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Title: Catchments as heterogeneous, multi-species reactors: An integral approach for identifying biogeochemical hot-spots at the catchment's scale.

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Keywords: biogeochemical processing; biogeochemical hot spots; Isometric Feature Mapping; chemical variability.

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Abstract: From a biogeochemical perspective, catchments can be regarded as reactors that transform the input of various substances via precipitation or deposition as they pass through soils and aquifers towards draining streams. Understanding and modeling the variability of solute concentrations in catchment waters require the identification of the prevailing processes, determining their respective contribution to the observed transformation of substances, and the localization of "hot spots", that is, the most reactive areas of catchments.

For this study, we applied a non-linear variant of the Principle Component Analysis, the Isometric Feature Mapping (Isomap), to a dataset composed of 1686 soil solution, groundwater and stream water samples and 16 variables (Al, Ca, Cl, Fe, K, Mg, Mn, Na, NH<sub>4</sub>, NO<sub>3</sub>, SO<sub>4</sub>, total S, Si, DOC, electric conductivity and pH values) from the Lehstenbach catchment in Germany, (i) to assess the contribution of the prevailing biogeochemical processes to the variability of solute concentrations in water samples taken from soils, in groundwater and in stream water in a catchment and (ii) to identify hot spots at the catchment scale with respect to 16 solutes along different flow paths.

The first three dimensions of the Isomap analysis explained 48%, 30% and 11%, respectively, i.e. 89% of the variance in the data set. Scores of the first three dimensions could be ascribed to three predominating bundles of biogeochemical processes: (i) redox processes, (ii) acid-induced podzolization, and (iii) weathering processes, based on the relationship between SO<sub>4</sub>, NO<sub>3</sub>, Mn, K, Mg, Ca, Fe and Si concentrations, electric conductivity and pH values with respect to the first dimension, between DOC, Fe, Al, SO<sub>4</sub>, Na and pH values with respect to the second dimension, and between Cl, Si, NH<sub>4</sub>, K, Na, Al and SO<sub>4</sub> concentrations and pH values with respect to the third dimension. Along the flow paths from upslope soils, the upper 90 cm layer could be considered as a hot spot both with respect to acid induced podzolization and weathering processes. Nearly 53% of the variance with respect to acid-induced podzolization could be traced back to the hot spot which represented only 2% of the total spatial volume of the catchment. Along the wetland flow paths, hot spots were found for all three bundles of biogeochemical processes, i.e. the upper 10 cm layer related both to redox processes and acid induced podzolization, and the upper 1 m layer with respect to weathering processes. Nearly 67% and 44% of the variance with respect to redox processes and acid-induced podzolization could be traced back to the respective hot spots, representing only 0.1% of the total spatial volume of the catchment. In contrast, biogeochemical processes in deep groundwater had only minor effects on the

biogeochemical turnover in catchment waters. Hot spots with respect to weathering processes along upslope and wetland flow paths could not be quantified due to effects of preferential sampling in soil solution samples. Predominating flow paths and biogeochemical processes crucial for the variability of stream water chemistry differed substantially for three streams but were consistent with presumed mixing ratios.

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Highlights:

- A systematic approach is used to identify biogeochemical hot spots in a catchment.
- Only three prevailing processes explained 89% of the variance of solute concentration.
- Hot spots were identified with respect to these different biogeochemical processes.
- Hot spots were found for all 15 solutes along different flow paths.
- Up to 97% of the biogeochemical transformation restricted to 2% of the regolith.

1 Catchments as heterogeneous, multi-species reactors: An integral approach for identifying  
2 biogeochemical hot-spots at the catchment's scale.

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22

23 Abstract

24 From a biogeochemical perspective, catchments can be regarded as reactors that transform the  
25 input of various substances via precipitation or deposition as they pass through soils and  
26 aquifers towards draining streams. Understanding and modeling the variability of solute  
27 concentrations in catchment waters require the identification of the prevailing processes,

1 determining their respective contribution to the observed transformation of substances, and the  
2 localization of “hot spots”, that is, the most reactive areas of catchments.

3 For this study, we applied a non-linear variant of the Principle Component Analysis, the  
4 Isometric Feature Mapping (Isomap), to a dataset composed of 1686 soil solution, groundwater  
5 and stream water samples and 16 variables (Al, Ca, Cl, Fe, K, Mg, Mn, Na, NH<sub>4</sub>, NO<sub>3</sub>, SO<sub>4</sub>,  
6 total S, Si, DOC, electric conductivity and pH values) from the Lehstenbach catchment in  
7 Germany, (i) to assess the contribution of the prevailing biogeochemical processes to the  
8 variability of solute concentrations in water samples taken from soils, in groundwater and in  
9 stream water in a catchment and (ii) to identify hot spots at the catchment scale with respect to  
10 16 solutes along different flow paths.

11 The first three dimensions of the Isomap analysis explained 48%, 30% and 11%, respectively,  
12 i.e. 89% of the variance in the data set. Scores of the first three dimensions could be ascribed to  
13 three predominating bundles of biogeochemical processes: (i) redox processes, (ii) acid-induced  
14 podzolization, and (iii) weathering processes, based on the relationship between SO<sub>4</sub>, NO<sub>3</sub>, Mn,  
15 K, Mg, Ca, Fe and Si concentrations, electric conductivity and pH values with respect to the  
16 first dimension, between DOC, Fe, Al, SO<sub>4</sub>, Na and pH values with respect to the second  
17 dimension, and between Cl, Si, NH<sub>4</sub>, K, Na, Al and SO<sub>4</sub> concentrations and pH values with  
18 respect to the third dimension. Along the flow paths from upslope soils, the upper 90 cm layer  
19 could be considered as a hot spot both with respect to acid induced podzolization and  
20 weathering processes. Nearly 53% of the variance with respect to acid-induced podzolization  
21 could be traced back to the hot spot which represented only 2% of the total spatial volume of the  
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28 minor effects on the biogeochemical turnover in catchment waters. Hot spots with respect to

1 weathering processes along upslope and wetland flow paths could not be quantified due to  
2 effects of preferential sampling in soil solution samples. Predominating flow paths and  
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4 substantially for three streams but were consistent with presumed mixing ratios.

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6 Keywords: biogeochemical processing, biogeochemical hot spots, Isometric Feature Mapping,  
7 chemical variability

## 10 1. Introduction

11 Catchments can be regarded as reactors for various dissolved organic and inorganic substances.  
12 Rainwater, fog, snow melt water and dissolved solutes infiltrate the soil or run off the soil  
13 surface on their way towards receiving streams (Neal et al., 1997; Stutter et al., 2006). Extensive  
14 field work and modeling studies have shown that subsurface water follows distinct flow paths  
15 rather than becomes completely mixed, even in shallow soil catchments (Biggs et al., 2006;  
16 Church, 1997; Hill, 1990; Rademacher et al., 2005). Along these flow paths a variety of  
17 biogeochemical processes occur that modify solute concentration (Biggs et al., 2006; McClain  
18 et al., 2003; Soulsby et al., 1998; Yang et al., 2012). Attempts have been made to better  
19 understand and to model the interplay of these processes (Church 1997, McClain et al. 2003,  
20 Stutter et al., 2006) and to relate them to the catchment's structure and properties (Biggs et al.,  
21 2006; Church, 1997; Grathwohl et al., 2013; Stutter et al., 2006) as well as to determine  
22 anthropogenic impacts (Church, 1997; Foster et al., 2001; Krám et al., 1999; Vidon et al., 2010).  
23 Single flow paths differ substantially from each other in transport velocity, travel time, and  
24 geochemical properties of the matrix (Botter, 2012; Liu et al., 2008; McDonnell et al., 2010;  
25 Neal et al., 1997; Yang et al., 2012) and are therefore exposed to a variety of processes.  
26 Changes of solute concentration along single flow paths depend on the respective process  
27 kinetics relative to exposure times (Oldham et al., 2013, and references therein) and to the  
28 concentration of reagents (McClain et al. 2003), on the density of reactive sites (e.g. Chapman

1 et al., 1997; Church, 1997; Stutter et al., 2012, and references therein), and on redox conditions  
2 (e.g. Cirmo and McDonnell, 1997; Olivie-Lauquet et al., 2001; Paul et al., 2006). Consequently,  
3 there will be hot spots along the flow paths where solute concentration changes more rapidly  
4 over time, or on shorter distances, compared to other zones. Such hot spots can exist on  
5 different spatial scales, from molecular to global, depending on the system of interest (McClain  
6 et al., 2003) and can be responsible for a large part of the material turnover in aquatic  
7 ecosystems (Vidon et al., 2010). Hot spots of organic matter mineralization were found to be  
8 important in the regulation of many biogeochemical cycles in riparian zones, as pointed out by  
9 Vidon et al. (2010). Groffman et al. (2009a) demonstrated that a high percentage of the  
10 denitrification activity in ecosystems occurs in hot spots, which in turn leads to a high  
11 uncertainty in denitrification models (Groffman et al., 2009b). Thus, understanding and  
12 modeling biogeochemical processes in catchments would benefit a lot from a systematic  
13 identification and characterization of these hot spots (Groffman et al., 2009a; McClain et al.,  
14 2003; Vidon et al., 2010). Otherwise, hot spots are often linked to the presence of multiple  
15 reactants that depend on the interplay of different biogeochemical processes (McClain et al.,  
16 2003; Vidon et al., 2010). However, up to now, researchers typically do not simultaneously  
17 study hot spots for multiple chemical species.

18 This study aims at testing an integral approach for (i) assessing the contribution of the  
19 prevailing biogeochemical processes to the variability of solute concentrations in water samples  
20 taken from soils, in groundwater and in stream water in a catchment, and (ii) identifying hot  
21 spots at the catchment scale with respect to 16 different solutes along different flow paths. We  
22 have performed a statistical analysis of the chemical composition of soil pore-water,  
23 groundwater and stream water from a forested catchment using the Isomap technique. Isomap is  
24 a non-linear variant of the Principal Component Analysis (Tenenbaum et al., 2000) which has  
25 been used previously to identify the prevailing biogeochemical processes responsible for the  
26 observed chemical composition of groundwater and stream water (Lischeid and Bittersohl, 2008;  
27 Lischeid et al., 2010), and of soil pore-water (Schilli et al., 2010).

