,6	*0,02*	
1	1	217-DE-BUR	DE	OBN-*kalktufbronnen*	30-3-2016	51,53702	8,58385	231	5	5,3	55,8	N	40	317,3	5201,4	615	9,3	7,57	3051,4	47,41	0,09	0,02	201,5	14,6	611,2	188,5	509,71	0,44	0,70	105,7	0,1	0,01	3098,8	*0,02*	
1	1	218-DE-BOX	DE	OBN-*kalktufbronnen*	30-3-2016	51,75299	8,12363	111	2	0,1	1,1	SW	90	372,2	6101,7	686	10	8,31	3403,2	95,56	0,68	0,07	312,3	21,5	570,5	249,7	495,39	1,16	0,64	113,0	0,8	0,03	3498,7	*0,03*	
1	1	219-DE-DMF	DE	RHDHV_2015	20-7-2015	50,32444	6,76889	380	5	5	39,4	E	10	359,9	5900,0	628	8,7	7,38	2357,3	667,08	0,45	0,00	242,1	14,6	462,7	241,7	306,08	3,32	0,23	107,0	0,1	0,02	3024,4	***0,28***	***+antropogenic?***
1	1	301 BE-CEL	BE	OBN-*kalktufbronnen*	14-3-2016	50,22875	4,99749	175	2	6,5	58,6	W	90	274,6	4501,2	588	10,7	8,31	2267,7	355,64	0,27	0,01	495,9	9,6	936,3	219,7	331,45	0,87	0,49	151,0	0,7	< 0,01	2623,4	*0,16*	
1	1	302 BE-BOF	BE	OBN-*kalktufbronnen*	14-3-2016	50,17768	4,72491	165	5	5,8	52,3	WNW	30	408,8	6701,8	771	10,1	7,19	3710,1	309,30	0,00	0,00	281,9	8,9	432,5	412,5	333,51	1,28	0,42	161,3	0,1	< 0,01	4019,4	*0,08*	
1	1	303 BE-VIR	BE	OBN-*kalktufbronnen*	16-3-2016	49,59422	5,54791	300	4	0,6	4,7	SW	85	311,2	5101,4	516	5,3	8,31	2659,7	67,94	0,40	0,03	119,7	0,4	99,7	169,2	11,20	1,62	0,38	125,0	0,8	< 0,01	2727,6	*0,03*	
1	1	304 BE-MON	BE	OBN-*kalktufbronnen*	16-3-2016	49,62939	5,5933	325	4	0,3	2,4	S	80	305,1	5001,4	485	8,7	7,51	2512,5	63,54	0,05	0,02	91,5	0,2	89,9	79,5	45,03	2,58	0,35	94,6	0,0	< 0,01	2576,0	*0,03*	
1	1	305 BE-MON	BE	OBN-*kalktufbronnen*	16-3-2016	49,6289	5,5938	330	5	4,2	33,1	S	10	256,3	4201,2	439	8,8	7,60	2251,2	57,24	0,01	0,00	75,9	0,3	63,1	102,2	52,44	0,82	0,33	113,1	0,5	< 0,01	2308,5	*0,03*	
1	1	306 BE-LAH	BE	OBN-*kalktufbronnen*	16-3-2016	49,63448	5,48231	320	4	3,1	24,4	E	40	256,3	4201,2	422	9,0	7,73	2187,1	37,16	0,00	0,00	66,7	0,2	58,2	84,6	48,33	0,70	0,29	109,9	0,1	< 0,01	2224,3	*0,02*	
1	1	307 BE-LAH	BE	OBN-*kalktufbronnen*	16-3-2016	49,63412	5,48035	315	1	0,8	6,3	SE	60	225,8	3701,0	375	8,7	7,91	1921,9	36,24	0,00	0,00	65,9	0,2	57,2	83,4	31,31	0,23	0,25	114,2	0,1	< 0,01	1958,1	*0,02*	
1	1	308 BE-LAH	BE	OBN-*kalktufbronnen*	18-3-2016	49,63421	5,49461	300	5	5,8	45,7	SE	25	335,6	5501,5	590	9,7	7,19	3036,4	62,10	0,05	0,00	87,1	0,2	76,0	86,0	325,81	1,26	0,23	127,3	0,1	< 0,01	3098,5	*0,02*	
1	1	309 BE-BLA	BE	OBN-*kalktufbronnen*	18-3-2016	50,188549	4,826957	100	5	0,7	6,3	W	85	414,9	6801,9	818	11,4	7,05	3700,1	314,90	0,03	0,00	505,5	7,1	1457,0	346,7	141,31	1,24	0,19	210,6	0,1	< 0,01	4015,0	*0,09*	
1	1	310 BE-BLA	BE	OBN-*kalktufbronnen*	18-3-2016	50,193315	4,831389	210	3	0,8	7,2	WSW	85	274,6	4501,2	655	10,2	7,58	2529,9	406,26	0,07	0,00	455,2	103,3	702,1	339,6	781,28	1,26	0,29	176,4	0,4	< 0,01	2936,2	*0,16*	
1	1	311-BE-BOE	BE	OBN-*kalktufbronnen*	5-4-2016	50,735665	5,903933	195	5	3	31,6	WNW	90	311,2	5101,4	725	9,2	8,00	3857,3	160,58	2,60	0,15	208,2	45,4	337,6	1103,2	51,56	1,39	0,36	452,5	3,6	0,04	4017,9	*0,04*	
1	1	312-BE-KRI	BE	OBN-*kalktufbronnen*	5-4-2016	50,74589	5,83142	155	3	5,2	54,7	SW	80	317,3	5201,4	692	11,1	7,47	3515,5	144,77	0,24	0,01	292,5	25,4	620,6	424,4	400,43	1,09	0,43	456,0	0,7	0,01	3660,2	*0,04*	
