Influence of catchment quality and altitude on the water and sediment composition of 68 small lakes in Central Europe

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ABSTRACT

68 lakes (63 Swiss, 2 French and 3 Italian) located in an altitudinal range between 334 and 2339 m spanning a wide range of land-use have been investigated. The aim of the study was to discuss influences of geographic location, vegetation and land-use in the catchment area on the water and sediment chemistry of small lakes. Detailed quantitative description of land-use, vegetation, and climate in the watershed of all lakes was established. Surface and bottom water samples collected from each lake were analyzed for major ions and nutrients. Correlations were interpreted using linear regression analysis. Chemical parameters of water and sediment reflect the characteristics of the catchment areas. All lakes were alkaline since they were situated on calcareous bedrock. Concentrations of nitrogen and phosphorus strongly increase with increasing agricultural land-use. Na and K, however, are positively correlated with the amount of urbanization within the catchment area. These elements as well as dissolved organic carbon (DOC), Mg, Ca, and alkalinity, increase when the catchment is urbanized or used for agriculture. Total nitrogen and organic carbon in the sediments decrease distinctly if large parts of the catchment consist of bare land. No correlations between sediment composition and maximum water depth or altitude of the lakes were found.
    Striking differences in the water compositions of lakes above and below approximately 700 m of altitude were observed. Concentrations of total nitrogen and nitrate, total phosphorus, DOC, Na, K, Mg, Ca, and alkalinity are distinctly higher in most lakes below 700 m than above, and the pH of the bottom waters of these lakes is generally lower. Estimates of total nitrogen concentrations, even in remote areas, indicate that precipitation is responsible for increased background concentrations. At lower altitudes nitrogen concentrations in lakes is explained by the nitrogen loaded rain from urban areas deposited on the catchment, and with high percentages of agricultural land-use in the watershed.

Introduction

The water composition of a lake as well as its sedimentary record are influenced by factors such as climate, geology, vegetation, and land-use in the catchment area

(e.g., Margalef, 1994). This close catchment and lake relationship renders the aquatic ecosystem sensitive to environmental changes (e.g., Schindler, 1987; Psenner and Schmidt, 1992; Larsen et al., 1996). A major issue is to understand the relevant processes that operate between catchment and lake as well as to recognize traces imprinted by prevailing environmental conditions. Spatial and temporal scale are of high importance for both factors. Knowledge of past lake development can only be gained by understanding the key processes of how environmental signals are archived via the water column into the sediment (e.g., Anderson and Battarbee, 1994). Therefore, investigations of the present-day situation in different lakes along environmental gradients (e.g., climate, trophic state, see Pienitz and Smol, 1993; Brenner and Binford, 1988) may help to better understand past lake development and thus assess the long term development of lacustrine ecosystems.

Sixty eight small lakes of comparable size situated along a climate and trophic gradient were sampled to assess the potential of different aquatic organisms (e.g., diatoms, cladocera, chironomids, chrysophytes) as quantitative indicators of past environmental change (Lotter et al., 1997a, b). Watershed-lake interaction can be studied easier with small lakes since specific influences are more apparent. Uniform catchments and short hydraulic residence times render small lakes more sensitive to influences of their water and sediment quality than large lakes. Specific chemical characteristics of anthropogenically influenced parameters are expressed more pronounced and can be traced and assigned easier. Analysis of the chemical data contributes to the characterisation of watershed-lake interactions and reveals distribution patterns of nutrients in small lakes. Knowledge of the processes that lead to these patterns are of importance when investigating alpine river systems and controlling new legislations and methods in farming. This study also contributes to regional limnology since especially the small lakes studied here are limnologically not well-known compared to larger Swiss lakes.

Here, we investigate the chemical information from water and surface sediments in relation to landuse and altitude and discuss the susceptibilities and chemical response of the lakes to anthropogenic impact. All selected lakes lay in carbonaceous catchment areas and have high buffer capacities against acids (high alkalinity). Therefore, the impact of acid deposition in the watersheds and its impact on lake acidification is of negligible significance. We follow the plea of Livingstone and Imboden (1996) to test if our data corroborate major in-lake processes rather than to obtain overall statistical relationships to search for new mechanisms. Focus is on reflections of geographic location and catchment areas in the processes that cause the observed limnological situation.

Methods

Sites selected for this study include small lakes between 0.007 and 0.67 km² situated in carbonate bedrock areas at elevations between 334 and 2339 m. An overview of their geographic locations is given in Figure 1. Geographic data are presented in Table 1. Sampling was carried out during spring and autumn 1993 and spring 1994. Several echo-sounding tracks helped to locate the deepest part of each lake where a continuous temperature and conductivity profile was recorded using an OTS
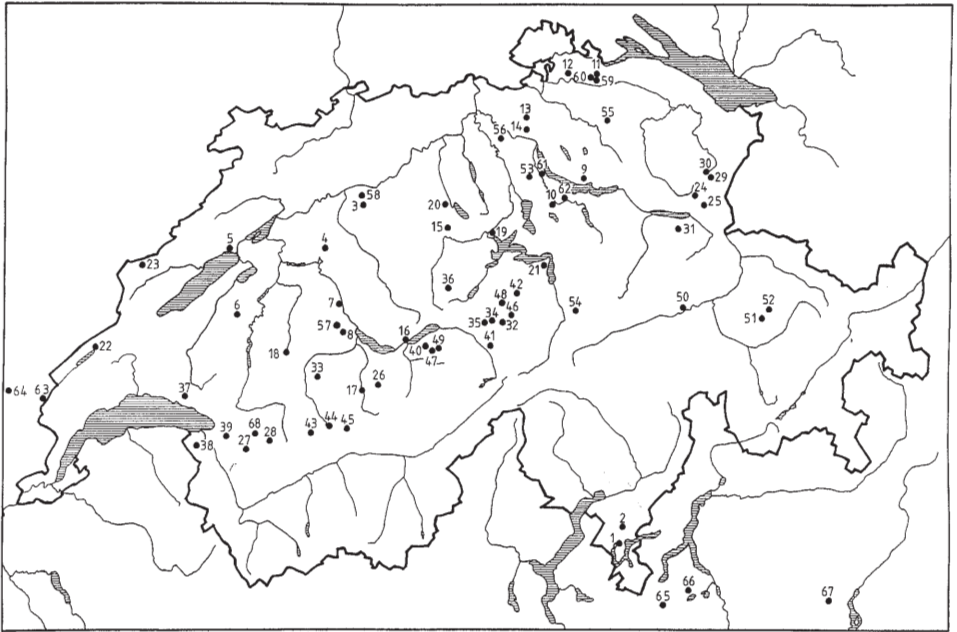
Figure 1. Map of Switzerland showing the geographic location of the 68 sampled lakes. Numbers refer to Table 1

probe (oxygen, temperature, conductivity; Meerestechnik GmbH, Trappenkamp, Germany). In thermally stratified lakes four samples were taken with a Niskin bottle (20 cm depth, above and below the thermocline; 1 m above the sediment surface). In unstratified lakes only three water samples were taken (surface; mid water depth; 1 m above the sediment). Only data from surface and bottom samples have been used for overall comparisons.

Oxygen content was determined by the Winkler method. pH was measured in the field because pH values measured in the laboratory the day after sampling deviated markedly from the field measurements due to CO_2 degassing. Alkalinity was determined by titration with strong acid to pH 4.3. DOC was measured by thermic oxidation with a Shimatsu TOC-500. Phosphate was determined photometrically with the molybdenum blue method (DEW 1996), nitrate with the salicylic acid method (DEW 1996), and silicate with the molybdosilicate method (DEW 1996). Total phosphorus (TP) and total nitrogen (TN) were determined in unfiltered samples by acidic digestion with $K_2S_2O_8$ in an autoclave for 2 h at 120 °C prior to analysis. Ca, Mg, K, and Na were determined with an inductively coupled plasma with optical emission spectroscopy (ICP–OES, Spectro Analytical Instruments). Chemical speciations were calculated with the program ChemEQL (Müller, 1995). Data for soluble reactive phosphorus (SRP) were collected either by additional sampling during the circulation period or obtained from the cantonal water protection authorities. These data were used to classify the lakes into the four categories of trophic states according to the OECD (1982) recommendation (see Table 1):

Table 1. Major hydrographical and limnological characteristics of the investigated 68 lakes. Numbers refer to Fig. 1. Trophic state is defined according to OECD (1982)