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## 2. Study area

The Lehstenbach watershed is located in the Fichtelgebirge Mountains in southeast Germany (Gerstberger et al., 2004) at 50°08'N and 11°52'E. The watershed area is 4.19 km<sup>2</sup> and the elevation ranges from 690 to 877 m a.s.l. (Fig. 1). The bedrock consists of granite. The thickness of the regolith is up to 40 m and more. Dystric cambisols and podzols predominate. Fibric histosols and dystric gleysols are found in the riparian zone, representing about one third of the watershed area (Küsel and Alewell, 2004). The area is drained by a dense network of natural streams and artificial channels (Lischeid et al., 2002). Dense Norway spruce stands (*Picea abies*) cover more than 95% of the watershed area. Annual mean air temperature is 5.3°C, and the annual mean precipitation is 1,162 mm (1971-2000 period) (Gerstberger et al., 2004). Snow pack usually develops in January, and final snow melt occurs in March (Lischeid et al., 2002). *(please place Figure 1 approximately here)*

Groundwater circulates mainly in the regolith which can be considered a porous aquifer with a saturated hydraulic conductivity of  $3 \cdot 10^{-6} \text{ m s}^{-1}$ . Mean residence time of water measured at the catchment outlet is 3.6 years (Lischeid et al., 2002). In the riparian zone, mean groundwater level is close to the surface during the whole year and more than 10 m below the surface in the upper part of the catchment.

Annual mean runoff was 470 mm during the period from 1991 to 2001 (Lischeid et al., 2010). Groundwater flow in the regolith parallel to the stream at the catchment outlet is likely to be a negligible portion of the total outflow (Lischeid et al., 2002). Stream discharge is generated by deep groundwater recharge during base flow conditions and does not fall below 0.25 mm per day, even during longer dry periods. During heavy rainstorms, the riparian zone is saturated up to the surface, thus hydrologically connected to the stream which can explain the strong increase (by a factor of 10 to 20 compared to base flow) in stream discharge during heavy rainstorms (Lischeid et al., 2002).

The watershed is still highly affected by atmospheric depositions (sulfur oxides, nitrogen oxides, protons, base cations) that peaked in the 1970s and steadily decreased thereafter (Matzner et al.,



1 2004). In general, Ca and Na are the predominating cations in streams and groundwater  
2 (Lischeid et al., 2004). The waters are acid and mostly hydrogen carbonate-free with a pH  
3 between 3.3 and 6.

### 4 5 6 3. Methods

#### 7 3.1 Sampling and chemical analysis

8 Soil solution, groundwater and stream water samples were taken along different flow paths in  
9 the catchment and were analyzed for different chemical variables. The sampling strategy was  
10 chosen with the aim to sample all water compartments relevant to assessing the chemical  
11 evolution along the different flow paths: flow paths from upslope soils to an upslope spring,  
12 from upslope soils to the catchment outlet, and wetland flow paths (Fig. 2). Sampled water  
13 compartments were chosen along the flow paths: soil solution from upslope soils and from the  
14 wetland, i.e. close to the input boundary; groundwater from upslope sites and from the wetland,  
15 and water from an upslope spring, the Moorbach stream and the eastern tributary of the  
16 Lehstenbach stream, representing solute output from the upslope sites, the wetland site and the  
17 catchment, respectively. It was assumed that these sampling sites represented to a sufficient  
18 degree the different water sources in the catchment. *(please place Figure 2 approximately here)*

19 Sampling was carried out between March 2005 and April 2008. Samples were taken at 10  
20 upslope sites (Coulissenhieb site, upslope groundwater sampling sites), the wetland site and 3  
21 spring and stream water sampling sites (Fig. 1), mostly at monthly intervals at least. In total, the  
22 data set included 16 variables of 1686 samples: Al, Ca, Cl, Fe, K, Mg, Mn, Na, NH<sub>4</sub>, NO<sub>3</sub>, SO<sub>4</sub>,  
23 total S, Si, DOC, electric conductivity, and pH values.

24 At the Coulissenhieb site, upslope soil solution was collected by 27 ceramic suction cups  
25 installed at 0.03, 0.2 and 0.9 m depth within nine plots. Three of the plots were subject to a  
26 freezing/thawing experiment (for more details see Muhr et al., 2008). At the upslope  
27 groundwater sampling sites, groundwater samples were taken with a submersed pump in 8  
28 observation wells gauged down to at least 10 m depth, and with a maximal gauging depth of 26

1 m. At the sampling sites GW03, GW13, GW15 and GW20, one or two additional piezometers  
2 beside the observation well allowed sampling the groundwater at lesser depths (shallow  
3 groundwater). They were installed in 2.2 m and 3.2 m (GW03), in 2.0 m and 3.0 m (GW13), in  
4 4.1 m (GW15), and in 0.9 and 1.9 m (GW20) below the surface. Spring water from the upslope  
5 spring near the catchment border was collected as grab samples.

6 The wetland site (Fig. 1) is a slightly acidic fen near the catchment outlet with an area of 0.08  
7 km<sup>2</sup> (Reiche et al., 2009). The thickness of the peat layer on top of the mineral soil ranges  
8 between 30 and 70 cm. Soil solution from this wetland site was collected by 18 ceramic suction  
9 cups installed in 0.1, 0.2 and 0.4 m depth within six different plots. The ceramic cups operated  
10 at a continuous suction of -25kPa. A dense network of 36 piezometers at 0.4 m depth and at 1 m  
11 depth, respectively, was installed within the six plots for groundwater sampling using an air-  
12 tight vacuum system pump to prevent water from mixing with oxygen during sampling. Three  
13 of the six plots were subject to two drying/rewetting experiments in August and in September  
14 2006, and from May to July 2007 (for more details see Reiche et al., 2009).

15 The wetland is drained by the ephemeral Moorbach stream. Stream water samples were taken  
16 with an automatic sampler at daily intervals. Samples taken during runoff events were selected  
17 and analyzed. Stream water samples from the eastern tributary of the Lehstenbach stream close  
18 to the catchment outlet were taken as grab samples, mainly during base flow conditions.

19 Samples from the western tributary were not included because of contamination from road salt  
20 (Lischeid and Bittersohl, 2008). The portion of wetland areas in the (sub)catchments of the  
21 upslope spring, the Moorbach stream and the Lehstenbach stream was 0%, 100% and 35%,  
22 respectively. Along the different flow paths, water samples were attributed to different sampling  
23 groups depending on the sampling depth of the water samples as summarized in Tab. 1. Two  
24 upslope groundwater sampling sites were the only ones with a sampling depth of 4.1 and 26 m,  
25 respectively and, in addition, were sampled only once. Thus, although included in the Isomap  
26 analysis, the 2 water samples from these sites were not explicitly considered for the water  
27 sampling groups. *(please place Table 1 approximately here)*

1 Soil solution, groundwater, spring water and water from the eastern tributary of the Lehstenbach  
2 stream were sampled at monthly intervals. Additional sampling campaigns were performed at  
3 the end of the drought period and after rewetting during both experiments at the wetland site for  
4 soil solution and groundwater sampling and for upslope soil solution sampling at the  
5 Coulissenhieb site.

6 Water and soil solution samples were filtered through a cellulose-acetate-membrane filter with  
7 0.45  $\mu\text{m}$  pore size. They were stored in polyethylene bottles in the dark at 2°C until further  
8 analysis. Element concentrations of Al, Ca, Fe, K, Mg, Mn, Na, total S and Si were analyzed by  
9 ICP-OES (Varian Vista-Pro CCD Simultaneous). Cl, NO<sub>3</sub> and SO<sub>4</sub> were analyzed using ion  
10 chromatography (IC Dionex DX 500), DOC by temperature combustion and subsequent  
11 determination of CO<sub>2</sub> (Analytik Jena Multi N/C 2100 F), NH<sub>4</sub> by Flow Injection Analysis (FIA-  
12 LAB by MLE). Quality assurance of the data was performed prior to this study by the  
13 BayCEER central laboratory. Electric conductivity was measured with a TetraCon<sup>®</sup> 325  
14 conductivity cell (WTW), pH values with a SenTix<sup>®</sup> 41-3 electrode (WTW).

15

### 16 3.2 Isometric Feature Mapping (Isomap)

17 The Isomap approach is based on classical multidimensional scaling (CMDS) (Tenenbaum et al.,  
18 2000). It has shown higher efficiency in representing the variance of a given data set compared  
19 to the linear Principal Component Analysis (PCA) (Tenenbaum et al., 2000, Mahecha et al.,  
20 2007). Geodesic distances between faraway points are estimated by summing up a sequence of  
21 euclidian distances between neighboring points in order to preserve non-linear structures in the  
22 dataset. In a first step for every data point the k nearest neighbors are determined. The selection  
23 of k is based on a trial-and-error approach. Then, Isomap estimates the geodesic distances  
24 between all pairs of points by determining the smallest sum of the interpoint distances  
25 determined in the first step. In the last step, CMDS is applied to the estimated geodesic  
26 distances, projecting the nonlinear structures of the dataset onto a low-dimensional ordination  
27 space. The method is described in detail in Lee and Verleysen (2007).

1 Values less than the limit of quantization were replaced by 0.5 times that limit. Missing values  
2 were replaced by the mean of the respective parameter. The data were then normalized to zero  
3 mean and unit variance for each variable separately. All statistical analyses were performed  
4 using the R statistical software environment (R Development Core Team, 2006).  
5 Each of the dimensions given by the Isomap analysis “represent” variables that are correlated  
6 with each other, irrespective of the type of relationship. These dimensions can be interpreted  
7 corresponding to the linear principal components. However, they are not necessarily linear.  
8 Thus, Spearman’s rank correlation coefficients between single dimensions and variables were  
9 calculated. The variables with the highest Spearman coefficient with each single Isomap  
10 dimension were selected and considered to be the key variables for the dimensions. The Isomap  
11 analysis has been performed with the package “vegan” (Oksanen et al., 2007).  
12 The performance of the Isomap approach was evaluated by the Pearson correlation between the  
13 interpoint distances in the high dimensional original data space with the interpoint distances in  
14 the low dimensional Isomap data space. The measure gives a value of one for a perfect fit, close  
15 to zero for a very poor fit, and is referred to as “explained variance” in the following.  
16 The median of the dimension scores and the variance were calculated for each of the sampling  
17 groups for the first three Isomap dimensions in order to assess the macro scale variability of  
18 dimension scores along the different flow paths and the variability within one sampling group,  
19 respectively.