1	1	401 FR-ETU	FR	OBN-*kalktufbronnen*	15-3-2016	47,8749	4,96532	299	5	25	263,2	NE	30	323,4	5301,5	502	10,6	8,17	2450,8	44,36	0,01	0,00	70,9	2,7	81,2	60,9	25,96	3,99	0,20	66,3	0,0	< 0,01	2495,2	*0,02*	
1	1	402 FR-LEG	FR	OBN-*kalktufbronnen*	15-3-2016	47,87533	5,24636	367	5	5,8	61,1	N	80	335,6	5501,5	544	9,8	7,64	2599,8	342,84	0,02	0,00	58,4	0,4	62,1	72,8	68,62	5,89	0,15	84,3	0,0	< 0,01	2942,6	*0,13*	
1	1	403 FR-CAM	FR	OBN-*kalktufbronnen*	15-3-2016	47,87653	5,24945	370	3	5,8	61,1	N	10	311,2	5101,4	525	9,8	7,45	2579,8	287,41	0,04	0,00	53,2	0,2	50,8	73,2	40,00	3,06	0,13	86,4	0,2	< 0,01	2867,2	*0,11*	
1	1	404 FR-ROL BOVEN	FR	OBN-*kalktufbronnen*	15-3-2016	47,95341	5,2601	338	5	50	526,3	NNW	50	353,9	5801,6	648	10,3	7,45	3146,2	274,98	0,01	0,00	170,6	0,4	167,8	122,7	384,95	2,24	0,10	82,4	0,7	< 0,01	3421,2	*0,09*	
1	1	405 FR-ROL MOERAS	FR	OBN-*kalktufbronnen*	15-3-2016	47,95679	5,253069	363	2	24	252,6	E	50	335,6	5501,5	630	9,3	7,76	2856,8	305,27	0,18	0,00	117,2	0,3	121,9	108,5	194,99	2,52	0,13	76,3	0,6	< 0,01	3162,1	*0,11*	
1	1	501 LU-MAM	LU	OBN-*kalktufbronnen*	17-3-2016	49,68478	6,09167	255	4	1,6	16,8	WSW	60	238,0	3901,1	577	7,9	8,06	2739,5	86,83	0,03	0,00	151,5	1,5	252,1	501,7	663,70	2,50	0,09	123,4	0,1	< 0,01	2826,4	*0,03*	
1	1	502 LU-MAM	LU	OBN-*kalktufbronnen*	17-3-2016	49,68636	6,08813	270	4	8,8	92,6	E	30	274,6	4501,2	604	8,9	7,62	2919,2	91,32	0,24	0,00	190,1	2,7	374,5	429,7	597,99	1,15	0,07	122,4	1,6	< 0,01	3010,5	*0,03*	
1	1	503 LU-MAM	LU	OBN-*kalktufbronnen*	17-3-2016	49,69892	6,08592	270	3	0,5	5,3	SE	80	299,0	4901,3	566	9,0	7,36	2446,4	541,56	0,37	0,00	116,7	8,5	117,0	440,3	60,09	1,28	0,09	112,4	1,5	< 0,01	2987,9	*0,22*	
		Minimum					Minimum	*45*		*0,03*	*0,4*		*0,0*	*225,8*	*3701,0*	*375*	*5,3*	*7,05*	*1529,4*	*36,2*	*0,0*	*0,0*	*53,2*	*0,2*	*20,4*	*60,9*	*0,7*	*0,23*	*0,07*	*66,3*	*0,0*	*0,01*	*1958,1*	*0,02*	
		Maximum					Maximum	*506*		*50*	*526,3*		*90,0*	*506,4*	*8302,3*	*1047*	*11,4*	*8,70*	*4690,6*	*2018,9*	*20,8*	*5,5*	*982,7*	*149,2*	*1991,2*	*2034,3*	*1890,3*	*5,89*	*4,44*	*469,6*	*35,5*	*0,20*	*5601,1*	*1,05*	
		Median					Median	*270*		*2,5*	*25,3*		*70,0*	*335,6*	*5501,5*	*628*	*9*	*7,75*	*2976,5*	*274,98*	*0,31*	*0,02*	*190,6*	*12,8*	*337,6*	*249,7*	*319,3*	*1,27*	*0,34*	*116,7*	*0,6*	*0,03*	*3359,0*	*0,08*	
		Average					Average	*243*		*7*	*67,6*		*58,3*	*350,1*	*5738,8*	*669*	*8,9*	*7,78*	*3090,9*	*469,59*	*2*	*0,24*	*287,7*	*20,0*	*439,9*	*374,4*	*442,8*	*1,58*	*0,59*	*174,7*	*2,7*	*0,05*	*3560,5*	*0,17*	
1	0	001-CR-PLI	CRO	RHDHV_Plitvice	27-01-2016			590	5	>500		NE/E/SE	20	286,8	4701,6	431	4,0	7,59	1367,3	920,99	0,06	0,03	13,2	8,5	15,3	36,3	33,3	2,65	0,08	39,3	0,9	<0,01	2288,3	***0,67***	***dolomite***
1	1	402 FR-LEG-tufa-delta	FR	OBN-*kalktufbronnen*	15-3-2016	47,8753	5,2464	363	4	5,8		N	80	335,6	5501,5	512	9,6	8,00	2499,7	331,36	0,02	0,00	57,4	0,4	63,1	71,9	69,26	5,89	0,15	82,6	0,0	< 0,01	2831,1	*0,13*	
1	1	404-FR-Rol-voet	FR	OBN-*kalktufbronnen*	15-3-2016	47,9534	5,2601	328	4	*5*		NNW	50	299,0	4901,6	555	9,5	7,74	2612,3	270,1	0,0	0,0	179,2	0,3	181,7	120,7	384,3	1,7	0,2	81,7	0,1	0,0	2882,4	*0,10*	
1	1	219-DE-DMF-voet	DE	RHDHV_2015	20-7-2015	50,3244	6,7689	370	5	*5*		E	30	274,6	4501,5	518	8,8	7,68	2084,8	643,2	0,0	0,0	248,1	18,4	518,9	242,4	310,6	4,0	0,1	107,9	0,1	0,0	2728,0	***0,31***	***+antropogenic?***