abbrev.	no.	lake	altitude [m]	surf. area [km²]	catchment area [km²]	max. depth [m]	residence time τ_w [a]	trophic state	sampling date
ABB	64	Lac de l'Abbaye	871	0.8	25.93	18	n.a.	m	19. Mai. 94
BAC	47	Bachsee	2265	0.07	1.87	16	0.22	m	11. Aug. 93
BAN	42	Bannalpsee	1587	0.16	8.23	17	0.13	m	20. Jul. 93
BIC	55	Bichelsee	590	0.09	2.7	6.5	0.22	e	22. Sep. 93
BLA	17	Blausee	887	0.01	0.09	10	0.34	m	30. Mär. 93
BRE	22	Lac Brenet	1002	0.63	2.85	17	1.60	m	18. Mai. 93
BRT	37	Lac de Bret	674	0.5	2.97	18	n.a.	e	29. Jun. 93
BUG	16	Burgseeli	613	0.09	1.18	19	0.63	e	30. Mär. 93
BUR	3	Burgäschisee	465	0.19	4.29	31	0.94	e	15. Mär. 93
CHA	14	Unterer Chatzensee	439	0.19	1.29	7.8	0.94	e	24. Mär. 93
CHV	27	Lac des Chavonnes	1690	0.05	0.74	29.5	0.93	m	2. Jun. 93
DIT	57	Dittligsee	652	0.07	3.13	16.5	0.25	e	18. Apr. 94
EGE	56	Egelsee	667	0.02	0.29	10	1.54	m	29. Sep. 93
END	67	Lago di Endine	334	0.49	8.34	8	n.a.	m	27. Mai. 94
ENG	32	Engstlensee	1850	0.45	7.4	49	0.84	m	15. Jun. 93
FÄL	29	Fälensee	1446	0.15	4.25	31	0.94	m	7. Jun. 93
FLU	44	Flueseeli	2045	0.04	0.79	8.5	0.17	m	28. Jul. 93
GAW	61	Gattiker Waldweiher	545	0.03	1.88	5.5	0.055	e	26. Apr. 94
GER	7	Gerzensee	603	0.27	2.7	10	0.93	e	17. Mär. 93
GRD	50	Lag Grond	1016	0.02	1.89	5	0.028	m	7. Sep. 93
GRO	31	Grosssee	1620	0.05	2.2	11.5	n.a.	m	8. Jun. 93
HAG	49	Hagelseewli	2339	0.03	0.36	18.5	0.59	m	18. Aug. 93
HAS	59	Hasensee	434	0.11	2.52	5.5	0.32	e	25. Apr. 94
HÜN	62	Hüttnersee	658	0.17	2.33	12	0.66	e	26. Apr. 94
HUS	12	Husemersee	409	0.08	1.33	14	n.a.	e	23. Mär. 93
HÜT	11	Hüttwilersee	434	0.35	3.71	15	1.93	e	23. Mär. 93
IFF	43	Iffigsee	2065	0.1	4.61	30	0.27	m	27. Jul. 93
INK	58	Inkwilersee	461	0.12	2.13	4.6	0.18	h	19. Apr. 94
LÄM	45	Lämmerensee	2296	0.07	1.55	2.5	0.057	m	28. Jul. 93
LIO	68	Lac Lioson	1848	0.07	1.5	25	n.a.	o	10. Aug. 94
LOC	5	Le Loclat	432	0.05	0.88	9.2	0.75	e	16. Mär. 93
LUT	48	Lutersee	1702	0.02	0.59	4.5	0.050	m	12. Aug. 93

LÜT	9	Lützelsee	500	0.13	6.02	6	0.10	e	22. Mär. 93
MAU	20	Mauensee	504	0.6	4.3	7	0.83	e	11. Mai. 93
MEL	35	Melchsee	1891	0.49	5.92	15.5	0.60	m	21. Jun. 93
MET	13	Mettmenhasler See	418	0.03	0.5	12.5	0.62	e	24. Mär. 93
MON	65	Lago di Montorfano	397	0.52	1.57	6.5	n.a.	m	26. Mai. 94
MOO	4	Moossee	521	0.31	10.41	21	0.56	m	15. Mär. 93
MUZ	1	Lago di Muzzano	337	0.22	2.2	3.2	0.14	h	3. Mär. 93
NER	39	Lac de Nervaux	1493	0.01	0.92	10	n.a.	e	30. Jun. 93
NUS	60	Nussbaumersee	434	0.25	5.87	8.2	0.47	m	25. Apr. 94
OBE	52	Obersee	1734	0.08	2.71	14.5	0.22	m	8. Sep. 93
ORI	2	Lago d'Origlio	416	0.07	1.19	6	0.15	m	10. Mär. 93
RET	28	Lac Retaud	1685	0.01	0.22	4.5	0.093	e	2. Jun. 93
ROT	19	Rotsee	419	0.5	4.6	16	0.94	e	11. Mai. 93
ROU	63	Lac des Rousses	1058	0.89	15.68	11.5	0.28	m	18. Mai. 94
SÄG	40	Sägistalsee	1935	0.07	3.85	9.7	0.080	m	7. Jul. 93
SAL	30	Seealpsee	1143	0.14	11.33	15	0.067	m	8. Jun. 93
SCE	51	Schwellisee	1933	0.03	9.58	12	0.019	m	7. Sep. 93
SCH	18	Schwarzsee	1046	0.46	19.7	9.5	0.13	m	31. Mär. 93
SCW	24	Schwendisee	1159	0.04	5.06	9.5	0.028	m	24. Mai. 93
SEB	33	Seebergsee	1831	0.06	0.23	15.5	2.39	m	16. Jun. 93
SEE	6	Lac de Seedorf	609	0.1	7.38	7.5	0.12	h	16. Mär. 93
SEG	66	Lago del Segrino	374	0.34	2.66	8.5	n.a.	m	26. Mai. 94
SEL	21	Seelisberg Seeli	738	0.18	2.7	37.5	0.73	m	12. Mai. 93
SEW	36	Sewenseeli	1689	0.03	0.21	4.5	0.26	m	28. Jun. 93
SOP	15	Soppensee	596	0.23	1.59	26.5	3.24	e	29. Mär. 93
SWL	54	Seewli See	2038	0.08	2.7	16	0.17	m	18. Sep. 93
TAI	23	Lac des Tailleres	1036	0.44	33.16	8.5	0.050	e	19. Mai. 93
TAN	34	Tannensee	1976	0.34	1.12	16	2.26	m	21. Jun. 93
TAY	38	Lac Tanay	1408	0.18	7.93	31	n.a.	m	29. Jun. 93
TRÜ	46	Trüebsee	1764	0.26	7.07	7	0.11	m	29. Jul. 93
TSC	26	Tschingelsee	1150	0.11	36.65	1.6	0.002	m	1. Jun. 93
TÜR	53	Türlersee	643	0.5	5.19	21	1.70	m	14. Sep. 93
UEB	8	Uebeschisee	641	0.15	2.16	14.5	0.71	e	17. Mär. 93
VOR	25	Voralpsee	1123	0.15	13.52	3.3	0.013	m	25. Mai. 93
WAN	41	Wannisbordsee	2103	0.02	1.64	14	0.047	o	8. Jul. 93
WIL	10	Wilersee	730	0.03	0.5	21	0.70	e	22. Mär. 93

o=oligotrophic (<10 μgP/L); m=mesotrophic (10–35 μgP/L); e=eutrophic (35–100 μgP/L); h=hypertrophic (>100 μgP/L). (n.a.: data were not available from hydrological atlas)

oligotrophic (<10 µgP/L), mesotrophic (10–35 µgP/L), eutrophic (35–100 µgP/L), hypertrophic (>100 µgP/L). In all figures, specific markers have been used for oligotrophic (triangles), mesotrophic (circles), eutrophic (diamonds), and hypertrophic lakes (squares).

Sediment cores were obtained from the deepest location of the lakes with a gravity corer. The cores were extruded on site and the uppermost 5 cm sampled in 1 cm sections. The samples were freeze-dried, pulverized, and digested with 4 ml of concentrated HNO_3 and 1 ml H_2O_2 in a microwave oven.

The relations between watershed descriptors, geographic and chemical information were ascertained using a Pearson correlation matrix with Bonferroni-adjusted probabilities (Wilkinson, 1988) of the dataset.

Results

Geographical data and sampling data for all 68 lakes are listed in Table 1, and their locations are depicted in Figure 1. Chemical data for water analysis, sediments, and land use are given in appendices I-III. The pH values of surface waters ranged from 7.8 to 9, alkalinity from 1 to 5 meq/L, and calcium from 0.5 to 3 mM. Conductivity measurements (κ, in µS cm^{-1}) are highly correlated with alkalinity (Alk, meq/L), suggesting that bicarbonate is the major anion in the investigated lakes, determining the ionic strength. The relationship obeys the following equation

$$\kappa = 0.22 + 0.0095 \cdot \text{Alk} \tag{1}$$

with a correlation coefficient r = 0.987 (n = 66).

pH values are generally higher in surface waters than in bottom waters in all lakes. Ca, alkalinity, TN, TP, and SRP, are slightly increased in bottom waters compared to the surface samples. Oxygen ranged from 9 to 15 mgO$_2$/L in surface waters but was totally depleted in the bottom waters of some lakes. Silicate was depleted in surface waters and enriched in the hypolimnion. Mg, DOC, NO_3^-, Na, and K, however, were distributed equally in the water column.

Dissolution of calcium carbonate dominates the composition of surface as well as bottom waters of the sampled lakes, depending on pH that, again, is influenced by the partial pressure of CO_2 (p_{CO_2}). Figure 2 shows ion products of measured Ca^{+2} and CO_3^{-2}; concentration of CO_3^{-2} was calculated from alkalinity and pH according to eq. (2):

$$[CO_3^{-2}] = \frac{\text{Alk}}{\dfrac{[H^+]}{K_2} + 2} \tag{2}$$

(assuming that all alkalinity originates from carbonate species) and the equilibrium constants log K_2 for 5 °C (hypolimnion) –10.56) and 20 °C (epilimnion) –10.38, respectively (Stumm and Morgan, 1996). It indicates calcite oversaturation in surface waters where photosynthetically decreased p_{CO_2} has increased the pH. The hypo-
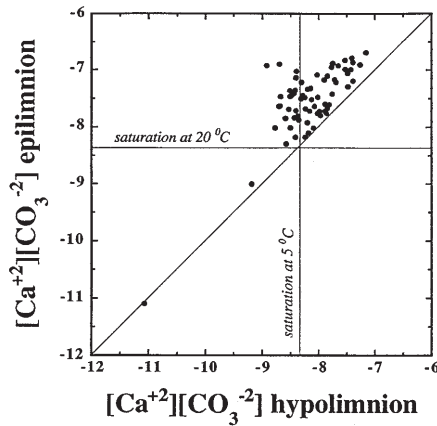
Figure 2. Ion products of $[Ca^{+2}]$ and $[CO_3^{-2}]$ as determined in surface and bottom waters. The lines for calcite saturation were calculated with constants for 20 °C for surface and 5 °C in bottom water (constants from Stumm and Morgan, 1996)

limnia, however, are at saturation with respect to calcite. pH values extend down to 7 due to mineralization processes. The ion product $[Ca^{+2}][CO_3^{-2}]$ for all lakes is higher in their epilimnia than in the hypolimnia.