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### 21 5.2.3 Quantifying the fraction of variance explained by hot spots

22 Considerable changes of the median of dimension scores on short distances along the flow paths  
23 were assumed to represent hot spots. These hot spots represent a certain fraction of the total  
24 variance of dimension scores explained by a certain Isomap dimension. The former was  
25 calculated using the difference between the minimum and the maximum median of dimension  
26 scores within a hot spot relative to the difference between the minimum and the maximum  
27 median of dimension scores of all water sampling groups, which was assumed to represent  
28 100% of the variance explained by the Isomap dimension. Furthermore, these hot spots only

1 constitute a fraction of the total spatial volume of the catchment. The latter was calculated using  
2 an assumed thickness of the regolith of 35 m, and the total catchment area of 4.19 km<sup>2</sup>. The  
3 fractions of the hot spots were calculated using the thickness of the hot spot, the portion of the  
4 non-wetland (65% of 4.19 km<sup>2</sup>) and the wetland area (35% of 4.19 km<sup>2</sup>) in the catchment for the  
5 hot spots of upslope soils and of wetland soils, respectively, relative to the total spatial volume  
6 of the catchment. The quantification was realized for those hot spots that were identified in the  
7 results and the discussion section and could not be realized for all hot spots (see section 5).

## 10 4. Results

### 11 4.1 Non-linear statistical analysis

12 The performance of the Isomap analysis depends on the choice of the parameter  $k$ , i.e. the  
13 number of neighbor points for determination of the geodesic distances (Tenenbaum et al., 2000).

14 In our study, the best performance was found for  $k = 1190$  by systematical variation of this  
15 parameter. *(please place Figure 3 approximately here)*

16 The first three Isomap dimensions represented about 89% of the variance (Fig. 3). Only the first  
17 three dimensions will be interpreted in this study that represented 48%, 30% and 11% of the  
18 variance of the interpoint distances of the data set, respectively. The 4<sup>th</sup> to 10<sup>th</sup> Isomap  
19 dimensions exhibited only minor contributions to the explained variance.

20 High scores of the 1<sup>st</sup> Isomap dimension were associated with high SO<sub>4</sub>, NO<sub>3</sub>, Mn, K, Mg and  
21 Ca concentrations and with high electric conductivity values, low scores with high Fe and Si  
22 concentrations and high pH values (Fig. 4). Some relationships exhibited strongly non-linear  
23 patterns, e.g., electric conductivity or Fe concentration versus scores of the first dimension (Fig.  
24 5). The second dimension was positively correlated with DOC, Fe and Al, and negatively with  
25 SO<sub>4</sub>, Na and pH (Fig. 4). The 3<sup>rd</sup> dimension was characterized by positive loadings of Cl, Si,  
26 NH<sub>4</sub>, K, Na and pH values and negative loadings of Al and SO<sub>4</sub>. *(please place Figure 4 and Figure*  
27 *5 approximately here)*

1 4.2 Changes of dimension scores along the flow paths (*please place Figure 6 approximately here*)  
2 The scores of the first three Isomap dimensions varied systematically among the different  
3 sampling groups along each flow path (Fig. 6). Scores of the 1<sup>st</sup> dimension were considerably  
4 lower for the wetland flow paths compared to those from the upslope soils and decreased with  
5 depth in the wetlands (Fig. 6). Correspondingly, scores of the Moorbach stream with 100%  
6 wetland area in its catchment were the lowest, and those of the upslope spring without any  
7 wetland in its catchment were the highest, similar to those of the upslope soils (Fig. 6). In the  
8 deep groundwater of the upslope sites only a minor decrease of dimension scores was observed.  
9 In contrast, both at the upslope soils and in the wetlands, considerable modifications of the  
10 scores of the 2<sup>nd</sup> and 3<sup>rd</sup> dimension were observed (Fig. 6), indicating hot spots in the uppermost  
11 soil horizons. In the upslope soils, scores of the 2<sup>nd</sup> dimension decreased down to a depth of 3  
12 meters with a sharp decrease within the uppermost 0.9 m soil layer, and leveled off in the deep  
13 groundwater at greater depth. Along the wetland flow paths, scores of the 2<sup>nd</sup> dimension were  
14 around 0 for the first 40 cm, i.e., within the peat layer, and then decreased down to 1 m depth.  
15 Similar to the 1<sup>st</sup> dimension, scores of the 2<sup>nd</sup> dimension were considerably lower for the  
16 wetland topsoil than those for the upslope topsoil. Among the stream water samples, those of  
17 the Moorbach stream exhibited the highest scores, whereas those of the upslope spring and of  
18 the catchment runoff were almost identical.  
19 Along the flow paths from the upslope soils, scores of the 3<sup>rd</sup> dimension decreased down to 0.9  
20 m depth and then increased again down to 16 m depth, whereas along the wetland flow paths a  
21 clear increase of scores was observed. Among the three streams, the catchment runoff exhibited  
22 the highest values of the scores of the 3<sup>rd</sup> dimension, and the upslope spring the lowest.  
23 For all three dimensions, the scores of all three streams were always within the range of soil  
24 solution and groundwater sampling groups (Fig. 6). Scores of the 1<sup>st</sup> dimension for the upslope  
25 spring were in the same range as was found for upslope soil solution samples, scores of the 2<sup>nd</sup>  
26 and 3<sup>rd</sup> dimension in the range of upslope soil solution in 0.9 m depth, and of shallow  
27 groundwater in 2 m depth.

28

### 4.3 Quantifying the fraction of variance explained by hot spots

Based on the results and the discussion (see section 5) of the hot spots, the fraction of variance explained by hot spots was calculated for the uppermost 0.1 m soil layer in the wetlands with respect to the 1<sup>st</sup> and the 2<sup>nd</sup> Isomap dimension and for the first 0.9 m of flow paths from upslope soils with respect to the 2<sup>nd</sup> dimension. Results are given in Tab. 2. The corresponding fractions of the spatial volume represented by these hot spots are given in Tab. 3.

*(please place Table 2 and Table 3 approximately here)*

## 5. Discussion

### 5.1 Process identification using the Isomap approach

Differing solute concentrations in water samples reflect reactions that occurred along the flow paths. The Isomap analysis revealed some very strong relationships between dimension scores and the concentration of specific constituents. This observation implies the following biogeochemical interpretation: Dimensions reflect characteristic chemical signatures generated by a variety of biogeochemical processes, provided that the water volume's exposure time to the respective biogeochemical processes is clearly longer than its characteristic reaction time. Only then will these processes exert an imprinting effect on the chemical composition of water samples (Oldham et al., 2013). Such preconditions are met at locations in the catchment where boundary conditions for the respective biogeochemical processes are favorable, depending on the concentration of reactants and the chemical state (e.g., redox state, pH, or ionic strength; Cirimo and McDonnell, 1997; Lohse et al., 2009). It is assumed that this creates the observed statistical variability of dimension scores. Based on these considerations, we attempt in the following to identify biogeochemical processes characteristic for each of the three dimensions.

#### 5.1.1 First Isomap dimension

High scores of the 1<sup>st</sup> Isomap dimension were associated with high SO<sub>4</sub>, NO<sub>3</sub>, Mn, K, Mg and Ca concentration and electric conductivity values, low scores with high Fe and Si concentration and pH values (Fig. 4, Fig. 5). A similar combination of variables correlated with the 1<sup>st</sup>

1 dimension was found by Schilli et al (2010) for a soil solution data set from the same catchment.  
2 They interpreted the dimension to represent geochemical signatures influenced by atmospheric  
3 deposition. Indeed, SO<sub>4</sub>, NO<sub>3</sub>, Ca, Mg and K originate from atmospheric deposition which  
4 played a major role for the biogeochemical functioning of many forested catchments (Matzner  
5 et al., 2004 and references therein). On the other hand, the correlation of SO<sub>4</sub>, NO<sub>3</sub>, Fe, Si and  
6 pH with an Isomap dimension in a groundwater data set from the same catchment has been  
7 interpreted to represent signatures affected by redox processes (Lischeid and Bittersohl, 2008).  
8 In fact, SO<sub>4</sub>, NO<sub>3</sub>, Mn and Fe are redox sensitive variables. There seems to be a threshold value  
9 for scores of that dimension of about 0 with a substantial increase of Fe concentration below  
10 (Fig. 5) which could indicate reduced conditions. Due to technical constraints of the soil suction  
11 cups, neither oxygen concentration data nor measurements of redox potential were available  
12 which could have confirmed this interpretation.

13 Redox processes like nitrification, denitrification, Fe oxidation and reduction as well as SO<sub>4</sub>  
14 reduction and sulfide oxidation processes have been identified to be relevant at the upslope sites  
15 (e.g. Alewell and Gehre, 1999; Durka et al., 1994; Hentschel et al. 2007) and in the wetlands of  
16 this catchment (Alewell et al., 2006; Knorr et al., 2009; Küsel and Alewell, 2004; Paul et al.,  
17 2006). Indeed, high dimension scores, corresponding to high concentrations of SO<sub>4</sub> and NO<sub>3</sub>,  
18 were found mainly for oxic environments (i.e. the upslope soils and deep groundwater) whereas  
19 low dimension scores with high Fe and Si concentrations and high pH values were found mainly  
20 for anoxic environments (i.e. the wetlands). The higher pH values were in line with H<sup>+</sup>  
21 consumption during reduction processes. Higher Si concentrations could be due to "acid"  
22 groundwater discharge in the wetlands as was argued by Lischeid and Bittersohl (2008).

23 The high correlation of manganese with the first dimension has to be interpreted with caution.  
24 This correlation was mainly determined by high Mn concentrations found in newly installed  
25 groundwater wells at the upslope sites (data not shown). These high concentrations clearly  
26 decreased with time since then. It is likely that Mn in the bentonite sealing was released due to  
27 drilling (Lischeid and Bittersohl, 2008) and will therefore not be discussed further. Ammonium  
28 was not correlated with the first dimension (Fig. 4), although it originated from atmospheric



1 deposition and mineralization processes as well. This was likely due to the occurrence of  $\text{NH}_4$  in  
2 only one single sampling group, i.e. the upslope topsoil layer, due to sorption to clay minerals  
3 and oxidation in deeper soil layers.