All figures on ortho-phosphate in this report are presented as ortho-P0$_4^{3-}$ <u>not as ortho-P</u>.

Appendix 4: Water chemistry of petrifying springs in databases and literature

Waterkwaliteit van kalktufbronnen ontleend aan databases en literatuurbronnen

Kalktufbronnen - (OBN 2015-75HE)

Data : 1 ***C/M*** : 0 =only chemistry; 1 = chemistry & bryophytes available

Data	*C/M*			*origin of data*	sampling date	*WGS84 Lat.*	*WGS84 Long.*	altitude m	travertine class	flow rate l/s	catchment ha (approx)	main exposition	shade %	HCO3 mg/l (veld)	**HCO3** µmol/l (veld)	**EGV** µS/cm (veld)	**temp** °C (veld)	**pH** (veld)	**Ca** µmol/l	**Mg** µmol/l	**Fe** µmol/l	**Mn** µmol/l	**Na** µmol/l	**K** µmol/l	**Cl** µmol/l	**S** µmol/l	**NO_3** µmol/l	**NH_4** µmol/l	**PO_4** µmol/l	Si µmol/l	Al µmol/l	Zn µmol/l	***Ca+Mg***	*Mg/Ca*	
2	0	OBROL0298 Hemelbeek zijtAC 9.00:	aNL	Waterschap RO										164,1	2689,6	800		8,20	3992,2	1193,17			870,0	33,2	1043,6	732,8	2113,27	46,41	0,42				5185,4	***0,30***	***+antropogenic***
2	0	OBROL0401B Berkenhofbeek zijtAC	aNL	Waterschap RO										246,2	4034,4	855		8,20	3992,2	740,59			1217,9	51,2	930,8	793,5	3227,03	46,41	0,42				4732,8	*0,19*	
2	0	OBROL0450 Terzieterbeek zijtAC 10	aNL	Waterschap RO										290,2	4756,0	561		8,11	3493,2	86,40			178,3	51,2	277,8	338,6	503,33	62,83	0,44				3579,6	*0,02*	
2	0	OBROL0650 Noor zijtAC 15.003TA br	aNL	Waterschap RO										278,2	4559,2	612		8,21	3243,7	135,77			239,2	40,9	471,0	443,6	963,82	65,68	0,42				3379,4	*0,04*	
2	0	OBRON0295 Voeding Roosbeek bro	aNL	Waterschap RO										329,3	5395,6	853		8,05	4740,8	1152,03			1174,4	156,0	1337,0	645,3	1427,89	54,26	0,42				5892,8	***0,24***	***+antropogenic***
2	0	OBRON0362 Vliekerwaterlossing zi	aNL	Waterschap RO										377,3	6182,8	857		8,04	4740,8	1028,59			565,5	79,3	614,9	517,7	2320,32	68,54	2,69				5769,4	***0,22***	***+antropogenic***
2	0	OBRON0372A Vliekerwaterlossing :	aNL	Waterschap RO										316,2	5182,4	815		7,30	3493,2	781,73			522,0	28,1	947,7	840,8	1456,45	17,14	0,52				4274,9	***0,22***	***+antropogenic***
2	0	OBRON0373 Vliekerwaterlossing zi	aNL	Waterschap RO										400,3	6560,0	923		7,30	3992,2	905,16			652,5	81,8	953,4	899,5	1627,79	22,13	0,61				4897,4	***0,23***	***+antropogenic***
2	0	OBRON0399 Strabekervloedgraaf zi	aNL	Waterschap RO										292,2	4788,8	896		8,00	3992,2	781,73			826,5	33,2	981,6	700,9	2934,31	10,71	0,42				4773,9	***0,20***	***+antropogenic***
2	0	OBRON0457 2e ZijtAC Fröschebron	aNL	Waterschap RO										258,2	4231,2				3243,7	119,32			195,7	30,7	246,5	470,3	449,78	18,56	0,51				3363,0	*0,04*	
2	0	OBRON0676 Noor zijtAC 15.003PH b	aNL	Waterschap RO										303,2	4969,2	621		8,23	3742,7	152,23			317,5	56,3	516,2	446,7	1092,33	46,41	0,53				3894,9	*0,04*	
2	0	OBRONKATTA Kattebeek zijtAC bro	aNL	Waterschap RO										227,2	3722,8	812		7,00	2994,2	493,73			1739,9	30,7	2798,1	302,6	530,46	19,28	0,42				3487,9	*0,16*	
2	0	1075	aNL	Bware n2011 (Bunderbos)	nov-13									352,1	5770,0			7,42	3575,3	840,33	9,72		680,3	27,1	960,0	772,1	1947,66	2,36	1,25		12,7		4415,7	***0,24***	***+antropogenic***
2	0	1074	aNL	Bware n2012 (Bunderbos)	nov-13									350,7	5746,8			7,20	3592,8	851,03	6,99		694,0	29,7	979,8	781,1	1967,28	2,44	1,62		12,0		4443,8	***0,24***	***+antropogenic***
2	0	1104	aNL	BWare n2013 (Bunderbos)	nov-13									358,0	5866,5			7,87	3917,2	908,64	16,23		529,8	11,9	1279,7	1493,3	475,32	3,04	0,27		20,4		4825,8	***0,23***	***+antropogenic***
2	0	1142	aNL	BWare n2014 (Bunderbos)	nov-13									336,5	5514,4			8,41	3527,9	862,96	1,08		598,0	30,4	1260,1	858,1	1217,94	2,75	0,49		1,4		4390,9	***0,24***	***+antropogenic***
2	0	1174	aNL	BWare n2015 (Bunderbos)	nov-13									403,7	6616,1			7,20	3797,4	918,93	6,68		692,9	18,9	1342,0	739,9	1328,28	2,13	0,87		12,2		4716,3	***0,24***	***+antropogenic***
2	0	1173b	aNL	BWare n2016 (Bunderbos)	nov-13									514,6	8432,5			7,65	4431,1	1166,26	15,26		759,5	34,0	1217,8	738,4	1164,78	3,81	1,70		0,1		5597,4	***0,26***	***+antropogenic***