The processes of assimilation and mineralization are reflected in the correlations of the chemical parameters in surface and bottom waters: High concentrations of O_2 in surface waters (Table 2a) coincide with high TP, TN, and DOC concentrations. In bottom waters (Table 2b) TP and O_2 are (weakly) negatively correlated, and high PO_4 and TN occur with high TP. Geogenic parameters (Ca, Mg, Na, K, Alk), with the exception of silicate, are correlated with high significance levels. High concentrations of DOC in hypolimnetic waters correlate with high concentrations of TN, alkalinity, K, Ca, Na, Mg, and CO_2. In both surface and bottom water layers we find generally positive correlations between nutrient parameters (NO_3^-, TN, SiO_2) and geogenic parameters (Ca, Mg, Na, K, alkalinity), except the phosphorus components, pH, and O_2. TP correlates with K and DOC. pH is allusively inversely correlated with the former parameters.

There are no obvious correlations of any chemical parameters with the maximum lake depths.

The influence of the catchment area

We classified the catchment according to the following five categories: bare land, green but unwooded land, forested land, agricultural land, and urban areas (see Appendix III). Increased levels of NO_3^-, TN, and TP occur preferentially in catchment areas with high percentages of agricultural land use. Land use is reflected in the water transparency since Secchi depth tends to be higher in catchments with little agriculture.

Figure 3a shows the distribution of TN in the epilimnetic waters in relation to agriculture in the catchment area. Consequently, the concentrations of nutrients are

Table 2. Pearson correlation matrix of chemical parameters (a) in surface waters, (b) in bottom waters, and (c) in sediments. Bold numbers signify correlations with significance levels $p < 0.01$

	SiO$_2$	K	Na	Mg	Ca	P$_{tot}$	PO$_4$	N$_{tot}$	NO$_3$	DOC	Alk	pH	O$_2$
SiO$_2$	1.000												
K	0.047	1.000											
Na	0.008	**0.721**	1.000										
Mg	0.218	**0.573**	0.456	1.000									
Ca	0.088	**0.728**	0.508	**0.598**	1.000								
P$_{tot}$	0.004	**0.729**	0.473	0.302	0.474	1.000							
PO$_4$	0.022	0.335	0.116	0.125	0.187	0.367	1.000						
N$_{tot}$	0.233	**0.805**	0.547	**0.690**	**0.818**	0.551	0.170	1.000					
NO$_3$	0.216	**0.631**	0.430	**0.584**	**0.693**	0.399	0.132	**0.896**	1.000				
DOC	−0.025	**0.794**	0.575	0.527	**0.769**	**0.605**	0.289	**0.756**	0.576	1.000			
Alk	0.088	**0.731**	0.547	**0.739**	**0.953**	0.460	0.167	**0.812**	0.667	**0.772**	1.000		
pH	−0.354	−0.110	−0.088	−0.047	−0.128	−0.038	−0.247	−0.188	−0.163	−0.037	−0.079	1.000	
O$_2$	−0.046	**0.636**	0.568	0.442	0.429	**0.633**	0.015	0.529	0.429	0.481	0.422	0.194	1.000

	SiO$_2$	K	Na	Mg	Ca	P$_{tot}$	PO$_4$	N$_{tot}$	NO$_3$	DOC	Alk	pH	O$_2$
SiO$_2$	1.000												
K	0.094	1.000											
Na	0.070	**0.574**	1.000										
Mg	0.329	0.541	0.328	1.000									
Ca	0.173	**0.709**	0.401	**0.578**	1.000								
P$_{tot}$	0.258	0.215	0.524	−0.058	0.184	1.000							
PO$_4$	0.136	0.158	**0.730**	−0.085	0.084	**0.885**	1.000						
N$_{tot}$	0.304	**0.675**	0.492	**0.575**	**0.713**	0.517	0.361	1.000					
NO$_3$	0.072	**0.627**	0.326	**0.655**	**0.697**	−0.081	−0.106	**0.724**	1.000				
DOC	0.155	**0.729**	0.425	0.485	**0.690**	0.189	0.117	**0.649**	0.524	1.000			
Alk	0.273	**0.707**	0.433	**0.720**	**0.902**	0.226	0.116	**0.770**	0.667	**0.772**	1.000		
pH	−0.395	−0.304	−0.340	−0.164	−0.247	−0.442	−0.362	−0.314	0.017	−0.432	−0.330	1.000	
O$_2$	−0.395	−0.025	−0.096	0.012	−0.043	−0.380	−0.325	−0.096	0.236	−0.176	−0.167	**0.632**	1.000

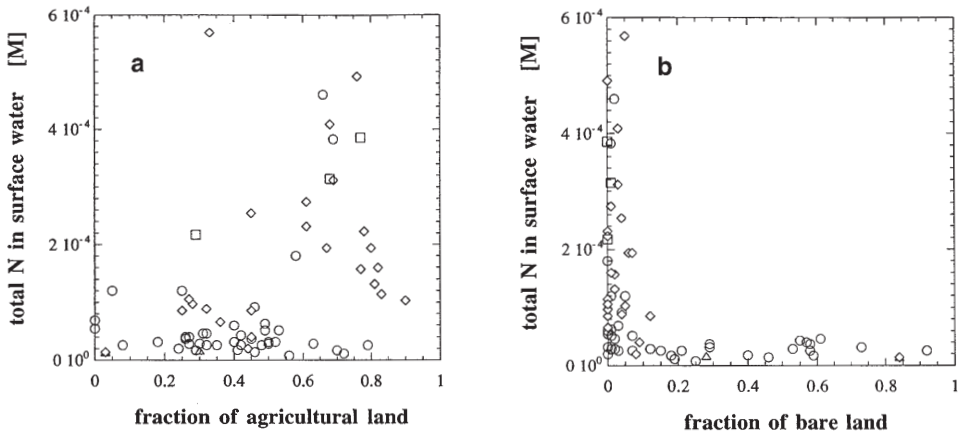|	N$_{tot}$	C$_{tot}$	C$_{inorg}$	C$_{org}$	CaCO$_3$	Ca	Mg	Na	K
N$_{tot}$	1.000								
C$_{tot}$	**0.767**	1.000							
C$_{inorg}$	−0.251	0.398	1.000						
C$_{org}$	**0.977**	**0.796**	−0.239	1.000					
CaCO$_3$	−0.251	0.396	**1.000**	−0.239	1.000				
Ca	−0.207	0.435	**0.989**	−0.192	**0.989**	1.000			
Mg	−0.140	−0.254	−0.121	−0.189	−0.121	−0.231	1.000		
Na	−0.358	**−0.598**	−0.359	−0.386	−0.359	−0.389	0.103	1.000	
K	−0.199	**−0.642**	−0.700	−0.218	−0.700	**−0.711**	0.187	0.433	1.000

Figure 3. Concentrations of TN in surface waters in relation to the percentage of agriculturally used land (a) and bare land (b) in the catchment area

very low in all catchments with high percentages of bare land (Fig. 3b). Generally, alkalinity, DOC, Ca, and Mg, are also negatively correlated with the percentage of bare land. The concentrations of Na and K increase with the percentage of urban areas. Very low concentrations of TN and total and organic carbon in the sediment occur regularly in areas with a high fraction of bare land in the catchment.

Some remarkable exceptions occur in Figure 3a where TN in lakes is very low in spite of the high percentage of agriculture in the watershed. Four mesotrophic lakes (OBE, TAN, MEL, and GRO, circles) are all located above 1600 m a.s.l., and "agriculture" is mostly extensive agriculture and pasture. The relatively low TN of eutrophic lakes (diamonds) in such areas are explained by their individual situation: WIL and MAU have artificial hypolimnetic syphons, BRT has a natural hypolimnetic discharge, HÜN is artificially aerated, and SOP is meromictic.