4 We conclude that high scores of the 1<sup>st</sup> dimension characterize soil solution, groundwater and  
5 stream water which exhibits high concentration of  $\text{NO}_3$ ,  $\text{SO}_4$  and accompanying cations under  
6 oxic conditions, whereas low scores represent samples from highly reduced environments. For  
7 the sake of clarity, this dimension will be referred to as “redox” dimension hereafter, although  
8 this is certainly a simplification of a bundle of related processes.

#### 9 10 5.1.2 Second Isomap dimension

11 The positive correlation between DOC, Fe and Al, and the scores of the 2<sup>nd</sup> dimension as well as  
12 the negative correlation with pH values (Fig. 4) is a typical signature for podzolization

13 processes (Lundström et al., 2000). This interpretation follows the reasoning of Schilli et al.  
14 (2010), who found similar results for a soil solution data set of the Lehstenbach catchment.

15 Scores of the 2<sup>nd</sup> dimension were the highest at shallow depth at the upslope soils (Fig. 6)  
16 reflecting the high values of DOC, Fe and Al in the forest floor and the accumulation horizons  
17 (Bh, Bs) of the podzol in about 20 cm depth. Scores decreased with depth, which can be  
18 interpreted by observations made in previous process studies in the catchment. Decreasing DOC,  
19 Fe and Al concentrations with increasing depth in the podzols of the catchment were attributed  
20 to microbial decay, sorption of DOC onto Fe and Al oxides/hydroxides, and (co)precipitation  
21 with Fe and Al (Kalbitz and Kaiser, 2008; Kalbitz et al., 2004).

22 Low scores of that dimension came along with enhanced  $\text{SO}_4$  and Na concentrations and higher  
23 pH values as were found in the deeper layers of upslope soils (shallow groundwater) and in  
24 deep groundwater (Fig. 6). The high  $\text{SO}_4$  concentrations would be consistent with the acidifying  
25 effects of high sulfur deposition mainly during the 1960s and 1970s (Matzner et al., 2004),  
26 which enhanced podzolization processes and mineral weathering (Huang et al., 2013; Maitat  
27 et al., 2000). The latter was reflected by the simultaneous correlation between  $\text{SO}_4$  and Na that

1 originates mainly from hydrolysis of feldspars (Weyer et al., 2008) occurring predominantly at  
2 greater depths in the deeply weathered granitic bedrock (Lischeid et al., 2002). A negative  
3 correlation between DOC and  $\text{SO}_4$  has been found in numerous streams across North America  
4 and northern and central Europe, simultaneously with the decline of  $\text{SO}_4$  deposition in these  
5 regions (Borken et al. 2011; Monteith et al., 2007).  
6 Denitrification and sulfide oxidation in the wetlands increase the alkalinity (Alewell and  
7 Matzner, 1993; Lindemann, 1997). Thus, acid-induced podzolization is not that relevant for the  
8 wetland site with fibric histosols and dystric gleysols. Correspondingly, the scores of the 2<sup>nd</sup>  
9 dimension in the peat layer of the wetland site (down to 0.4 m depth) were lower compared to  
10 those of the upslope soils (Fig. 6). To conclude, this dimension seems to reflect chemical  
11 signatures affected by acid-induced podzolization and associated reactions.

12

### 13 5.1.3 Third Isomap dimension

14 High scores of the 3<sup>rd</sup> dimension were found in the forest floor and in the deeper layers of  
15 upslope soils (shallow groundwater), in the deep groundwater, and in the deeper layers at the  
16 wetland site and were associated with higher values of Na, Si,  $\text{NH}_4$ , K, Cl and pH. Low scores  
17 were observed in waters sampled at 0.2 and 0.9 m depth of upslope soils and at 0.1 m depth at  
18 the wetland site and were associated with high values of Al and  $\text{SO}_4$  (Fig. 4, Fig. 6).

19 Silicon and Na originate mainly from silicate weathering in deeper layers of the catchment  
20 (Weyer et al., 2008) which was in line with the high scores in shallow and deep groundwater  
21 (Fig. 6). The same holds true for the deeper layers at the wetland site, where high clay content  
22 was found. The positive correlation between the 3<sup>rd</sup> Isomap dimension and the pH values seems  
23 to corroborate weathering as the key process for the chemical signature reflected by this  
24 dimension.

25 High dimension scores were also found in the organic layer of the topsoil of upslope soils where  
26 silicate weathering is an unlikely process. Instead, base cation release by cation exchange was  
27 indicated by the correlation of the third dimension with  $\text{NH}_4$  and K that originate from  
28 atmospheric deposition or internal cycling of organic matter.

1 In addition, Cl was positively correlated with the 3<sup>rd</sup> dimension (Fig. 4). In contrast to Si and Na,  
2 weathering of the granite can be excluded as a Cl source. Instead, the catchment receives  
3 considerable amounts of Cl via deposition (Matzner et al., 2004). It is the only one of the  
4 predominating three anions in soil solution and groundwater (Cl, NO<sub>3</sub>, SO<sub>4</sub>) which is not subject  
5 to biological or redox processes or to sorption to the matrix. Hydrogen carbonate plays only a  
6 minor role due to low pH values. Thus, any process that reduces NO<sub>3</sub> and SO<sub>4</sub> concentration, e.g.  
7 via nitrogen uptake by plants, denitrification, or sorption of sulfate will result in a relative  
8 enrichment of chloride and thus explain the positive correlation.

9 Soil acidification caused by high sulfur deposition up to the 1980s (Matzner et al., 2004) lead to  
10 high SO<sub>4</sub> concentrations and Al saturation of more than 97% of the cation exchange capacity in  
11 the mineral soil of this catchment (Gerstberger et al., 2004), indicating weathering of Al  
12 containing minerals. Similar, low scores and high Al and SO<sub>4</sub> concentration were found in the  
13 topsoil at the wetland site (Fig. 6). The lack of correlation between Al and DOC with respect to  
14 the 3<sup>rd</sup> dimension is likely due to the large C pool in the peat layer that likely did not change due  
15 to Al dynamics.

16 We propose that the chemical signature represented by the third dimension reflects the release  
17 of base cations and silicon via silicate weathering and cation exchange which had been  
18 intensified by high sulfur deposition. To give a concise label, it will be referred to as the  
19 weathering dimension in the following discussion.

20

## 21 5.2 Hot spots of biogeochemical transformation along flow paths

22 A change of Isomap dimension scores along the flow paths was assumed to indicate a change of  
23 the respective contribution of the biogeochemical transformation processes, resulting in a  
24 change of solute concentrations. Flow paths have not been determined directly, but it was  
25 assumed that seepage flux in the unsaturated zone was vertical and that groundwater flow was  
26 horizontal. This presumably holds true for shallow groundwater in the wetlands (Fig. 2). Thus,  
27 the gradients of dimension scores over depth in the unsaturated zone cannot be compared  
28 directly with those in the deep groundwater and at the wetland site. In addition, transport

1 velocity presumably differs between the different sampling sites and sampling depths and will  
2 not be constant in time. Thus, our results do not allow direct inference of transformation rates of  
3 different processes. Nevertheless, zones of major change of dimension scores on short distances  
4 likely represent the most reactive areas of the catchment with respect to these processes.

#### 5 6 5.2.1 First Isomap dimension

7 The chemical signature described by the 1<sup>st</sup> dimension seems to be hardly modified in the  
8 unsaturated zone of the upslope soil and aquifer as it remained constant throughout the entire  
9 catchment except in wetlands (Fig. 6). In contrast, in wetland soils a sharp decrease of oxygen  
10 concentrations is typically found within the upper 10 cm of wetland soil profiles in the  
11 Lehstenbach catchment (Knorr et al., 2009), pointing to a considerable impact of anoxic  
12 mineralization processes. In fact, despite the same input signal (open field precipitation and  
13 throughfall), the scores of the 1<sup>st</sup> dimension for the wetland topsoil were lower than those for the  
14 upslope topsoil. This suggests that the uppermost 10 cm layer of the wetland soils had a major  
15 impact on the chemical composition of the water with respect to the redox processes. In fact, the  
16 highest rates of Fe(II) formation and SO<sub>4</sub> consumption were found between 0 and 10 cm depth  
17 in anoxic microcosm experiments (Küsel et al., 2008). Below 10 cm depth, scores of the 1<sup>st</sup>  
18 dimension decreased only slightly. Thus, the uppermost 10 cm layer of the wetland soils can be  
19 considered as a major hot spot that accounts for the largest fraction of biogeochemical turnover  
20 by redox processes.

#### 21 22 5.2.2 Second Isomap dimension

23 Scores of the 2<sup>nd</sup> dimension decreased down to 3 m depth with a sharp decrease within the  
24 uppermost 0.9 m layer at the upslope sites (Fig. 6). Correspondingly, scores of the 2<sup>nd</sup>  
25 dimension decreased with depth in wetland soils. It is remarkable that scores at 0.9 m depth are  
26 about the same in upslope and wetland soils, whereas those at 10 cm depth were clearly lower in  
27 the wetland soils compared to the upslope soils. As has been observed for the 1<sup>st</sup> dimension, the  
28 uppermost 10 cm layer of the wetland soils seems to play a major role for acid-induced

1 podzolization processes associated with the 2<sup>nd</sup> dimension. In fact, the top of the small  
2 hummocks in the wetland was not permanently water saturated which likely lead to at least  
3 temporary oxic conditions (Frei et al. 2010). Likewise, the oxic topsoil layer at another wetland  
4 site in the same catchment saturated only during single rainstorms and snowmelt events  
5 (Lischeid et al. 2007).

6 The impact of podzolization processes seems to be restricted to the uppermost 3 m layer at the  
7 upslope sites. This pattern may have been amplified by the acidifying effects of historical high  
8 sulfur deposition, the location of which has now moved to a few m depth (Lischeid, 2001;  
9 Lischeid et al., 2004; Matzner et al., 2004), enhancing podzolization and mineral weathering.

#### 10 11 5.2.3 Third Isomap dimension

12 In the wetland soils, a continuous increase of scores of the 3<sup>rd</sup> dimension down to 1 m depth  
13 (Fig. 6) points to a considerable change of the chemical state affecting processes related to  
14 weathering and cation exchange. However, at the upslope sites, a corresponding increase of  
15 scores with depth is restricted to depths below 0.9 m, and is tending to level off at greater depths  
16 in the aquifer. In contrast, there is a clear decrease of scores from the topsoil down to 0.9 m  
17 depth, which is exactly the opposite of the pattern found in the wetland soil (Fig. 6).