2	0	1013	aNL	BWare n2017 (Bunderbos)	nov-13									387,2	6345,8			7,28	3959,6	960,91	1,23		816,6	171,2	975,5	862,8	1786,68	2,11	1,30		1,3		4920,5	***0,24***	***+antropogenic***
2	0	1110	aNL	BWare n2018 (Bunderbos)	nov-13									295,4	4841,2			7,42	3053,9	721,81	2,21		444,2	28,4	762,3	1152,2	645,96	1,90	0,24		0,8		3775,7	***0,24***	***+antropogenic***
2	1	Ename, Enamebos a	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,8538	3,3759	54	3				95	385,0	6309,7	995		7,70	4601,0	740,59			591,6	53,7	1497,8	995,2	914,56	5,71	0,21				5341,6	*0,16*	
2	0	Ename, Enamebos b	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,.8535	3,6494	52	5				75	360,0	5900,0	994		7,90	4251,7	637,73			600,3	51,2	1466,7	928,3	946,69	2,78	0,08				4889,4	*0,15*	
2	0	Galmaarden a	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7623	3,9414	46	2				95	423,0	6932,5	853		7,80	4546,1	682,99			574,2	110,0	953,4	1237,0	323,42	6,43	0,08				5229,1	*0,15*	
2	0	Galmaarden b	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7617	3,9419	43	3				95	409,0	6703,1	910		8,00	4276,7	621,27			548,1	84,4	894,1	1123,8	346,26	2,78	0,08				4897,9	*0,15*	
2	0	Halle, Steenputbeek c	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7854	3,3759	73	3				95	334,0	5473,9	713		8,10	3331,0	423,78			517,6	30,7	671,3	808,9	124,94	6,07	0,23				3754,8	*0,13*	
2	0	Hoesselt, Wijngaardbos a	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,8167	5,4808	106	1				95	416,0	6817,8	856		7,20	3892,4	699,44			735,1	30,7	913,9	665,9	554,02	7,21	0,08				4591,9	*0,18*	
2	1	Hornebeek a	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7217	5,2385	106	2				50	387,0	6342,5	986		7,30	4386,4	802,30			535,0	38,4	1602,1	987,0	692,53	5,78	0,08				5188,8	*0,18*	
2	1	Kwaremont, Feelbos a	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,8379	3,6493	74	4				75	342,0	5605,0	869		7,70	3959,8	403,21			726,4	71,6	1153,6	857,3	812,47	5,78	0,18				4363,0	*0,10*	
2	0	Kwaremont, Feelbos b	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7720	3,5374	72	5				75	315,0	5162,5	842		8,00	3850,0	386,75			735,1	89,5	1207,2	843,9	752,50	2,78	0,13				4236,7	*0,10*	
2	0	Kwaremont, Feelbos c	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7721	3,5369	61	5				75	311,0	5097,0	831		8,10	3667,8	333,26			730,8	84,4	1176,2	929,3	697,52	2,78	0,16				4001,1	*0,09*	
2	0	Mater b	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,8490	3,6767	49	3				25	422,0	6916,1	1065		7,30	5167,4	584,24			787,3	127,9	1317,2	1834,0	2,14	2,78	0,08				5751,7	*0,11*	
2	0	Michelbeke, Boterhoek a	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,8379	3,7759	63	4				25	404,0	6621,1	788		7,20	3510,7	724,13			482,8	158,6	798,2	721,4	2,14	6,14	0,34				4234,8	*0,21*	
2	0	Moen, Vaarttaluds b	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7118	4,2774	29	3				0	300,0	4916,7	956		8,00	3328,5	1061,51			1187,5	626,6	1272,1	2059,3	2,14	2,78	0,08				4390,0	***0,32***	***+antropogenic***
2	1	Remersdaal, Mabroek a	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7275	5,9013	202	5				95	266,0	4359,5	669		7,00	3318,5	123,43			234,9	40,9	459,8	848,0	593,29	5,21	0,32				3442,0	*0,04*	
2	0	Remmersdaal, Mabroek b	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7273	5,9015	197	3				95	231,0	3785,8	616		7,90	2946,8	106,97			234,9	38,4	431,6	747,2	678,96	3,64	0,28				3053,7	*0,04*	
2	1	Sint-Martens-Voeren, Krindaal a	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7457	5,8320	154	3				95	333,0	5457,5	685		7,80	3578,0	111,09			313,2	69,1	657,2	480,6	450,50	5,64	0,08				3689,1	*0,03*	
2	0	Sint-Martens-Voeren, Krindaal b	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7459	5,8311	153	4				75	315,0	5162,5	710		7,80	3388,4	106,97			291,4	43,5	586,7	420,9	558,30	2,78	0,08				3495,4	*0,03*	
2	1	Sint-Martens-Voeren, Kwinten a	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7508	5,8124	138	3				95	323,0	5293,6	719		7,50	3685,3	102,86			274,0	40,9	569,8	473,4	893,14	5,43	0,16				3788,2	*0,03*	