Altitude

Parameters indicative for human impact in the catchment areas, such as nitrogen and phosphorus, as well as geogenic parameters, show a remarkable pattern with respect to the elevation of the lakes. It is important to note that there is only a very weak correlation between agricultural land use and altitude (r=0.35). TN in surface and in bottom waters of lakes situated below 700 m a.s.l. are all higher than 0.05 mM (surface) and 0.08 mM (bottom) and reach as high as 0.6 mM. Above 700 m a.s.l., however, TN concentrations in surface and in bottom waters are all below 0.05 mM and 0.08 mM, respectively (Fig. 4a). The same pattern occurs with NO_3^- (Fig. 4b) and TP (Fig. 4c) in epilimnetic water: NO_3^- concentrations reach up to 0.5 mM in lakes below 700 m a.s.l. but are below 0.03 mM in all lakes at higher altitudes; TP reaches concentrations up to 2.7 µM in lakes below 700 m a.s.l., but only up to 1 µM below 700 m a.s.l. Lakes with high concentrations of SRP in their surface or bottom waters occur more numerous in low areas. For most lakes, how-
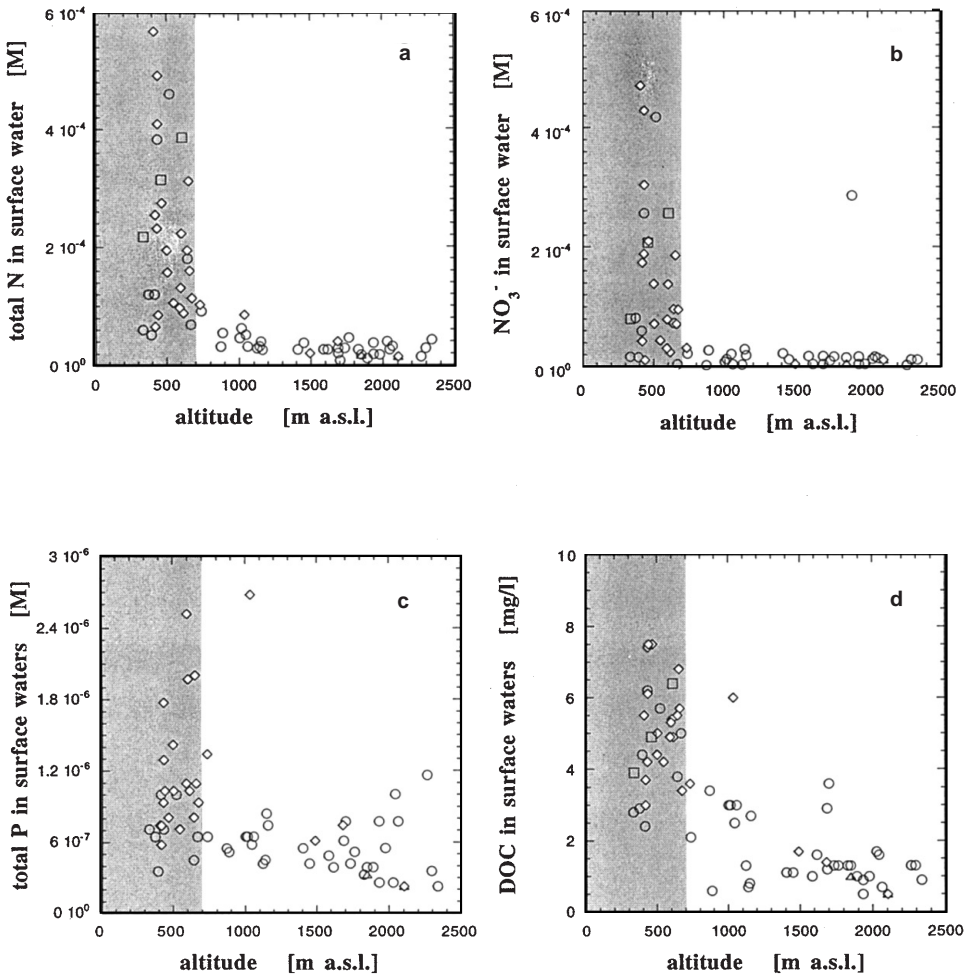
Figure 4. Distribution of TN, NO$_3^-$, TP, DOC, Ca, Mg, Na, and K, in relation to elevation

ever, concentrations for SRP are at the analytical detection limit. Concentrations of DOC in lakes below 700 m a.s.l. exceed those of lakes higher than 700 m a.s.l. (Fig. 4 d) about twofold. The wider range of concentrations at lower altitudes may reflect the wider range of land-use practices: we find more urban areas and more wooded land than at higher altitudes, and almost no bare land. Agriculture, however, is almost evenly distributed at all altitudes.

Moreover, the concentration range of seemingly purely geogenic parameters differs remarkably in lakes above and below 700 m a.s.l. While in all lakes above 700 m a.s.l. Ca ranges between 0.5 mM and 1.5 mM, more than 50 % of the lakes below 700 m a.s.l. (surface as well as bottom waters) show concentrations between 1.5 mM and 3 mM (Fig. 4 e). The situation for alkalinity is almost identical since
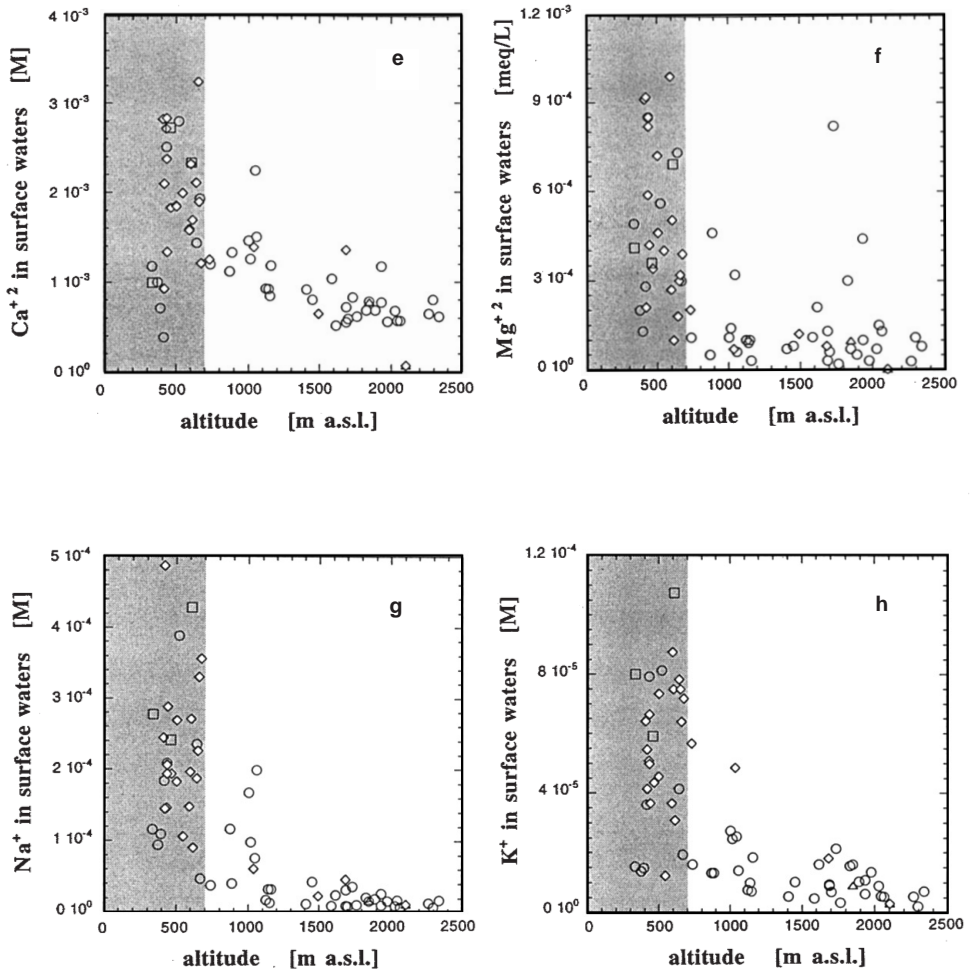
Figure 4 (continued)

Ca^{+2} and alkalinity are strongly correlated. Alkalinities are 1–3 mM above and 1–5.5 mM below 700 m a.s.l. This effect is even more pronounced for Mg, where average concentrations – with few exceptions – are below 0.2 mM for altitudes higher than 700 m a.s.l., but above 0.2 mM and up to 1 mM for more than 80 % of the lakes at lower altitudes (Fig. 4f). pH in surface as well as bottom waters tends to be lower below 700 m a.s.l. Distribution of silicate with altitude is not very pronounced with a few outliers with high concentrations at lower altitudes. Na and K, however, also reflect this pattern very strongly (Fig. 4g, h): in almost all lakes above 700 m a.s.l. Na concentrations are below 0.1 mM (K below 0.03 mM) but below 700 m a.s.l. values up to 0.5 mM (K up to 0.1 mM) are reached.
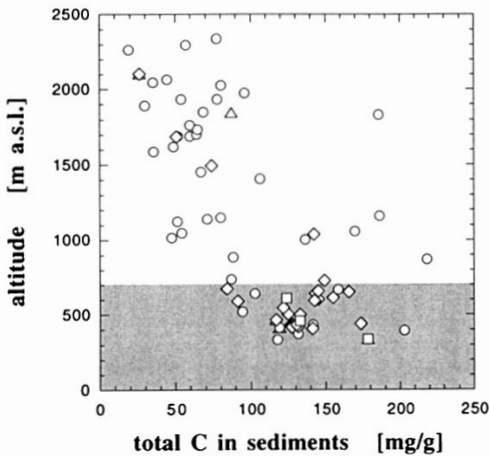
Figure 5. Concentrations of total carbon in the sediments in relation to elevation

Sediments

The effect of altitude is also reflected in the composition of the sediments. The contents of inorganic and organic carbon are up to two times higher in lake sediments below 700 m a.s.l. than in those above (Fig. 5). The contents of Fe, Na, and K in the sediments are higher above 700 m a.s.l., Ca and Sr, however, decrease. Concentrations of Mg and Mn in lake sediments are not sensitive to altitude.

The maximum lake depth seems to only slightly affect nutrients in the sediments. All lakes with TN in the sediments exceeding 10 g/kg and 70 g/kg of total organic carbon are shallower than 20 m. Apart from that there was no correlation of chemical sediment parameters with lake depth.

Among the sediment parameters TN is highly correlated with organic carbon (Table 2c) at a weight ratio of C_{org}:TN = 10:1. Practically all inorganic carbon and all Ca originates from calcite. Ca concentrations are high in sediments of lakes with high Ca concentrations in their bottom waters. Na in sediments, however, is high in lakes with low Na concentrations in bottom waters. The same is true for K, though less pronounced.

The concentrations of N and DOC show strong seasonal fluctuations in the water column. Therefore, our set of samples is not suited to reveal the relationship between sediment and overlaying waters with regard to these parameters. Except for an overall increase in TN and organic carbon in the sediments of lakes with a high hypolimnetic concentration of DOC, none of these sediment parameters (TN, C_{inorg}, C_{org}) show any correlations with dissolved ions in the bottom waters. Furthermore, neither of these parameters show any correlation with water depth, O_2 contents, alkalinity, or pH of the hypolimnion.