18 This contradicts the assumption of an approximately monotonous transformation of solute  
19 concentration along the flow path. There is some evidence that samples from suction cups at  
20 different depths may not represent a continuum of the same flow path, but rather the immobile  
21 fraction of soil solution (Brandi-Dohrn et al., 1996; Landon et al., 1999). The immobile fraction  
22 is characterized by a rather long residence time. In addition, the immobile soil water fraction is  
23 located more in small diameter pores with a large interface between soil solution and soil matrix.  
24 This immobile fraction interacts with the soil matrix, whereas there is less influence of soil  
25 matrix on the mobile fraction at the same depth. This holds especially true during the growing  
26 season, when the topsoil desiccates and suction cups sample only the immobile fraction. Below  
27 1 m depth, soil water content hardly decreased during the growing season. In contrast, the  
28 wetland topsoil was close to saturation even during the growing season. Thus, the effect of

1 preferentially sampling the immobile soil solution fraction due to the use of suction cups was  
2 restricted to the upslope top soil, and was the largest in the uppermost soil layer. The effect of  
3 sampling with suction cups is less critical at greater depths because of greater mixing of soil  
4 solution from different pore sizes at greater depth (Guber et al., 2008; Hohenbrink and Lischeid,  
5 2014; Kamgar et al., 1993).

### 6 7 5.2.3 Quantifying the fraction of variance explained by biogeochemical hot spots

8 The hot spots identified above are assumed to account for a large fraction of biogeochemical  
9 turnover with respect to different biogeochemical processes. This fraction of biogeochemical  
10 turnover was estimated using the medians of dimension scores (Tab. 2). The difference between  
11 the minimum and the maximum median of dimension scores of all water sampling groups was  
12 assumed to represent 100% of the biogeochemical turnover with respect to the biogeochemical  
13 processes. Correspondingly, the difference between the minimum and the maximum median of  
14 dimension scores within a hot spot represents a certain fraction of the total turnover in the  
15 catchment. Nearly 67% of the variance traced back to redox processes and nearly 53% and 44%  
16 traced back to acid induced podzolization could be explained by the hot spots along the flow  
17 paths from upslope soils and along the wetland soils, respectively (Tab. 2). These seem to be  
18 plausible numbers, given the role of riparian zones for redox processes and the role of the upper  
19 soil layer for podzolization processes. For the hot spots of weathering processes, quantification  
20 was not possible because of the effects of preferential sampling of soil solution samples. Given  
21 the results for the fractions of the spatial volume of the whole catchment represented by the hot  
22 spots (Tab. 3), these results emphasize the important role of hot spots for biogeochemical  
23 turnover in the catchment, which is restricted to a very small part of the spatial volume.

### 24 25 5.2.4 Streams

26 Spring and stream sampling sites could not be ascribed to specific positions along a single flow  
27 path, as they integrate the contributions of most flow paths. However, different flow paths can

1 contribute in varying degrees to surface water chemistry. Thus, the results of the Isomap  
2 analysis help to identify the respective predominant ones.  
3 Scores of all three dimensions at the upslope spring water were in the range of those of soil  
4 solution (at 0.9 m depth) and of shallow groundwater (2 m depth). This is in line with the  
5 findings of Lischeid and Bittersohl (2008), who found waters from several upslope springs very  
6 similar to upslope groundwater from shallow depths. Similarly, waters discharging to the spring  
7 were clearly marked by oxic mineralization processes (1<sup>st</sup> dimension), moderately influenced by  
8 acid induced podzolization (2<sup>nd</sup> dimension) but rather strongly influenced by Al releasing  
9 weathering reactions (3<sup>rd</sup> dimension) as was typical for groundwater from shallow depths  
10 outside the wetlands.

11 The concept of near-surface runoff generation in the wetlands (given by Lischeid and Bittersohl  
12 (2008)) is consistent with dimension scores of the Moorbach stream samples which are similar  
13 to those of shallow wetland soils. The Isomap results point to strong evidence of anoxic  
14 mineralization processes (1<sup>st</sup> dimension) and of Al releasing weathering reactions (3<sup>rd</sup>  
15 dimension), and to minor evidence of acid induced podzolization (2<sup>nd</sup> dimension).

16 For the eastern tributary of the Lehstenbach stream near the catchment outlet, scores of all three  
17 dimensions were intermediate between deep groundwater and water from the wetland flow  
18 paths, as was expected. One third of the catchment area is covered by wetlands. Thus, wetland  
19 runoff as well as deep groundwater discharging from upslope soils mix in the Lehstenbach  
20 stream (Küsel and Alewell, 2004; Lischeid et al., 2002). In our study, the Lehstenbach stream  
21 was sampled mainly during base flow conditions, when mainly groundwater was discharging to  
22 the stream (Lischeid et al., 2002). During runoff events, the riparian zones are hydrologically  
23 connected to the stream, presumably shifting dimension scores towards those of the wetland  
24 samples.

25  
26 The results of our study showed that up to 97% of the biogeochemical transformation of the  
27 chemical composition of soil solution, groundwater and stream water in the Lehstenbach  
28 catchment was restricted to less than 2% of the catchment's regolith, i.e., to the uppermost 0.1

1 or 0.9 m soil layer. Biogeochemical processes in the deeper aquifer played a negligible role. In  
2 addition, processes that were described by the 1<sup>st</sup> Isomap dimension were restricted to material  
3 turnover in wetland soils. For those associated with the 2<sup>nd</sup> and 3<sup>rd</sup> Isomap dimension, the  
4 uppermost 1 m layer of upslope and wetland soils was equally important. For the 3<sup>rd</sup> dimension,  
5 we found some evidence that preferential sampling of the immobile water fraction in the  
6 upslope topsoil blurred clear gradients.

7 Hot spots are frequently described in terms of processes linked to the nitrogen or carbon cycle  
8 (Andrews et al., 2011; Groffman et al., 2009a; McClain et al., 2003; Vidon et al., 2010). Our  
9 study considered 15 different solutes and electric conductivity, and found clear evidence of hot  
10 spots for all of these solutes.

## 11 12 13 6. Conclusions

14 Regarding a catchment as a heterogeneous, multi-species reactor, our study aimed at identifying  
15 biogeochemical hot spots along different flow paths in a forested catchment based on numerous  
16 soil solution, groundwater and stream water samples. According to the results of the Isomap  
17 analysis, about 89% of the total variance could be ascribed to three different bundles of  
18 biogeochemical processes that exhibited different patterns along subsurface flow paths. In all  
19 cases, the uppermost 1 m layer of the catchment's regolith was identified as a hot spot for the  
20 respective biogeochemical processes, although the exact location differed for different process  
21 bundles at upslope sites and in wetland soils. It is remarkable that these hot spots constitute the  
22 largest fraction of the biogeochemical transformation of all of the investigated 15 solutes. On  
23 the other hand, most solutes were affected by more than one of these three process bundles, each  
24 of which had different hot spot patterns.

25 We conclude that an integral approach like that presented in this study would be a useful  
26 prerequisite for a biogeochemical modeling approach by reducing the number of processes to  
27 the predominating ones ultimately included in the model, focusing on hot spots and including



1 spatial patterns where necessary and appropriate. Thus, the approach can help develop accurate  
2 and parsimonious models commonly used for water management purposes.

3

4

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1 Figure captions:

2

3 Fig. 1: Map of the Lehstenbach watershed in the Fichtelgebirge Mountains in southeast  
4 Germany and sampling sites. Gauss-Krüger coordinates [m] are given at the axes. Black  
5 symbols: sampling sites; black dashed line: catchment border; black solid lines: streams; solid  
6 grey line: public road; grey area: riparian zone. At the sampling sites GW03, GW13, GW15 and  
7 GW20, 1 (GW15) or 2 (GW03, GW13, GW20) additional piezometers were installed at  
8 different depths.

9

10 Fig. 2: Scheme of the flow paths from upslope soils and of the wetland flow paths.

11

12 Fig. 3: Pearson correlation coefficients between the interpoint distances in the 18-dimensional  
13 data space and in the low-dimensional projection, referred to as “explained variance”, for the  
14 first 10 Isomap dimensions.

15

16 Fig. 4: Spearman coefficients ( $\rho$ ) between the analyzed variables and the first three Isomap  
17 dimensions. Grey shading is proportional to Spearman  $\rho$ . El. Cond.: electric conductivity

18

19 Fig. 5: Scatter plots of the first Isomap dimension (y-axis) versus electric conductivity [ $\mu\text{S cm}^{-1}$ ]  
20 and Fe concentrations [ $\text{mg l}^{-1}$ ] (x-axis)

21

22 Fig. 6: Median of dimension scores for different sampling groups vs. sampling depth for the  
23 first three Isomap dimensions for different flow paths. Crossbars represent median values of  
24 dimension scores; boxes are representative for the variance of the dimension scores, and the  
25 whiskers give the 10% and 90% confidence intervals. Samples from the upslope soils at 0.9 m  
26 depth comprised soil solution and shallow groundwater samples. Samples from upslope soils at  
27 2 and 3.1 m depth were groundwater samples taken between 1.9 and 2.2 m depth and between  
28 3.0 and 3.2 m depth, respectively, and have been grouped for better visibility. Samples from the

1 wetland sites at 0.4 m depth comprised soil solution and shallow groundwater samples. Spring:  
2 Upslope spring, MB: Moorbach stream, LB: eastern tributary of the Lehstenbach stream

3

4

5 Table captions:

6

7 Tab. 1: Number of samples included in the Isomap analysis. The sampling group “Lehstenbach  
8 stream” consists of samples from the eastern tributary of the Lehstenbach stream.