2	0	Sint-Martens-Voeren, Kwinten b	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,7513	5.8125	144	5				50	303,0	4965,8	703		7,90	3543,1	90,52			265,3	40,9	547,2	474,4	890,29	3,64	0,08				3633,6	*0,03*	
2	0	Willebringen, Fonteinbeek b	BE-Fl	Denys & Oosterlynck, 2015	2013/12	50,8100	4,8444	67	3				50	406,0	6653,9	867		7,90	3632,9	933,96			574,2	138,1	772,9	788,3	550,45	6,93	0,41				4566,9	*0,26*	
2	0	03DB12 Deinschawanger Bach (Fran	DE	Arp et al., 2010	10-10-2006			500	3		800,0			313,7	5140,0	603	8,5	8,35	2030,0	1090,00			335,0	31,2	56,2	180,0	485,00		2,03	101,0			3120,0	***0,54***	***+antropogenic***
2	0	03Wb-Wo3Westerhofer Bach (Harz	DE	Arp et al., 2010	23-5-2006			200	5		350,0			327,1	5360,0	1025	9,1	7,82	3900,0	1720,00			341,0	53,0	297,0	2950,0	92,00		0,24	158,0			5620,0	***0,44***	***dolomite/gypsum***
2	0	P13 Reingraben	DE	Arp et al., 2010	6-8-2002			200	3		100,0			307,6	5040,0	1200	12,8	8,10	5120,0	1120,00			617,0	44,0	584,0	376,0	59,00		1,37	153,0			6240,0	*0,22*	
2	0	SRE01/3 Steinerne Rinne (Franconi:	DE	Arp et al., 2010	13-10-2006			500	5		100,0			334,4	5480,0	627	8,9	7,96	3430,0	134,00			188,0	17,0	140,0	270,0	81,00		2,63	84			3564,0	*0,04*	
2	0	Hohenroden-Aftetal	DE	Hartkopf-Froder et al., 1989	29-5-1988			263	4	0,5	3,9			269	4408,2	665	9,1	7,60	3418,2	41,14	sp	sp	130,5	25,5102	733,4	467,9	596,7						3459,3	*0,01*	
2	0	Blaen Onnen (runnel with Palustrie	UK	Farr et al., 2014										228,0	3736,7	564		7,83	1931,2	374,00	13,45		1335,4	24,1	1703,7	111,4	24,0						2305,2	*0,19*	
2	0	Blaen Onnen (spring at head of site	UK	Farr et al., 2014										268,0	4392,2	666		7,24	2066,0	469,04	7,50		1648,6	22,3	2081,6	<0,1	38,3						2535,0	*0,23*	
2	0	Brest Rhiw 1	UK	Farr et al., 2014												634		7,23	3168,8	199,55	2,74		565,5	26,9	820,8	261,3	7,7						3368,4	*0,06*	
2	1	Cors Erddreiniog 4	UK	Farr et al., 2014										261,0	4277,5	489		8,14	2445,2	145,24	11,94		427,6	21,7	623,4	183,2	147,6						2590,5	*0,06*	
2	1	Ddol	UK	Farr et al., 2014										354,0	5801,7	668		7,42	3094,0	440,24	<0,55		691,6	55,5	823,6	267,5	425,8						3534,2	*0,14*	
2	1	Fedw Faw Beach 2	UK	Farr et al., 2014										259,0	4244,7	547		8,29	2275,6	319,69	3,92		752,5	145,5	1043,6	166,6	251,6						2595,2	*0,14*	
2	1	Fedw Fawr Beach 1	UK	Farr et al., 2014										266,0	4359,5	539		8,45	2255,6	473,15	3,06		835,2	66,5	1074,7	156,2	96,6						2728,8	*0,21*	
2	0	Foel Fawr Site 2	UK	Farr et al., 2014										417,0	6834,2	860		12,20	3518,1	15,92	3,92		107,0	26,1	160,8	137,4	14,2						3534,1	*0,00*	
2	1	McWalters Dingle (1)	UK	Farr et al., 2014										404,0	6621,1	886		7,83	3393,4	1312,49	<0,55		1239,7	177,5	1698,0	677,7	251,6						4705,9	*0,39*	***salt?***
2	0	Via Gellia, Derbyshire 1 (t=1 mean)	UK	Columbu et al., 2013	2011/12			160						286,5	4695,4	414		7,94	2638,6	61,10			189,2	16,7	175,2	179,1	236,3						2699,7	*0,02*	
2	0	White Hole Farm Spring A	UK	Thomas, 2007	2002/3									263,0	4310,0	574	9,9	7,00	2794,6	337,38	0,38		304,5	71,4	428,7	127,0	121,0						3131,9	*0,12*	
2	0	White Hole Farm Spring B	UK	Thomas, 2007	2002/3									243,0	3982,0	536	9,9	7,70	2594,9	297,47	0,59		295,8	71,6	423,1	121,8	115,5						2892,4	*0,11*	
2	1	Clapham Beck	UK	Pentecost & Zhaohui 2002	23-4-1990			250						146,5	2400,0		9,9	8,09	1350,0	170,00			200,0		270,0	90,0							1520,0	*0,13*	
2	1	Shelsley Walsh	UK	Pentecost & Zhaohui 2002	19-9-1991			100						248,4	4070,0		12,8	8,03	2040,0	640,00			1200,0		0,0	260,0							2680,0	***0,31***	
2	1	Waterfall Beck	UK	Pentecost & Zhaohui 2002	6-4-1993			360	5			N		152,6	2500,0		11	8,29	1370,0	30,00			160,0		120,0	80,0							1400,0	*0,02*	
2	1	West Malling	UK	Pentecost & Zhaohui 2002	23-4-1990			30						258,7	4240,0		20,4	8,22	2710,0	110,00			380,0		730,0	480,0							2820,0	*0,04*	
2	0	Grag cave	IRE	Frisia et al., 2010				60	5					297	4868,9	552	10,4	7,70	2277,9	385,44			761,2	42,6	665,7	254,7	230,61						2663,4	*0,17*	