Discussion

Agricultural land-use and altitude

The chemical composition of a lake reflects the geology, vegetation, and human activities in its catchment area. Our data of epi-, meta-, and hypolimnetic waters from 68 small lakes show high concentrations of Ca, Mg, and alkalinity typical for hard water lakes in carbonaceous bedrock catchments. The lakes thus are not sensitive to atmospheric acid deposition. The only exception (WAN) is explained by its geological setting in an area of mixed carbonaceous and siliceous bedrock.

Concentration of nutrients (N and P) in lake waters and sediments are significantly increased in areas with high agricultural land use as illustrated for TN in Figures 6a and 6b. This connection is evident even in our temporally widespread water samples and it shows that agricultural activity has by far the most dominant influence on these lake ecosystems. Large fractions of nutrients from agricultural land are known to be transported into rivers and lakes mainly by surface runoff and transport through macropores (e.g., Gächter et al., 1996). Moreover, phosphorus also may be transported by wind erosion from fertilized ground as dust particles. Its contribution to eutrophication as wet and dry deposition, however, is considerably smaller compared to the above mentioned processes (Berner and Berner, 1996). The concentrations of Na and K in the investigated lakes are positively correlated with the area of urbanization in the catchment.

The concentrations of all chemical parameters in waters and sediments are lowest in catchments with high amounts of bare land (Fig. 3b). This indicates low erosion and weathering and, therefore, low nutrient concentrations and sediments with very low contents of N, P, and organic carbon. The main reason for this observations is the increasing fraction of agricultural land at lower altitudes. Bare land and land unsuitable for farming increases with altitude (above 1100 m a.s.l.). Therefore, we observe increasing nutrient concentrations with increasing agriculture, and decreasing nutrients with increasing altitude as exemplified in Figure 6 for TN in the epilimnetic waters. The most prominent contribution to nutrient concentrations in lakes are agricultural activities in the catchment areas followed by urbanization, whereas green or forested land are minor sources.

However, the geogenic parameters increase at lower altitude due to increased weathering rates and erosion. Higher concentrations of Ca, Mg, and alkalinity at lower altitudes indicate increased dissolution of calcareous rocks. As mentioned above, we find decreasing concentrations of Ca, Mg, alkalinity, and DOC with increasing fraction of bare land in the catchment. However, even at altitudes above 1100 m, only a few lakes have catchments areas with >7–8% bare land. This indicates that chemical weathering rates are lower at high elevations and larger at low elevations. This phenomenon is supported by the work of Zobrist and Drever (1990) and Drever and Zobrist (1992) who showed exponentially increasing weathering rates of silicate rocks with decreasing elevation in river systems. Low temperatures, thin or absent soils, and short contact times result in less chemical weathering at higher altitudes. Mineral dissolution rates are lower
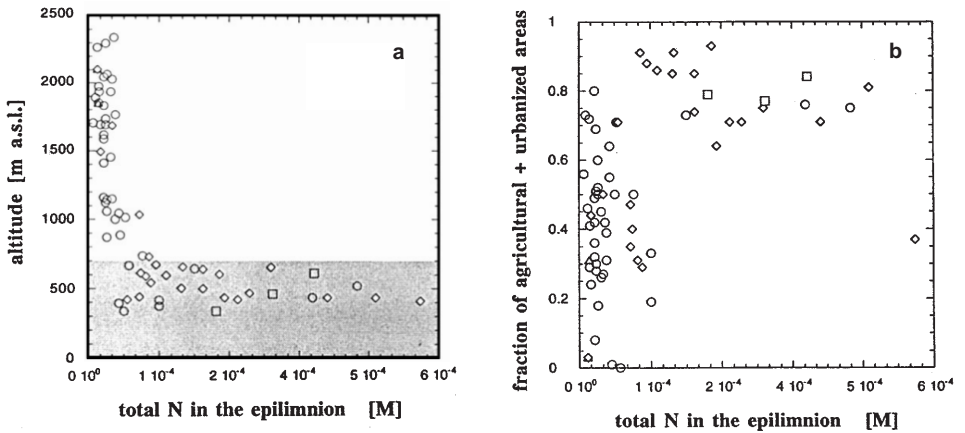
Figure 6. Distribution of epilimnetic TN concentrations in relation to altitude (a) and in relation to land-use (b) in the catchment

at high altitudes not only because of the lower average temperatures (Velbel et al. 1990) but also because of the relative surface area of rocks that is available for weathering reactions. Soil formation produces both large surface areas of minerals and a long residence time of the water compared with naked rock or thin soils. Additionally, the oxidation of reduced nutrients brought out in intensively farmed areas below 700 m a.s.l. (manure, fertilizer) introduces acidity into the soil. These causes result in the increase of weathering rates that results in higher concentrations of the geogenic parameters. pH values were found to decrease with decreasing altitude of the lakes. Therefore, bottom waters of lakes below 700 m a.s.l. tend to be higher in alkalinity, Ca, and Mg. Further contributions to this effect are infiltration of CO_2 rich groundwater with high concentrations of dissolved minerals as well as input and transport of reduced matter to the sediment whose mineralization causes the formation of CO_2, a drop in pH, dissolution of calcite, and an increase in alkalinity. This finding also indicates that groundwater infiltration to small lakes at high altitudes forms not a major contribution to the water composition.

However, correlations of the main elements are stronger with altitude than with the amount of agricultural land use. Therefore, other processes can be expected to contribute to this dependency. The sharp separation of lakes with high and low nutrient concentrations along the altitudinal gradient coincides with the altitude of meteorological situations where cold air is trapped under layers of warmer air. This climatic inversion situation is quite common in perialpine and alpine regions in Switzerland during the winter months (Barry, 1992). Due to the stabilization of the air layers, polluted air can be trapped, spread, and deposited within relatively confined areas below 700–800 m a.s.l. Because pollutant concentrations of aerosols and dry deposition can be extremely high (POLLUMET, 1990) they may contribute significantly to the direct and indirect nutrient input into the investigated lakes.

Nutrients

Most of the investigated lakes have low concentrations of SRP (< 1 µmol/L) soon after stratification, but increased PP concentrations were observed in the bottom waters. No significant decrease of NO_3^- and only sporadic increases in bottom water TN occurred, however. Concentrations of NO_3^- and TN exceed P concentrations by a factor $100–1000$. Apart from two lakes (WIL, BUG) which were extremely high in SRP at the deepest sampling point and where no annual mixing took place, only one lake (SOP) had an average SRP concentration as high as 2 µmol/L. A second sampling of some lakes in the following winter (mixing situation), however, revealed very high concentrations of SRP (>2 µmol/L) in the epilimnion of several lakes (LOC, SEE, SOP, ROT, INK) although SRP was below 0.5 µmol/L in the springtime of the previous year. Only SRP, and not NO_3^-, was increased in these lakes.

   Two lakes sampled at the end of March (WIL, BUG) were devoid of hypolimnetic oxygen and showed very high concentrations of dissolved and particulate phosphorus. Both lakes are meromictic. Concentrations of SRP were exceedingly high (25 µmol/L and 12 µmol/L) and so were concentrations of TP (29 µmol/L and 36 µmol/L). In all lakes there was no significant increase in SRP as long as there were traces of O_2 detectable. However, PP increased by approximately a factor of two in all cases where O_2 was below 1 mg/L, but still detectable (ROT, CHV, GRO, SEB, BRT, OBE, TÜR, EGE, DIT). This could be due to adsorption of phosphate onto iron oxide particles (Hupfer et al., 1995). Therefore, PN does not follow the increase of particulate phosphorus in these cases. Nitrate was at the detection limit in the bottom waters of both lakes due to denitrification. TN was increased, however, and so were alkalinity, Ca, and SiO_2 (but not DOC), resulting in a very high ion concentration as reflected also by the conductivity data. Obviously, these lakes did not undergo mixing during the cold season due to high salt density gradients in their bottom waters (Wüest et al, 1992; Imboden and Wüest, 1995). An indication for density induced stabilization is also the higher water temperature of the bottom waters compared to the overlaying waters.

   With its extremely low ion concentrations, low concentrations of PN, P, and DOC, and low pH, one lake (WAN) immediately attracts attention. The fact that this is the only lake whose catchment is situated at a geological transition zone between carbonaceous and siliceous bedrock explains the special situation. Nevertheless, the general trends in concentration differences between surface and bottom waters agree with the processes discussed for the other lakes.

The origin of nitrogen: a conceptual approach

To discuss the origin of nitrogen in the 68 investigated lakes in more detail we use a simple, conceptual approach. Mass balances of nitrogen in lakes are described in a one box model by the input (from soils and atmosphere), outflow, and the amount of nitrogen eliminated by sedimentation and denitrification:

$$V \frac{dN}{dt} = Q\,[N_{in}] - Q\,[N_{out}] - \sigma V\,[N] \qquad\qquad (3)$$

Lake volumes (V) were taken either from literature if available or estimated using lake surface area, maximum depth, and a multiplication factor of 0.56 estimated from literature data on areas, volumes, and depths of lakes. Throughflows of water (Q) were estimated from detailed data in the Swiss Hydrological Atlas (1992) on annual precipitation and the amount of water flowing out of certain catchment areas averaged over 20 years (1961–1980). σ indicates the fraction of nitrogen in the lake eliminated by sedimentation and denitrification. Mean water residence times τ_w ($=V/Q$) or the flow rate ρ ($=1/\tau_w$) were calculated from these data. In steady state conditions ($dN/dt=0$) eq. 3 turns to:

$$N = N_{in} \cdot \frac{\rho}{\rho + \sigma} \tag{4}$$

Our data show increasing values for the flow rates and decreasing TN concentrations for lakes with increasing altitudes. Nitrogen concentrations in high altitude lakes are rather low. This may be due to several reasons. First, there is increasing precipitation at high altitudes resulting in higher mean flow rates per catchment area compared to lowland lakes. Second, flows at high altitudes depend on the season, showing extremely high rates at snowmelt in spring and summer and very low rates during winter when the catchment is snow-covered or frozen. At a very slow flow rate (i.e., a long residence time) the effect of elimination reactions on the concentration of TN may be considerable, whereas it becomes less important with increasing flow rate. Third, the factor for elimination of nitrogen from lake water (σ) decreases with increasing altitude due to reduced photosynthetic activity, and denitrification rates may be smaller due to lower temperatures. Similarly, less phosphate results in smaller production, less uptake of nitrate, less sedimentation of nitrogen and, therefore, smaller σ.