9

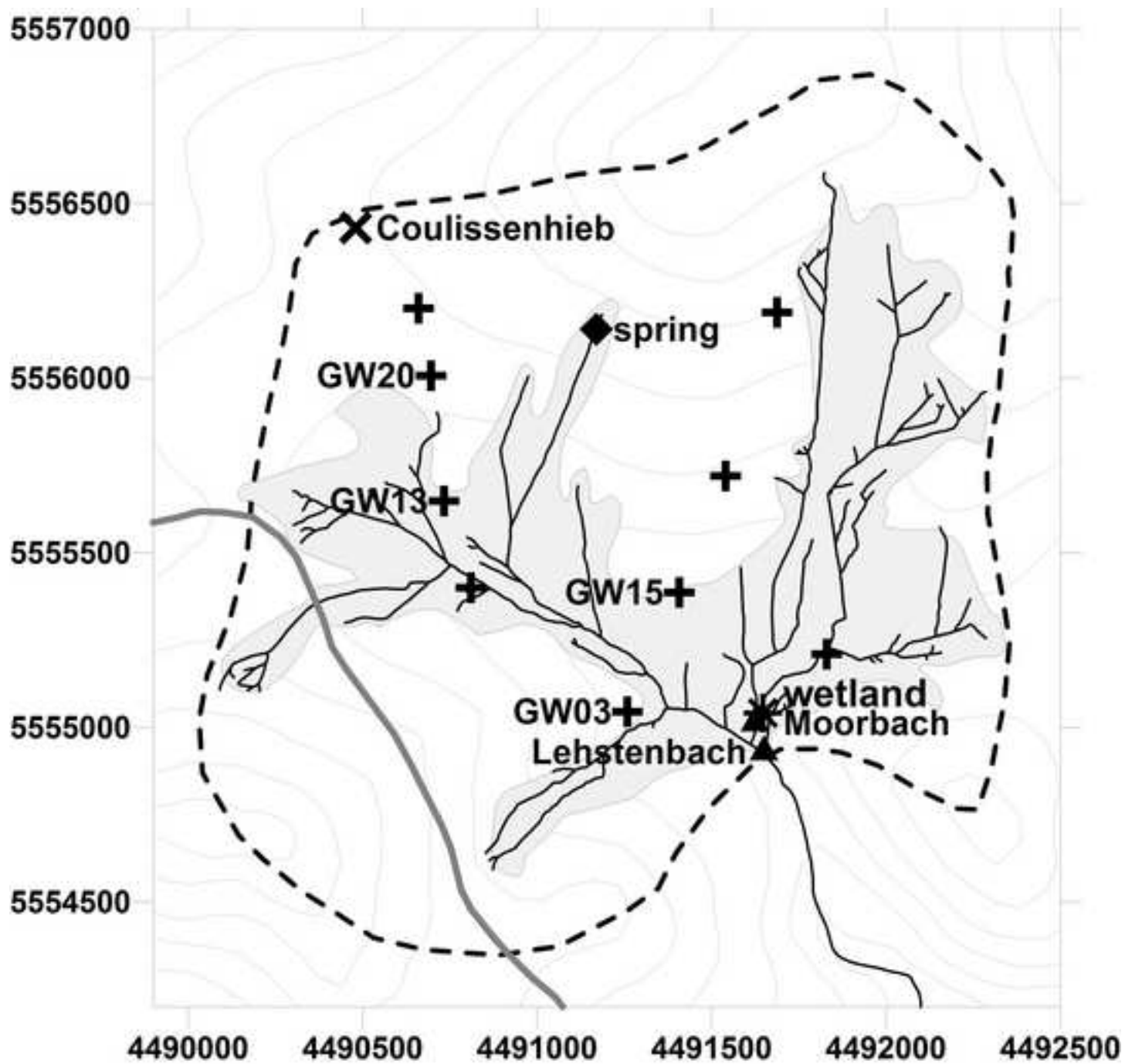
10 Tab. 2: Relative quantification of the identified hot spots with respect to the 1<sup>st</sup> and 2<sup>nd</sup> Isomap  
11 dimension, representing redox processes and acid-induced podzolization processes, respectively.

12 Sampling group: sampling groups representing the minimum and maximum median of  
13 dimension scores of all sampling groups in the catchment or of the hot spot, respectively. The  
14 fraction of variance explained was calculated as the ratio between the difference between the  
15 minimum and the maximum median of dimension scores for the hot spot, and the difference  
16 between the minimum and maximum median of dimension scores of the whole catchment.

17

18 Tab. 3: Fraction of the catchment’s spatial volume represented by the identified hot spots with  
19 respect to the 1<sup>st</sup> and 2<sup>nd</sup> Isomap dimension, representing redox processes and acid-induced  
20 podzolization processes, respectively.

Figure 1  
[Click here to download high resolution image](#)



- |                         |   |
|-------------------------|---|
| ✕ upslope soil solution | * wetland soil solution and groundwater |
| + upslope groundwater   | ▲ stream sampling sites                 |
| ◆ upslope spring        |   |