Appendix 5: Water chemistry of petrifying springs in Eastern European spring mires

Waterkwaliteit van de kalktufbronnen in Oost-Europese bronvenen.

Kalktufbronnen - (OBN 2015-75HE)

Data : 1 ***C/M*** : 0 =only chemistry; 1 = chemistry & bryophyte available

Data	*C/M*			*origin of data*	sampling date	*WGS84 Lat.*	*WGS84 Long.*	altitude m	travertine class	flow rate l/s	catchment ha (approx)	main exposition	shade %	HCO3 mg/l (veld)	**HCO3** µmol/l (veld)	**EGV** µS/cm (veld)	**temp** °C (veld)	**pH** (veld)	**Ca** µmol/l	**Mg** µmol/l	**Fe** µmol/l	**Mn** µmol/l	**Na** µmol/l	**K** µmol/l	**Cl** µmol/l	**S** µmol/l	**NO_3** µmol/l	**NH_4** µmol/l	*ortho* **PO_4** µmol/l	Si µmol/l	Al µmol/l	Zn µmol/l	***Ca+Mg***	*Mg/Ca*	
2	1	601-PL-RE	PL (Ab)	SURF-A1															1478,9	309,44	3,92	1,85	202,9	29,5	129,5	195,9	3,3	9,26		274,1			1788,3	0,21	
2	1	602-PL-RE	PL (Ab)	SURF-A2															1492,3	311,17	0,29	3,88	197,1	31,1	128,3	190,0	1,3	5,71		276,2			1803,5	0,21	
2	1	603-PL-RE	PL (Ab)	SURF-A3															1512,6	312,24	0,20	1,61	202,9	34,0	133,3	197,2	3,6	4,88		281,7			1824,8	0,21	
2	1	604-PL-RE	PL (Ab)	SURF-B1															1501,8	315,20	2,64	3,41	200,2	38,2	133,9	190,7	2,4	7,37		277,9			1817,0	0,21	
2	0	605-PL-RE	PL (Ab)	SURF-B2															1515,8	313,84	0,85	3,37	198,6	33,7	132,3	187,8	1,8	5,54		279,6			1829,6	0,21	
2	1	606-PL-RE	PL (Ab)	SURF-B3															1515,8	314,59	1,48	2,39	203,0	36,0	131,7	183,8	3,1	4,95		284,3			1830,4	0,21	
2	1	607-PL-ZLO	PL (Ab)	SURF-A1															3146,4	382,56	0,32	4,34	240,9	24,8	132,0	13,2	0,7	8,68		196,9			3528,9	0,12	
2	1	608-PL-ZLO	PL (Ab)	SURF-A2															3113,9	412,67	17,51	12,37	314,2	61,8	164,1	12,4	0,3	17,01		285,4			3526,6	0,13	
2	1	609-PL-ZLO	PL (Ab)	SURF-A3															2542,5	267,97	321,77	38,24	279,9	88,7	394,3	32,0	0,7	16,57		341,7			2810,5	0,11	
2	0	610-PL-ZLO	PL (Ab)	SURF-B1															2244,6	276,45	1,29	6,07	265,8	81,8	210,0	41,7	1,2	8,80		292,9			2521,1	0,12	
2	1	611-PL-ZLO	PL (Ab)	SURF-B2															2001,8	243,20	0,76	4,54	239,1	48,6	244,1	108,2	2,4	0,74		245,4			2245,0	0,12	
2	1	612-PL-ZLO	PL (Ab)	SURF-B3															2259,3	252,95	0,35	7,94	241,8	20,0	256,0	111,1	3,6	0,88		252,0			2512,3	0,11	
2	0	613-PL-LAS	PL (Ab)	SURF-L										299,1	4902				3459,5	671,65	4,70		372,2	57,3	624,8	678,0							4131,1	0,19	
2	0	614-PL-LAS	PL (Ab)	SURF-L3										300,5	4924				3640,9	663,49	4,51		420,9	57,5	636,1	706,9							4304,4	0,18	
2	0	615-PL-LAS	PL (Ab)	SURF-L6										300,2	4920				3706,2	672,94	4,51		402,6	58,0	687,3	773,5							4379,1	0,18	
2	0	616-PL-LAS	PL (Ab)	SURF-L9										299,7	4912				3625,0	694,85	4,88		520,6	61,9	820,2	898,0							4319,9	0,19	
2	0	617-PL-LAS	PL (Ab)	SURF-L12										295,6	4844				3957,7	701,72	8,00		415,5	63,6	824,2	889,4							4659,4	0,18	
2	0	618-PL-LAS	PL (Ab)	SURF-L15										280,0	4588				3892,4	696,99	19,37		634,1	59,0	894,8	1023,4							4589,4	0,18	
2	0	619-PL-LAS	PL (Ab)	SURF-LA1										305,6	5008				3464,3	717,62	4,15		316,7	48,9	489,6	734,4							4181,9	0,21	
2	0	620-PL-LAS	PL (Ab)	SURF-LA5										300,6	4926				3491,3	742,10	11,67		332,4	47,7	565,3	744,0							4233,4	0,21	
2	0	621-PL-MOS	PL (Ab)	GRW-M1										383,2	6280				3274,2	700,00	5,43		518,8	144,4	702,3	394,6							3974,2	0,21	
2	0	622-PL-MOS	PL (Ab)	SURF-M1										362,5	5940				3139,1	746,40	5,62		339,1	74,4	562,5	467,4							3885,5	0,24	
2	0	623-PL-MOS	PL (Ab)	SURF-M3										345,3	5658				3172,8	774,75	5,98		424,0	77,0	565,5	581,2							3947,6	0,24	
2	0	624-PL-MOS	PL (Ab)	SURF-M5										310,7	5092				2790,0	773,89	5,07		350,2	70,7	588,8	571,4							3563,9	0,28	
2	0	725-LAT-SLI	LAT (Ab	GRW-A1										534,7	8763				3535,4	871,19	16,82	4,56	113,2	33,0	153,0	20,0	50,1	7,76	0,07	0,1		1,45	4406,6	0,25	
2	1	726-LAT-SLI	LAT (Ab	SURF-A1										537,9	8815				3632,7	869,14	0,81	0,16	141,4	33,7	151,1	53,4	115,1	9,21	0,11	0,1		0,98	4501,9	0,24	
2	1	727-LAT-SLI	LAT (Ab	SURF-A2										425,0	6965				2776,9	860,08	0,32	1,20	124,4	31,5	130,9	98,4	157,4	8,07	0,10	0,5		5,96	3637,0	**0,31**	**dolomite**
2	1	728-LAT-SLI	LAT (Ab	SURF-A3										415,2	6805				2632,2	869,96	0,22	0,34	150,8	50,5	181,8	71,8	83,4	7,20	0,07	0,8		1,28	3502,2	**0,33**	**dolomite**
2	1	729-LAT-MAZ	LAT (Ab	SURF-B1										356,2	5838				3041,4	1023,46	1,75	1,05	167,9	29,0	368,4	1063,6	126,3	114,26	0,11	0,3		8,03	4064,9	**0,34**	**dolomite**
2	1	730-LAT-MAZ	LAT (Ab	SURF-B2										328,5	5383				3463,1	1313,99	1,53	0,11	181,8	35,0	198,6	2095,7	41,2	33,57	0,11	0,1		4,21	4777,1	**0,38**	**dolomite**
2	1	731-LAT-MAZ	LAT (Ab	SURF-Spring										335,5	5498				3051,4	1149,38	38,98	3,50	229,8	26,4	185,1	1483,6	109,0	17,67	0,13	-0,1		0,74	4200,8	**0,38**	**dolomite**
2	0	801-SLO-POP	SLO (Ab	GRWP6												737		7,30	2214,3				461,7	44,5	541,6	2468,8	8,5	10,72	0,76						
2	0	802-SLO-POP	SLO (Ab	GRWP7												820		7,05	2577,3				467,0	24,8	428,8	1929,7	4,5	9,22	1,02						
2	0	803-SLO-POP	SLO (Ab	GRWP10												805		7,60	2366,5				572,2	40,7	592,1	2365,6	5,3	5,06	1,26						
2	0	804-SLO-POP	SLO (Ab	GRWP11												760		7,32	2381,5				471,7	26,9	739,9	2475,0	5,2	13,89	0,36						
2	0	805-SLO-POP	SLO (Ab	GRWP12												724		7,20					477,8	37,1	419,7	2140,6	4,0	0,33	0,67						
2	0	806-SLO-POP	SLO (Ab	GRWP6															2213,2	1455,6			461,7	44,6	540,8	2461,1	8,5	10,72	0,77				3668,8	**0,66**	**dolomite**
2	0	807-SLO-POP	SLO (Ab	GRWP7															2576,1	1651,9			467,0	24,9	428,2	1923,7	4,5	9,22	1,03				4227,9	**0,64**	**dolomite**
2	0	808-SLO-POP	SLO (Ab	GRWP8															2728,2	2011,5			522,6	32,8	414,1	1512,5	4,0	0,00	0,67				4739,7	**0,74**	**dolomite**
2	0	809-SLO-POP	SLO (Ab	GRWP10															2365,3	1544,9			572,2	40,8	591,3	2358,3	5,3	5,06	1,27				3910,2	**0,65**	**dolomite**
2	0	810-SLO-POP	SLO (Ab	GRWP11															2380,3	1481,5			471,7	26,9	738,9	2467,3	5,2	13,89	0,37				3861,8	**0,62**	**dolomite**