Hence, we can explain steady state nitrogen concentrations at higher altitudes to be close to input concentrations, whereas elimination reactions are more effective at lower altitudes.

Estimates can be made whether the nitrogen concentrations may be explained by mere atmospheric input through rain or whether additional sources must be considered. The input of nitrogen by rain was calculated from the annual rainfall and the TN concentrations in rainwater of two locations (Zobrist, 1983). Jungfraujoch in the Swiss Alps (3570 m a.s.l.) is an example for unpolluted rain (10^{-5} mol/L), whereas Dübendorf, close to the city of Zürich, is characteristic for a polluted urban area ($3.4 \cdot 10^{-5}$ mol/L). Values for Q were calculated as described above.

Despite the rough estimates the conclusions from the data are unambiguous. The concentrations of TN of 24 lakes are smaller (less than 50%) than estimated from the unpolluted rain. These lakes – with one exception – are all located above 1000 m a.s.l. The average part of agriculture in the catchment area is 38%. These lakes are characterized by very short residence times (average $\tau_w = 26$ days).

TN concentrations of 11 lakes are comparable to the concentrations estimated from unpolluted rain ($\pm 100\%$). Six of them are situated above 880 m a.s.l. The agricultural part of the catchment of only 3 of these lakes is larger than 45%, and the residence times are short (average $\tau_w = 2.9$ months). Furthermore, ten out of these

eleven lakes have K concentrations similar (within a factor of two) to those measured in the Jungfraujoch precipitation, and five have similar Na concentrations.

Our dataset contains 16 lakes whose lakewater TN concentrations agree with the estimate of a polluted rain such as from Dübendorf; 14 of these lakes are below 700 m a.s.l., and eight lakes have >70% agricultural land in the catchment. Mean residence time is 5.5 months.

TN concentrations in 8 lakes are more than a factor of two higher than estimated from the polluted rain. All of them are located below 640 m a.s.l.; 68% of the land is in agricultural use, and the mean hydrological residence times is 11 months.

These findings indicate that precipitation is responsible for a certain background concentration of nitrogen and that increasing amounts of nitrogen originate from agricultural activities especially in lakes at low altitudes with long hydrological residence times.

Conclusions

The chemical analyses of epilimnetic and hypolimnetic water and surficial sediments of 68 circumalpine lakes show that environmental factors of the catchment areas strongly affect the water composition of the lakes. Lakes with a high percentage of agricultural and urban land-use show significantly higher concentrations of nitrogen and phosphorus than lakes with a high fraction of bare, green, or forested land in their catchment. Increased concentrations of TN occur in locations of low altitude and high percentage of agricultural land-use. We explain our set of nutrient data with two causes, namely precipitation and intense farming activities in the catchment. Low levels of TN in remote lakes can be attributed to unpolluted precipitation, and contribution from farming is not obvious. Two thirds of the lakes located below 700 m a.s.l. show TN concentrations corresponding to the composition of a polluted urban precipitation. Nitrogen contents of the remaining eight lakes are distinctly higher, indicating that agriculture which covers two thirds of the land in their catchment is the likely cause.

Nutrient concentrations in the lakes increase with residence times which also increase in lakes at lower altitude. Concentrations are generally two to three times lower and vary in a narrower range at altitudes above 700 m a.s.l., than in lakes located below 700 m a.s.l. This may reflect the wider range of land-use practices in catchments below 700 m a.s.l.

A strong correlation of Ca, Mg, Na, K, and alkalinity with altitude indicates increased weathering rates at lower altitude. The concentrations of Na and K increase with increasing percentage of urbanized areas in the watershed.

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Appendix I: Chemical analysis of surface water (20 cm)

no	Abb.	O₂ mg/L	pH	Alk meq/L	DOC mg/L	NO₃ µmol/L	TN µmol/L	SRP µmol/L	TP µmol/L	Ca mmol/L	Mg mmol/L	Na µmol/L	K µmol/L	SiO₂ µmol/L
1	MUZ	13.40	8.25	2.37	3.9	80.0	217.1	0.1	2.4	0.99	0.41	277.4	80.1	97.2
2	ORI	11.76	7.80	0.99	2.4	59.3	120.0	0.1	1.0	0.38	0.28	183.9	36.1	118.9
3	BUR	12.76	8.00	3.02	7.5	209.3	274.3	0.1	0.8	1.82	0.34	193.5	43.5	29.5
4	MOO	15.34	8.25	5.02	5.7	417.9	460.0	0.1	1.0	2.79	0.56	387.8	81.3	104.7
5	LOC	16.63	8.55	5.20	4.2	188.6	231.4	0.1	0.9	2.71	0.59	146.1	50.9	6.1
6	SEE	28.88	8.50	4.50	6.4	256.4	385.7	0.2	4.2	2.33	0.69	428.3	107.4	3.9
7	GER	16.32	8.55	4.48	5.4	137.9	222.9	0.1	2.0	2.31	0.50	270.9	74.9	1.8
8	UEB	14.62	8.40	3.78	5.5	95.7	194.3	0.1	0.8	2.11	0.18	187.0	78.3	4.3
9	LÜT	16.31	8.50	4.28	4.4	138.6	194.3	0.2	1.4	1.85	0.72	182.6	45.5	27.1
10	WIL	15.38	9.00	2.65	3.6	31.4	102.9	0.1	1.3	1.25	0.20	873.9	56.8	4.3
11	HÜT	14.35	8.40	4.59	7.4	303.6	408.6	0.5	1.3	2.37	0.82	206.5	66.5	35.6
12	HUS	12.93	8.35	5.07	5.5	471.4	568.6	0.2	0.7	2.82	0.91	244.8	64.2	41.7
13	MET	12.27	8.20	4.85	3.7	173.6	254.3	0.1	0.7	2.10	0.92	487.0	54.7	11.7
14	CHA	15.34	8.90	2.90	7.5	10.7	85.7	0.4	1.0	1.33	0.42	287.8	36.6	1.1
15	SOP	9.19	7.80	3.16	5.3	79.3	131.4	1.3	2.5	1.59	0.27	196.5	87.5	6.4
16	BUG	12.34	8.30	3.14	4.9	24.3	88.6	0.2	1.0	1.69	0.10	90.0	30.9	12.1
17	BLA	11.00	8.10	2.72	0.6	27.1	54.3	0.3	0.5	1.33	0.46	40.0	13.3	58.0
18	SCH	12.70	8.20	2.59	2.5	21.4	51.4	0.2	0.6	2.24	0.32	76.1	25.6	38.1
19	ROT	13.61	8.73	1.79	3.0	42.1	65.7	0.1	0.6	0.93	0.21	144.8	41.4	3.2
20	MAU	12.29	8.33	3.75	5.0	70.7	157.1	0.1	1.0	1.84	0.46	268.7	73.4	6.4
21	SEL	11.97	8.49	2.17	2.1	22.1	91.4	0.1	0.6	1.20	0.11	37.4	16.1	31.0
22	BRE	10.38	8.48	2.65	3.0	7.9	45.7	n.d.	0.6	1.46	0.11	167.4	27.4	2.8
23	TAI	11.77	8.84	2.51	6.0	n.d.	85.7	n.d.	2.7	1.38	0.07	60.9	48.6	2.8
24	SCW	9.21	8.09	2.32	2.7	n.d.	25.7	n.d.	0.7	1.19	0.03	32.6	18.4	7.1
25	VOR	11.77	8.89	1.79	1.3	2.9	28.6	n.d.	0.4	0.93	0.10	17.0	7.7	3.6
26	TSC	11.86	8.20	1.58	0.8	18.6	40.0	0.1	0.8	0.84	0.10	13.5	7.2	21.7
27	CHV	9.71	8.35	1.46	1.2	17.1	28.6	0.1	0.6	0.72	0.13	9.6	9.5	19.9
28	RET	11.31	8.40	2.39	1.4	n.d.	40.0	0.1	0.7	1.35	0.08	46.5	18.2	12.1
29	FÄL	11.40	8.80	1.70	1.1	11.4	37.1	0.1	0.4	0.80	0.08	43.0	10.2	8.9
30	SAL	10.61	8.55	1.87	0.7	29.3	31.4	0.1	0.5	0.92	0.09	32.2	10.0	17.1
31	GRO	10.10	8.90	1.43	1.6	4.3	25.7	0.1	0.4	0.51	0.21	24.3	16.1	5.7
32	ENG	9.00	8.40	1.48	1.3	15.0	17.1	0.1	0.4	0.78	0.07	15.7	16.1	24.9
33	SEB	12.99	8.84	1.82	1.3	n.d.	25.7	0.1	0.3	0.68	0.30	21.3	15.6	17.1
34	TAN	9.87	8.30	1.11	1.0	4.3	17.1	0.1	0.5	0.56	0.03	15.7	13.6	10.7
35	MEL	9.88	8.60	1.30	1.0	285.7	11.4	0.1	0.4	0.68	0.05	19.1	10.5	15.3
36	SEW	9.54	8.61	1.06	2.9	3.6	20.0	0.1	0.6	0.55	0.03	31.7	9.0	17.4
37	BRT	12.40	8.55	2.65	3.4	95.0	114.3	0.1	0.9	1.21	0.39	355.7	71.9	18.2
38	TAY	10.01	8.80	1.90	1.1	22.1	25.7	0.2	0.5	0.92	0.07	12.2	5.4	15.7
39	NER	11.37	8.75	1.60	1.7	3.6	20.0	0.0	0.6	0.65	0.12	23.0	n.d.	8.9
40	SÄG	9.18	8.27	2.29	0.9	3.6	17.9	0.1	0.8	1.17	0.10	10.0	6.4	21.0
41	WAN	10.77	7.15	0.21	0.5	10.7	14.3	0.1	0.2	0.06	0.00	11.3	3.1	24.9
42	BAN	9.39	8.44	2.07	1.0	17.1	25.7	0.1	0.5	1.04	0.11	9.1	4.9	20.3
43	IFF	9.85	8.50	1.31	0.7	14.3	31.4	0.1	0.8	0.57	0.13	7.4	5.4	18.9
44	FLU	9.98	8.40	1.35	1.6	16.4	25.7	0.1	1.0	0.57	0.15	17.4	5.6	24.9
45	LÄM	8.80	8.55	1.82	1.3	11.4	28.6	0.1	0.4	0.80	0.11	7.0	2.0	16.7
46	TRÜ	9.26	8.39	1.08	1.3	16.4	45.7	0.1	0.5	0.61	0.02	10.4	3.3	16.0
47	BAC	10.99	8.66	1.29	1.3	2.1	14.3	0.1	1.2	0.65	0.03	13.0	5.4	18.5
48	LUT	11.25	8.84	1.27	3.6	n.d.	7.9	0.1	0.8	0.59	0.06	8.7	6.9	9.6
49	HAG	10.12	8.32	1.25	0.9	11.4	42.9	0.1	0.2	0.61	0.08	17.4	7.2	37.0
50	GRD	10.80	8.10	2.87	3.0	12.9	62.9	0.1	0.6	1.25	0.14	98.3	24.8	42.7
51	SCE	11.80	8.40	1.98	0.5	16.4	37.1	0.1	0.3	0.77	0.44	26.5	11.0	57.7
52	OBE	11.80	8.65	2.60	1.3	9.3	28.6	0.1	0.4	0.83	0.82	36.1	21.5	85.8
53	TÜR	9.70	8.46	3.60	3.8	72.9	180.0	0.1	0.5	1.43	0.73	235.2	41.4	10.0
54	SWL	10.80	8.60	1.58	1.7	12.1	40.0	0.1	0.3	0.68	0.07	9.1	9.0	19.9
55	BIC	12.40	8.40	4.53	4.9	30.7	97.1	0.1	1.1	1.57	0.99	147.8	36.6	10.7
56	EGE	7.10	8.05	3.95	5.0	3.6	68.6	0.1	0.6	1.93	0.30	47.0	19.4	38.4
57	DIT	10.50	7.98	6.07	6.8	186.4	311.4	0.2	2.0	3.24	0.30	226.1	74.9	15.7
58	INK	11.50	8.09	4.63	4.9	207.1	314.3	0.4	1.8	2.72	0.36	241.3	59.1	115.3
59	HAS	n.d.	8.27	5.67	6.1	428.6	491.4	0.1	1.8	2.83	0.85	193.9	49.9	34.2
60	NUS	11.50	8.34	5.24	6.2	256.4	382.9	0.1	0.7	2.51	0.85	209.1	79.3	24.2
61	GAW	11.20	8.39	4.36	4.2	43.6	105.7	0.2	0.7	1.99	0.40	106.1	12.3	112.5
62	HÜN	13.80	8.70	4.24	5.7	71.4	160.0	0.1	1.1	1.89	0.32	330.4	63.9	3.6
63	ROU	10.20	8.55	3.11	3.0	4.3	31.4	0.1	0.6	1.50	0.06	199.1	14.1	4.6
64	ABB	9.80	8.40	2.63	3.4	2.1	31.4	0.1	0.5	1.12	0.05	117.0	13.3	2.1
65	MON	11.20	8.46	1.81	4.4	15.7	51.4	0.1	0.4	0.71	0.13	109.6	14.8	4.3
66	SEG	12.00	8.25	2.64	2.9	81.4	120.0	0.1	0.6	1.00	0.20	93.9	13.8	19.2
67	END	14.80	8.33	3.01	2.8	16.4	60.0	0.1	0.7	1.18	0.49	116.1	15.3	5.7
68	LIO	8.20	8.55	1.69	1.0	5.7	16.4	0.2	0.3	0.78	0.10	16.5	9.2	15.3