Figure 2

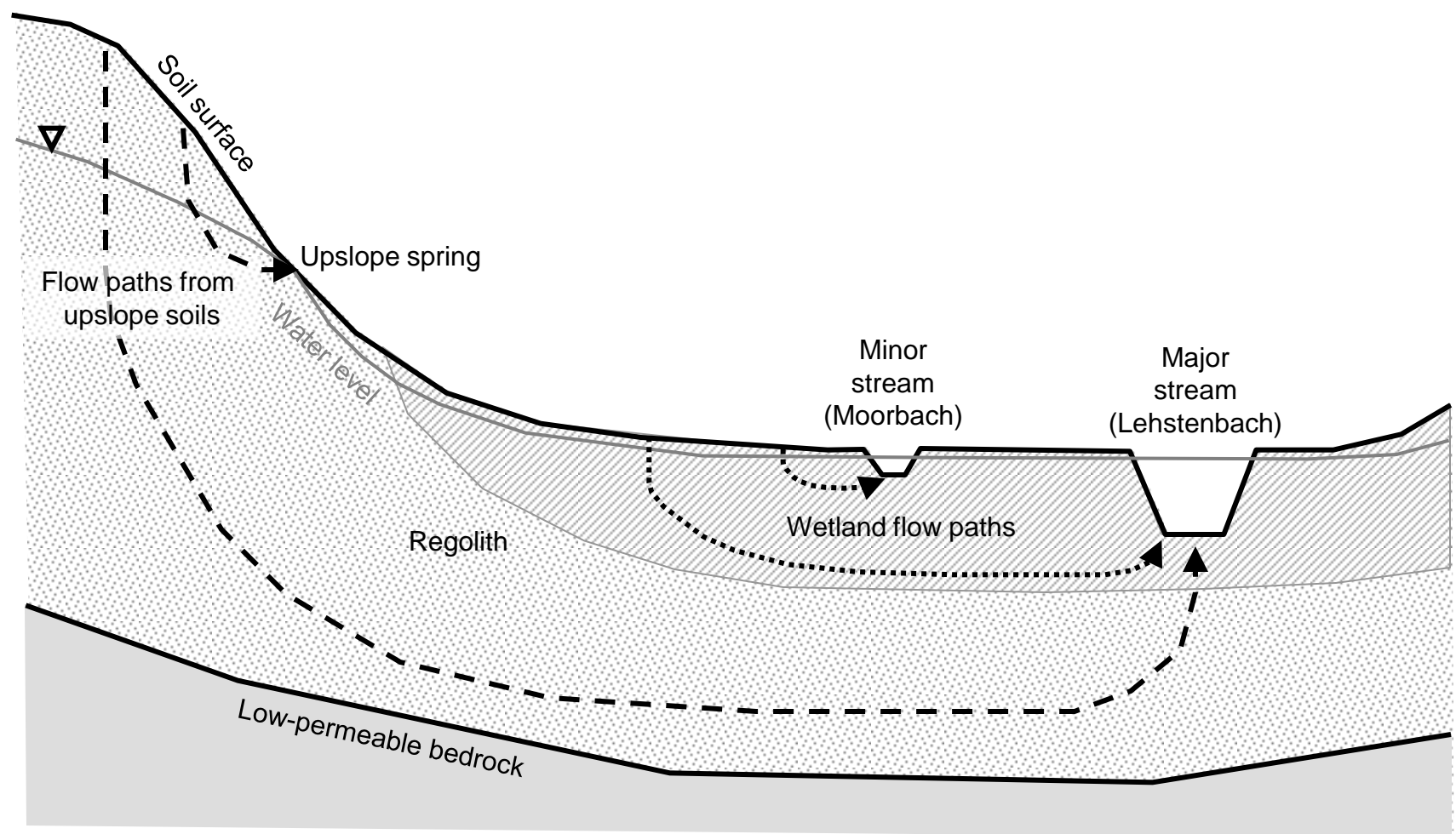


Figure 3

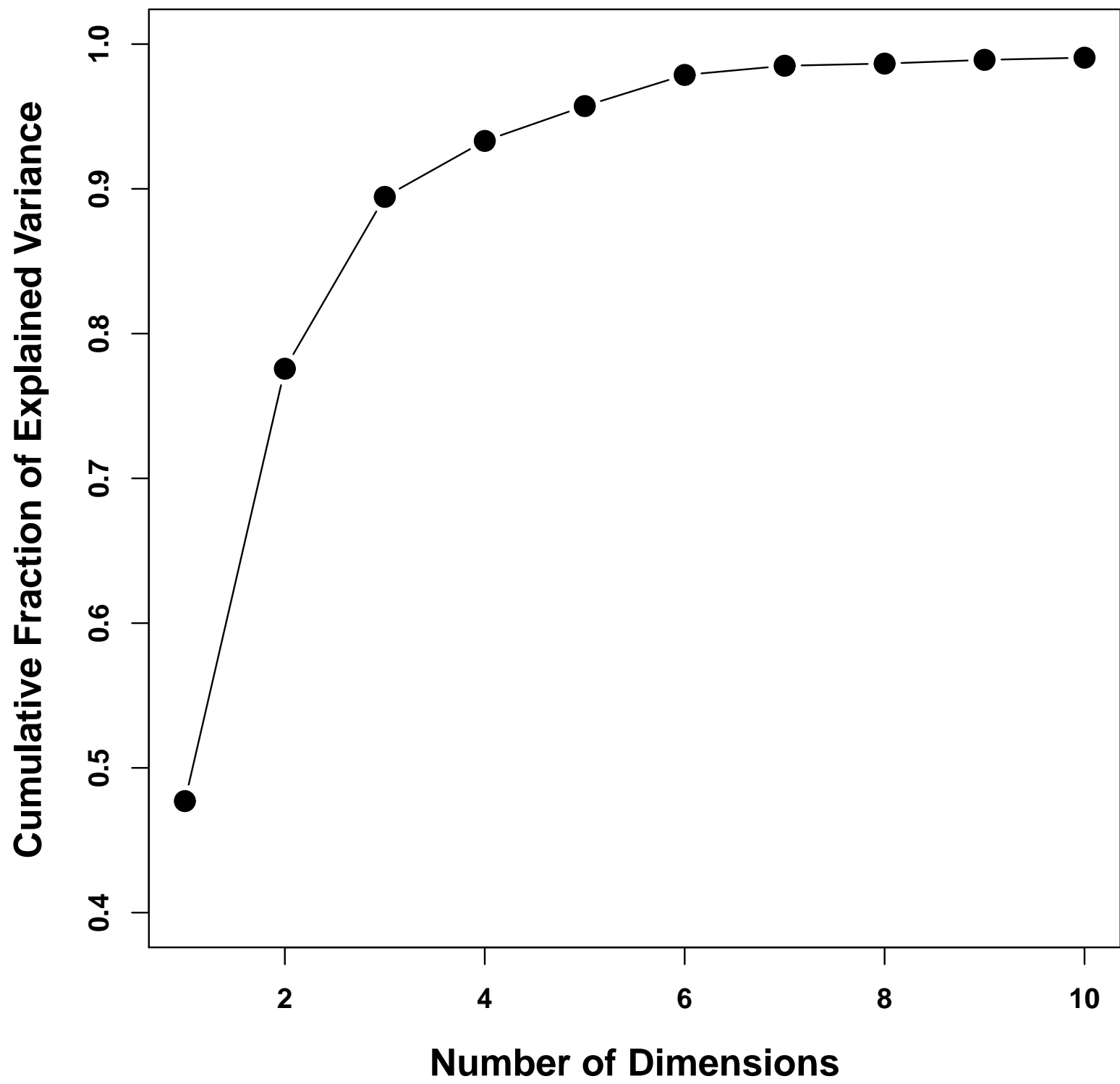


Figure 4

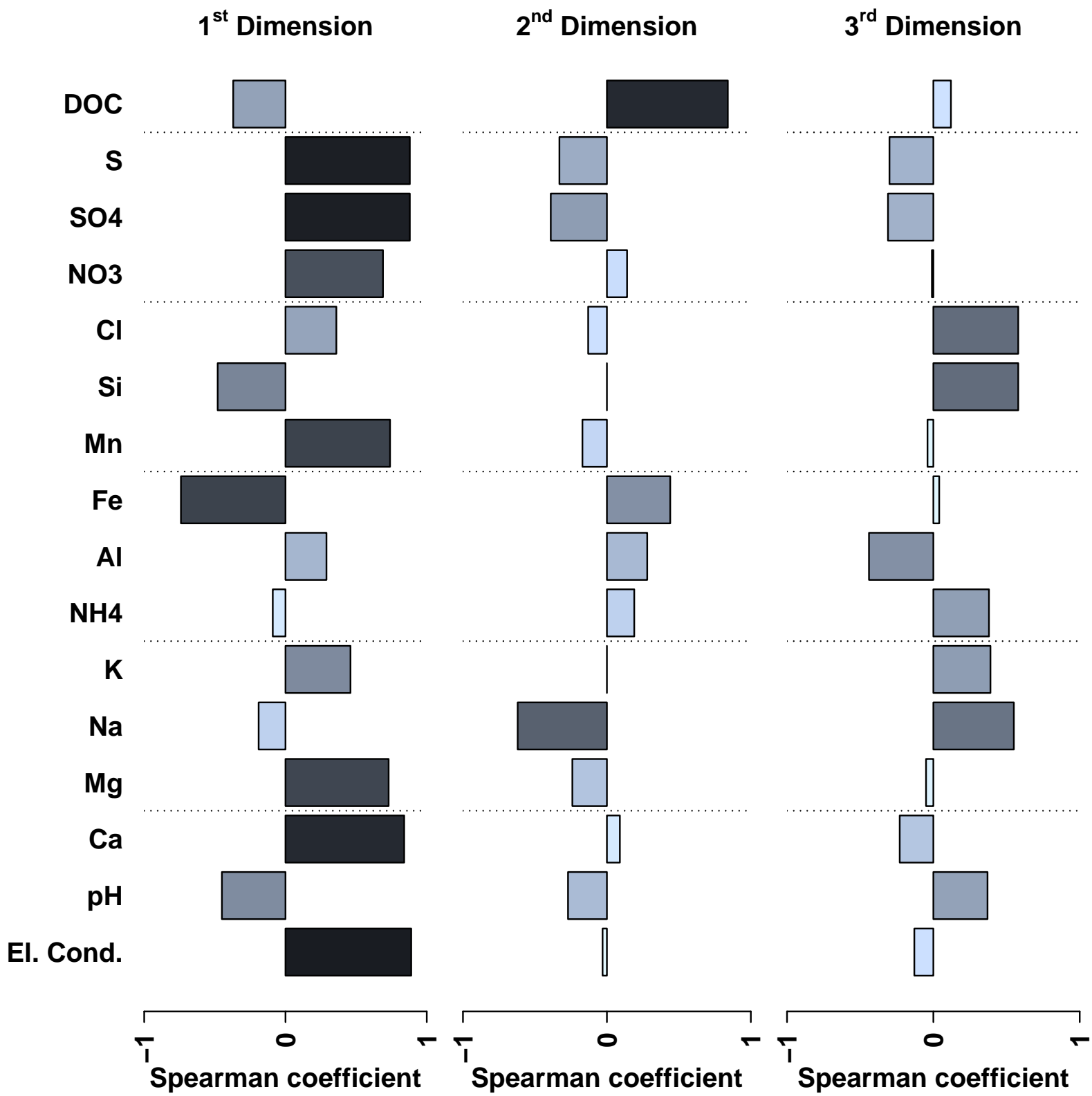


Figure 5

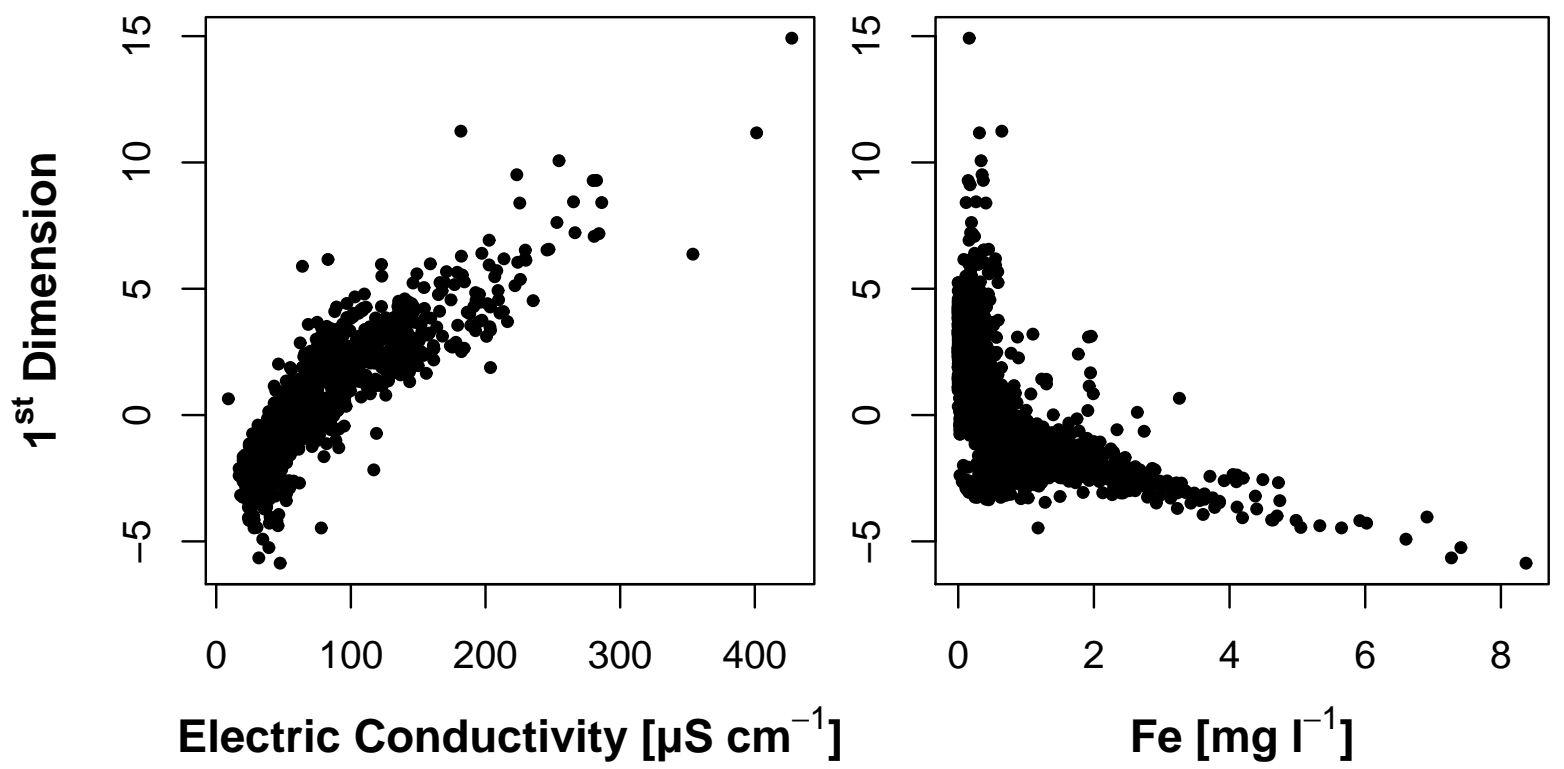


Figure 6

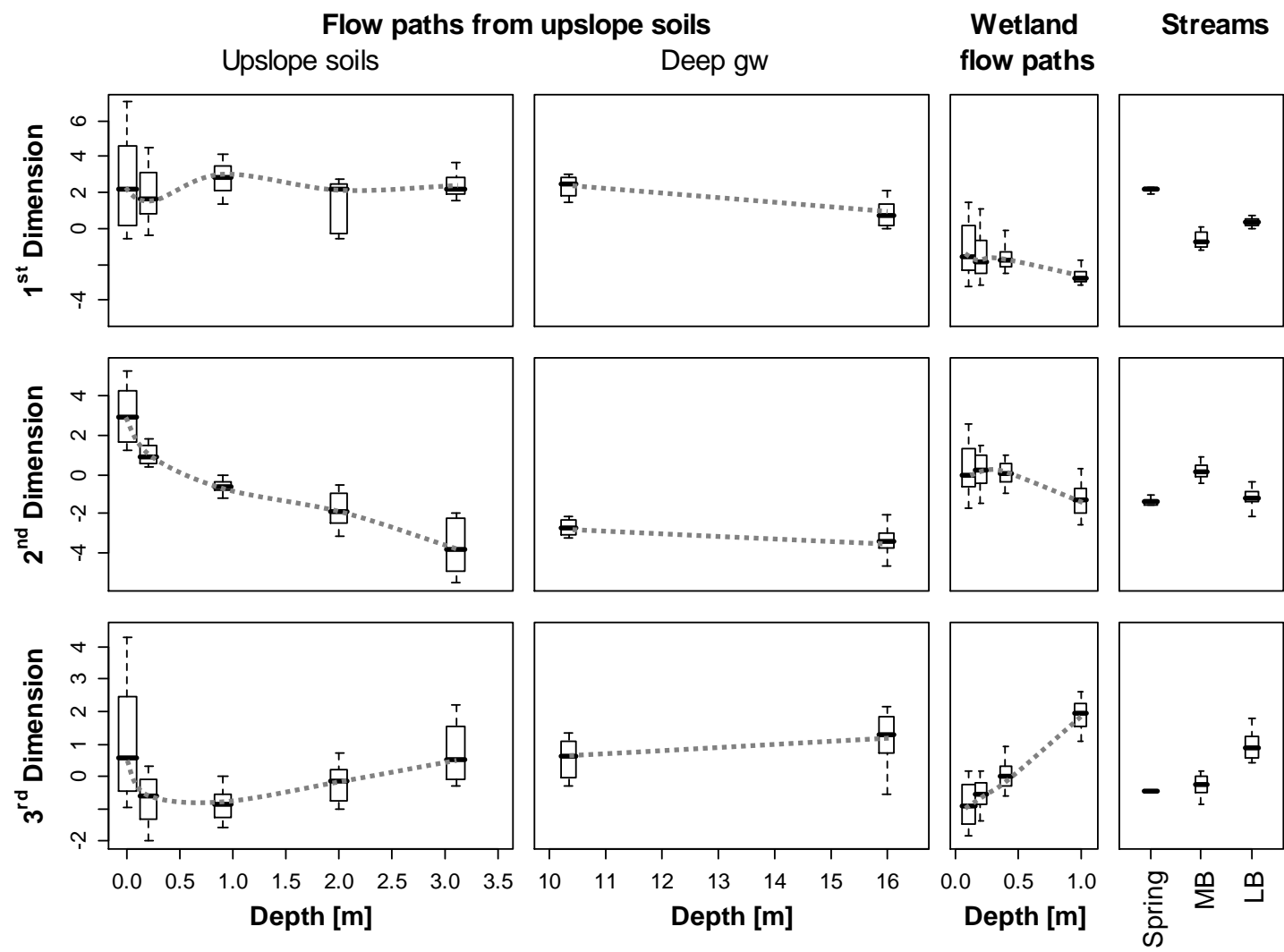




Figure 3

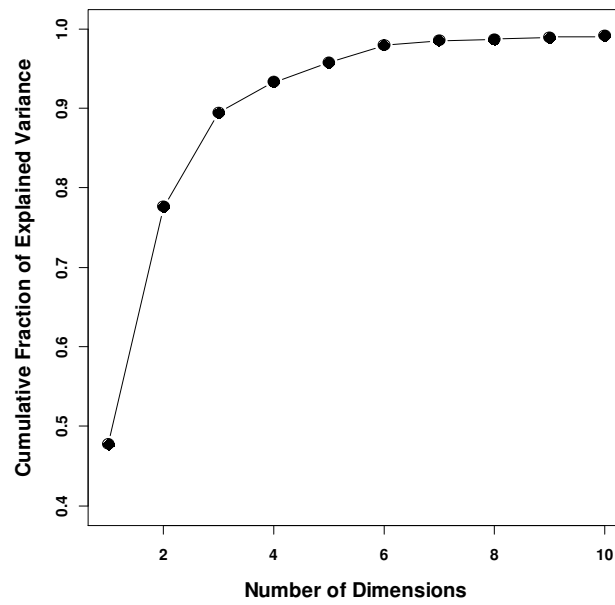


Figure 4

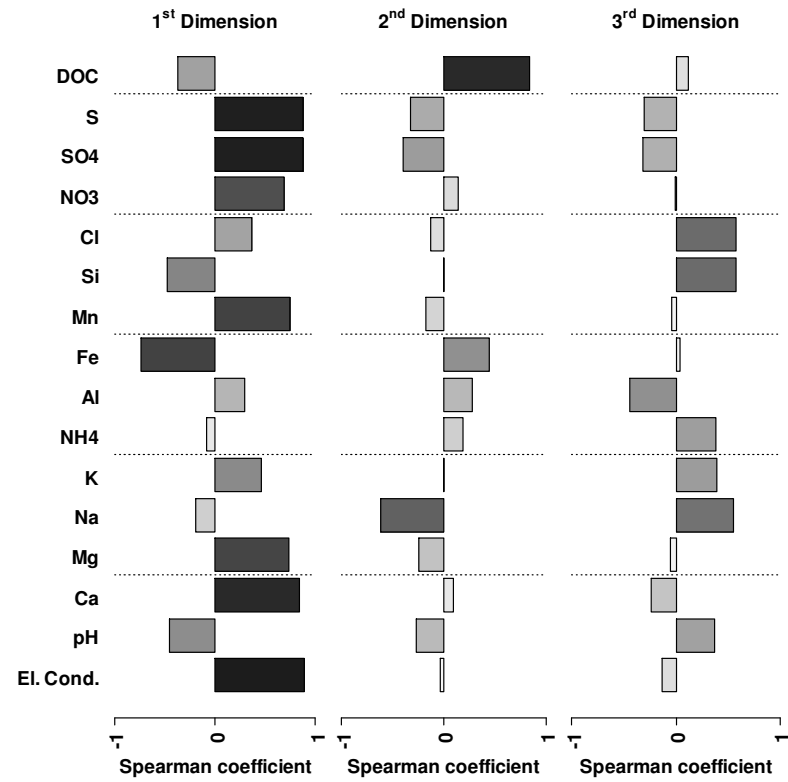


Figure 5

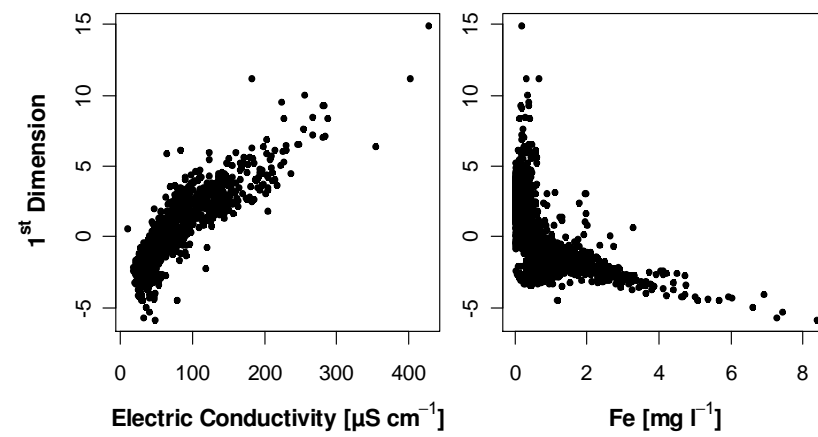


Table1

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	<b>Sampling Group</b>	<b>Comprised of</b>	<b>Number of Samples</b>
Flow paths from upslope soils	Upslope soils 0.03 m	soil solution from organic layer	139
	Upslope soils 0.2 m	soil solution	161
	Upslope soils 0.9 m	soil solution and shallow groundwater	161
	Upslope soils 2 m	shallow groundwater sampled between 1.9 and 2.2 m depth	35
	Upslope soils 3.1 m	shallow groundwater sampled between 3.0 and 3.2 m depth	31
	Deep groundwater 10 m	deep groundwater sampled in 10 or 10.7 m depth	51
	Deep groundwater 16 m	deep groundwater	17
Wetland flow paths	Wetlands 0.1 m	soil solution	158
	Wetlands 0.2 m	soil solution	135
	Wetlands 0.4 m	soil solution and shallow groundwater	333
	Wetlands 1.0 m	shallow groundwater	154
Surface waters (Solute output)	Upslope spring		7
	Moorbach stream		282
	Lehstenbach stream		18

Table 2