Appendix 6: Bryophyte relevees and Moss vegetation types of petrifying springs

Mos-opnamen en onderscheiden mos-typen van de bemonsterde kalktufbronnen

	101-TEH	102-GEU	103-ULE	104-PAP	105-RAV	106-WAL	107-MAT	108-NOO	109-NOO	110-PUT	111-TEZ	200-TEU	201-TEU	202-BEB	203-HIL	204-BOC	205-LEI	206-LEI	207-LEI	208-MER	209-MER	210-RIM	211-HIL	212-BIN	213-NEN	214-BIN	215-LEI	216-LEI	217-BUR	218-BOX	219-DMF	301-CEL	302-BOF	303-VIR	304-MON	305-MON	306-LAH	307-LAH	308-LAH	309-BLA	310-BLA	311-BOE	312-KRI	401-ETU	402-LEGb	402-LEGm	403-CAM	404-ROL	405-ROL	501-MAM	502-MAM	503-MAM
Aneura pinguis (echt vetmos)																1	1					1						2	1		1																					
Brachythecium rivulare (beekdikkopmos)							2	2	2		2	2		3	2		2	2	1		3	3		4	4	3	3	4	5		4			3					2	2	6	5	6		2	6				2	2	2
Brachythecium rutabulum (gewoon dikkopmos)												3				1				2	1	1								5		2						2														
Bryum pseudotriquetrum (veenknikmos)												3		1			2		1	1		1				1	4		1		1		7		3		2		5					5								
Calliergonella cuspidata (puntmos)												1			1						3		5		1					1									4													
Campylium stellatum (sterrengoudmos)														1													1										2															
Chiloscyphus polyanthos (lippenmos)																																																				2
Climacium dendroides (boompjesmos)								2																																							6					
Conocephalum conicum (kegelmos)																																		2			2													2		2
Cratoneuron filicinum (gewoon diknerfmos)	3	5	7	5	7	7	2	6	5	6	7	3	7	5	7	3	7	5	3	5	7	7	1	5	1	6	5	5	6	4		2	2	2			2			2	6	3	3					2	5			4
Ctenidium molluscum (kammos)																																	2																		2	
Didiymodon sinuosus (bros dubbeltandmos)																																2																				
Eucladium verticillatum (tufmos)										2			6				2	4	2		1	4					2	4	4		x				3	3	2		4	3				2				2			2	
Eurhynchium striatum (geplooid snavelmos)																																									2				2							2
Fissidens adianthoides (groot vedermos)																											1								2		2		2													
Fissidens incurvus (gekromd vedermos)																																2																				
Fissidens taxifolius (Kleivedermos)										3	1		1	2	1	2						2							2		x	2									2		2			2					2	3
Gymnostotum calcerum (klein kalkmos)																																																2				
Hylocomium splendens (glanzend etagemos)																																																				2
Hypnum cupressiforme (gesnaveld/gewoon klauwtjesmos)																																									2											
Kindbergia praelonga (fijn laddermos)																																2									2						2					
Lophocolea bidentata (gewoon kantmos)														1	1			2			4	1					1	2		1																	2					2
Marchantia polymorpha (parapluutjesmos)																																2																				
Mnium hornum (gewoon sterrenmos)															2		2													2											2											
Mnium stellare (ongezoomd sterrenmos)																				1																																
Neckera complanata (glad kringmos)																																																		2		
Oxyrrhynchium hians (kleisnavelmos)																		1			1													2						2	2											
Oxyrrhynchium speciosum (moerassnavelmos)																										1				2																				2		
Palustriella commutata (geveerd diknerfmos)							5	3						7	7	8	6	6	7	4	1	6				5	7	8	7		8		8		7	7	7	8	7	8	2			7	7		7	8		8	7	4
Palustriella falcata (geklauwd diknerfmos)																										2							2				2							2							2	
Pellia endiviifolia (gekroesd plakkaatmos)	2	2	7			3	2	2		5	3		5	2		2	2			1	1	3		2				4	1		2	2	2	2	2	3	2	2		1	1	3	6				2			1	2	3
Philonotis calcarea (groot staartjesmos)																																							5													
Plagiochila porelloides (klein varentjesmos)											1																																									
Plagiochilla asplenioides (groot varentjesmos)																																									2				2		2					
Plagiomnium affine (rond boogsterrenmos)																	2										1	4																								
Plagiomnium rostratum (gesnaveld boogsterrenmos)															1						4			1		4	3			2																					2	
Plagiomnium undulatum (gerimpeld boogsterrenmos)		2			3			2							2		1	1	2	4	1	1		2			4		2	2	x	2		2												2	2			2	2	
Pohlia wahlenbergii (bleek peermos)																																2					2															
Rhizomnium punctatum (gewoon viltsterrenmos)															2		2				1			1			1			2								2												2		
Rhynchostegium riparioides (watervalmos)													6									1										2									2										2	
Rhytidiadelphus triquetrus (pluimstaartmos)												1									1		1																2													2
Riccardia chamedryfolia (gewoon moerasvorkje)																																									2											
Sphagnum palustre (gewoon veenmos)																										1																										
Thamnobryum alopecurum (struikmos)																																2		2						2									2			
Thuidium tamariscinum (gewoon thujamos)																																		2				2			2						2					
Moss vegetation type (see also hs 4.3)	2	2	2	2	1	2	3	2	2	2	2	1	2	2	1	2	3	3	3	1	1	2	1	1	2	1	3	2	2	1	3	1	3	2	3	3	4	3	3	3	2	2	2	3	4	2	4	3	2	4	3	2
Habitat quality (see als hs 6.2)	p	p	p	p	p	p	m	m	m	m	m	m	m	m	m	g	m	m	m	m	m	m	p	m	m	m	m	g	m	p	g	p	m	m	m	m	m	g	m	g	m	m	m	m	m	m	m	g	p	g	m	m
p = poor; m = moderate; g = good.																																																				