Appendix II: Chemical analysis of bottom waters (1 m above sediment)

no	Abb.	O$_2$ mg/L	pH	Alk meq/L	DOC mg/L	NO$_3$ µmol/L	TN µmol/L	SRP µmol/L	TP µmol/L	Ca mmol/L	Mg mmol/L	Na µmol/L	K µmol/L	SiO$_2$ µmol/L
1	MUZ	12.30	8.15	2.40	3.7	83.6	208.6	0.1	2.6	1.02	0.42	276.5	85.7	101.1
2	ORI	12.82	7.80	0.97	2.3	60.0	125.7	0.1	0.8	0.39	0.28	183.9	34.5	114.2
3	BUR	6.00	7.60	3.62	7.9	242.1	317.1	0.7	1.8	2.12	0.38	211.7	39.4	70.8
4	MOO	10.61	7.85	5.25	4.5	417.9	454.3	0.2	1.7	2.91	0.58	430.0	81.6	133.5
5	LOC	14.21	8.25	5.23	4.3	182.1	222.9	0.1	1.1	2.73	0.60	148.3	47.6	15.7
6	SEE	19.68	8.05	5.03	6.4	265.7	377.1	0.2	3.7	2.62	0.69	430.9	109.0	4.3
7	GER	9.93	8.00	4.57	4.7	132.1	231.4	0.1	4.3	2.34	0.51	271.3	76.0	17.4
8	UEB	5.88	7.60	3.91	5.1	79.3	197.1	0.1	1.4	2.17	0.18	193.5	83.9	17.4
9	LÜT	13.68	8.15	4.72	4.6	162.1	228.6	0.2	1.0	2.03	0.76	191.7	45.0	41.6
10	WIL	n.d.	7.10	3.60	4.5	2.9	337.1	24.8	29.0	1.60	0.22	1452.2	62.7	62.6
11	HÜT	4.64	7.70	4.91	6.3	275.0	411.4	0.3	1.1	2.49	0.85	212.6	66.8	63.3
12	HUS	4.08	7.60	5.52	5.3	442.9	600.0	0.2	0.9	2.95	0.92	248.7	65.2	106.0
13	MET	8.24	7.55	5.37	2.3	225.7	311.4	0.1	0.9	2.37	0.99	521.7	56.0	71.9
14	CHA	13.12	7.00	3.08	6.0	6.4	117.1	0.2	0.9	1.40	0.42	294.3	36.6	53.0
15	SOP	3.34	7.50	3.20	4.2	68.6	137.1	2.4	3.8	1.58	0.28	201.7	91.3	19.2
16	BUG	n.d.	7.00	4.86	4.0	2.1	628.6	11.9	36.0	2.28	0.11	96.5	41.7	165.1
17	BLA	11.27	8.10	2.70	1.3	27.1	42.9	0.2	0.4	1.36	0.46	39.6	13.0	55.9
18	SCH	9.63	7.90	2.82	2.0	20.0	45.7	0.2	0.6	2.85	0.40	85.7	29.2	50.2
19	ROT	0.44	7.49	2.75	2.9	41.4	128.6	0.2	2.4	1.41	0.22	161.7	48.1	37.0
20	MAU	9.79	7.95	4.03	4.6	41.4	128.6	0.1	1.3	2.06	0.46	265.2	73.1	18.9
21	SEL	8.91	7.88	2.21	1.8	26.4	77.1	0.1	0.7	1.22	0.11	38.3	16.1	47.0
22	BRE	5.13	7.80	2.73	3.0	12.9	57.1	0.3	1.7	1.50	0.10	169.1	27.6	10.0
23	TAI	1.24	7.56	2.70	5.7	n.d.	77.1	n.d.	3.1	1.48	0.07	61.3	48.6	15.3
24	SCW	2.11	7.26	3.14	3.5	n.d.	60.0	n.d.	1.7	1.63	0.10	41.3	36.6	56.9
25	VOR	12.27	8.85	1.85	1.3	2.9	37.1	n.d.	0.6	0.95	0.10	14.8	7.2	5.7
26	TSC	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
27	CHV	0.50	7.50	2.05	1.5	n.d.	82.9	0.3	2.7	0.95	0.15	37.4	8.2	98.9
28	RET	10.42	7.90	2.76	1.5	n.d.	51.4	0.1	1.2	1.60	0.08	41.7	25.1	41.6
29	FÄL	4.60	7.60	1.97	1.0	30.7	40.0	0.2	1.8	0.98	0.09	26.5	11.3	71.2
30	SAL	12.52	8.40	1.97	0.7	33.6	182.9	0.1	0.5	0.96	0.10	24.3	22.5	24.2
31	GRO	0.38	7.45	2.60	2.0	n.d.	62.9	0.1	1.9	0.97	0.37	44.3	39.1	68.3
32	ENG	8.40	8.15	1.74	1.1	13.6	14.3	0.1	0.4	0.93	0.09	12.6	10.0	41.6
33	SEB	0.60	7.72	2.33	1.6	n.d.	51.4	0.1	1.7	0.92	0.35	27.0	18.7	35.9
34	TAN	9.94	8.19	1.11	0.5	6.4	22.9	0.1	0.3	0.56	0.03	15.2	11.5	11.4
35	MEL	9.82	8.10	1.47	0.7	6.4	14.3	0.1	0.3	0.73	0.06	19.1	9.7	22.4
36	SEW	13.97	7.97	1.55	2.3	3.6	20.0	0.1	0.8	0.79	0.04	67.4	12.5	55.9
37	BRT	0.54	7.55	3.66	2.7	92.9	182.9	0.5	3.5	1.77	0.38	359.1	70.6	43.4
38	TAY	4.72	7.80	2.12	1.1	27.9	37.1	0.3	0.9	1.03	0.09	13.5	17.1	41.3
39	NER	7.16	7.35	2.65	3.1	3.6	68.6	0.2	2.8	1.26	0.15	32.2	20.5	67.3
40	SÄG	7.48	7.70	2.99	0.4	6.4	14.3	0.1	0.3	1.40	0.14	17.0	7.7	40.2
41	WAN	10.60	7.22	0.24	0.5	6.4	14.3	0.1	0.4	0.08	0.01	13.0	4.9	26.0
42	BAN	10.00	8.35	2.19	0.7	21.4	22.9	0.1	0.4	1.14	0.11	8.7	4.6	23.8
43	IFF	10.37	8.45	1.58	0.5	17.9	22.9	0.4	0.5	0.66	0.17	6.5	7.2	29.5
44	FLU	10.94	8.45	1.38	0.8	17.1	34.3	0.5	0.5	0.62	0.16	17.8	2.6	27.4
45	LÄM	8.66	8.55	1.79	0.9	4.3	54.3	0.1	0.4	0.83	0.10	7.8	2.3	16.0
46	TRÜ	10.39	8.50	1.09	1.2	17.1	40.0	0.1	1.1	0.62	0.02	14.3	10.5	16.4
47	BAC	9.84	8.24	1.35	0.9	5.0	5.7	0.1	0.4	0.67	0.04	8.7	3.8	26.0
48	LUT	8.98	8.02	1.48	4.0	n.d.	31.4	0.1	1.0	0.69	0.05	4.3	5.1	12.5
49	HAG	4.35	7.76	2.19	0.8	1.4	8.6	0.4	1.0	1.11	0.27	56.5	8.2	100.4