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Isomap dimension / biogeochemical process bundle		sampling group	maximal and minimal median of dimension scores, respectively	difference between maximal and minimal median of dimension scores	fraction of variance explained [%]
<b>1st dimension: processes</b>	<b>redox</b>	<b>whole catchment</b>	upslope soils 0.9 m	2.79	<b>100</b>
			wetland soils 1 m	-2.75	
	<b>hot spot wetland 0.1 m</b>		upslope soils 0.03 m	2.17	<b>66.8</b>
			wetland soils 0.1 m	-1.54	
<b>2nd dimension: acid- induced podzolization</b>		<b>whole catchment</b>	upslope soils 0.03	2.96	<b>100</b>
			upslope soils 3.1 m	-3.80	
	<b>hot spot upslope soils 0.9 m</b>		upslope soils 0.03 m	2.96	<b>52.5</b>
			upslope soils 0.9 m	-0.59	
<b>hot spot wetland 0.1 m</b>		upslope soils 0.03 m	2.96	<b>43.7</b>	
		wetland soils 0.1 m	0.01		

Table 3

[Click here to download Table: Weyer et al Tab 3.xls](#)

Isomap dimension / biogeochemical process bundle		thickness of the regolith / hot spot	fraction of catchment area (non-wetland/ wetland)	3-D domain [km <sup>3</sup> ]	fraction of 3-D domain of the whole catchment [%]
whole catchment (4.19 km <sup>2</sup> )		35 m		0.14665000	100
1st dimension: redox processes	hot spot wetland 0.1 m	0.1 m	0.35	0.00014665	0.1
2nd dimension: acid- induced podzolization	hot spot upslope soils 0.9 m	0.9 m	0.65	0.00245115	1.7
	hot spot wetland 0.1 m	0.1 m	0.35	0.00014665	0.1