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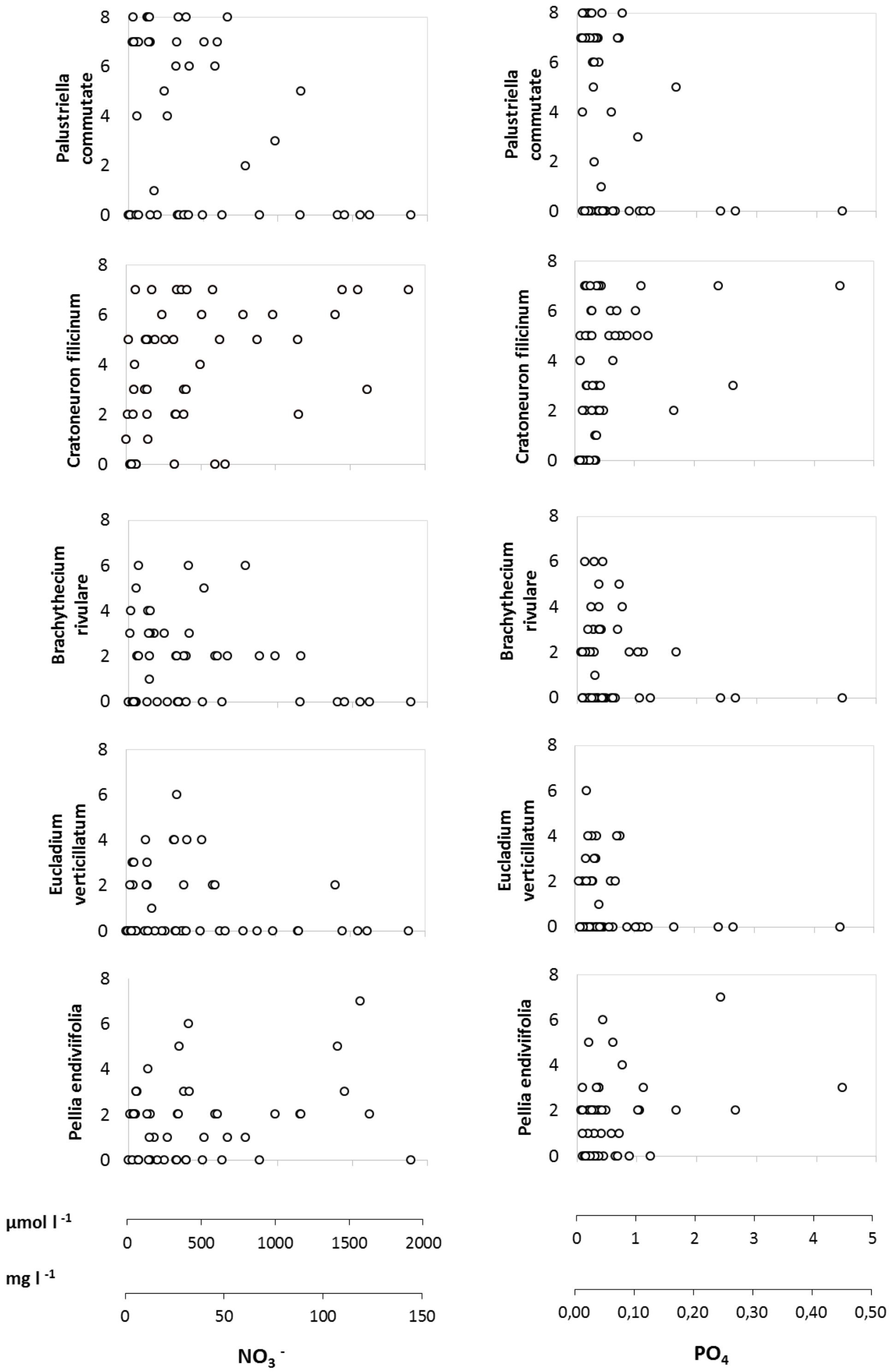
Appendix 7: Coverage of five bryophyte species typical for petrifying springs in relation to the surface water nitrate and phosphate concentrations

De bedekkingsgraad van vijf typische kaltufmossen in relatie tot het nitraat-en fosfaatgehalte van het bronwater

(coverage: 0=0%, 1=<1%, 2=±1%, 3=2-4%, 4=±5%, 5=6-15%, 6=16-25%, 7=26-50%, 8=>50%)



ontwikkeling+beheer natuurkwaliteit

o+bn

Het Kennisnetwerk Ontwikkeling Beheer Natuurkwaliteit:

- is een onafhankelijk en innovatief platform waarin beheer, beleid en wetenschap op het gebied van natuurherstel en -beheer samenwerken;
- ontwikkelt en verspreidt kennis met als doel het structureel herstel en beheer van natuurkwaliteit.