50	GRD	9.20	8.00	2.83	2.5	12.9	65.7	0.1	0.8	1.32	0.14	100.9	25.6	49.8
51	SCE	9.90	8.40	1.98	0.5	22.1	217.1	0.5	0.5	0.79	0.47	27.4	15.6	56.9
52	OBE	0.70	7.65	3.06	1.8	8.6	71.4	0.3	2.0	0.96	0.87	48.7	28.9	305.3
53	TÜR	0.70	7.48	3.98	3.3	23.6	102.9	0.1	3.1	1.48	0.71	250.4	38.1	69.4
54	SWL	5.90	8.67	1.57	2.0	12.1	57.1	0.1	0.4	0.70	0.06	7.8	7.4	24.9
55	BIC	2.50	7.30	5.42	7.8	14.3	234.3	0.1	2.4	1.32	0.73	111.3	33.5	69.0
56	EGE	0.30	7.25	4.72	5.4	3.6	280.0	0.1	2.3	2.23	0.32	54.3	27.4	172.6
57	DIT	0.50	7.48	6.20	8.2	155.0	260.0	0.3	2.2	2.75	0.31	236.5	81.3	124.9
58	INK	11.40	8.08	4.58	5.2	207.9	308.6	0.4	2.0	2.70	0.38	257.4	67.0	113.5
59	HAS	10.50	8.08	5.88	4.9	428.6	491.4	0.1	1.1	2.79	0.84	196.5	52.7	35.2
60	NUS	5.80	7.84	5.36	5.7	212.9	348.6	0.1	1.1	2.17	0.83	202.6	73.9	46.6
61	GAW	10.10	8.14	4.32	3.7	43.6	97.1	0.2	0.7	2.00	0.39	105.7	10.7	122.1
62	HÜN	10.70	8.22	4.24	4.9	76.4	162.9	0.2	1.7	2.03	0.33	339.6	62.4	39.9
63	ROU	8.60	8.20	3.18	2.6	7.9	51.4	0.1	0.6	1.40	0.05	185.7	13.6	14.6
64	ABB	7.20	7.95	2.69	3.4	4.3	40.0	0.1	0.8	1.13	0.05	112.2	15.3	10.7
65	MON	10.50	8.06	1.86	4.1	13.6	77.1	0.1	0.5	0.71	0.13	110.0	25.6	6.4
66	SEG	4.60	7.60	3.01	2.7	62.1	171.4	0.5	1.2	1.18	0.20	104.8	14.3	82.9
67	END	4.40	7.53	3.71	2.4	8.6	125.7	0.3	1.3	1.40	0.49	114.8	25.3	74.4
68	LIO	7.00	8.15	1.95	1.1	7.1	16.4	0.2	0.4	0.91	0.12	16.5	16.1	45.9

Appendix III: Chemical analysis of sediments, and land use

no	Abb.	TN mg/g	C_tot mg/g	C_inorg mg/g	C_org mg/g	CaCO₃ %	Ca mg/g	Mg mg/g	Na mg/g	K mg/g	agric.	urban	bare	wooded	green
1	MUZ	20.5	178.3	5.1	173.1	4.3	23.4	9.3	0.3	4.0	0.29	0.50	0.00	0.17	0.04
2	ORI	10.4	119.1	0.7	118.3	0.6	4.1	4.1	0.2	5.9	0.05	0.14	0.01	0.79	0.01
3	BUR	5.9	117.0	52.0	65.0	43.3	180.2	5.3	0.2	2.6	0.61	0.10	0.01	0.26	0.03
4	MOO	4.2	94.3	50.9	43.5	42.4	170.7	6.9	0.3	3.8	0.66	0.09	0.02	0.22	0.01
5	LOC	4.5	126.3	80.8	45.4	67.4	256.2	4.1	0.2	2.2	0.61	0.03	0.00	0.33	0.03
6	SEE	7.0	123.8	59.9	63.9	49.9	204.4	5.6	0.4	2.8	0.77	0.07	0.00	0.15	0.01
7	GER	5.8	145.1	88.6	56.5	73.8	293.9	1.2	0.1	0.7	0.78	0.15	0.00	0.05	0.02
8	UEB	6.0	143.2	80.7	62.5	67.3	263.4	0.4	0.1	1.1	0.80	0.05	0.06	0.06	0.02
9	LÜT	8.3	132.9	48.9	83.9	40.8	164.6	9.8	0.1	2.7	0.67	0.07	0.07	0.10	0.09
10	WIL	9.3	149.1	44.6	104.5	37.2	155.7	6.2	0.3	3.9	0.90	0.01	0.05	0.04	0.00
11	HÜT	4.7	127.8	86.5	41.3	72.1	282.8	5.0	0.1	1.1	0.68	0.03	0.03	0.25	0.00
12	HUS	5.8	141.0	87.3	53.7	72.8	294.2	2.0	0.1	0.4	0.33	0.04	0.05	0.54	0.04
13	MET	5.4	127.3	73.9	53.4	61.5	245.3	3.7	0.2	1.0	0.45	0.26	0.04	0.20	0.06
14	CHA	10.5	173.5	75.4	98.1	62.8	255.8	4.8	0.1	0.8	0.25	0.10	0.12	0.45	0.08
15	SOP	6.6	142.5	75.6	66.9	63.0	263.7	2.1	0.1	1.2	0.81	0.05	0.02	0.12	0.00
16	BUG	8.2	155.0	58.0	97.0	48.3	187.7	3.6	0.1	2.4	0.32	0.08	0.04	0.51	0.05
17	BLA	1.8	88.5	69.4	19.1	57.8	207.0	11.7	0.3	3.1	0.00	0.01	0.00	0.89	0.10
18	SCH	3.4	54.2	21.9	32.3	18.3	78.1	13.2	0.2	9.5	0.53	0.02	0.07	0.27	0.11
19	ROT	8.4	131.7	54.7	77.0	45.6	193.9	5.2	0.2	2.6	0.36	0.35	0.00	0.19	0.10
20	MAU	5.1	124.9	80.6	44.2	67.2	292.3	4.0	0.3	1.8	0.77	0.08	0.02	0.12	0.01
21	SEL	5.6	87.0	26.2	60.8	21.8	104.2	2.3	0.1	2.8	0.46	0.04	0.04	0.46	0.00
22	BRE	4.8	136.3	89.1	47.2	74.3	334.4	1.4	0.1	1.1	0.32	0.07	0.02	0.56	0.03
23	TAI	11.0	142.1	34.7	107.3	28.9	139.2	4.6	0.1	4.2	0.45	0.02	0.00	0.53	0.00
24	SCW	17.6	186.4	3.1	183.3	2.6	23.8	2.6	0.2	3.1	0.48	0.01	0.07	0.37	0.06
25	VOR	3.0	51.3	21.4	29.9	17.8	80.3	7.4	0.3	6.4	0.50	0.01	0.12	0.28	0.09
26	TSC	0.6	80.1	71.1	9.0	59.2	218.2	9.3	0.3	3.5	0.26	0.01	0.57	0.10	0.06
27	CHV	5.4	51.4	0.7	50.7	0.6	7.8	4.8	0.7	5.6	0.27	0.01	0.01	0.67	0.04
28	RET	4.9	50.5	13.2	37.3	11.0	45.6	5.8	0.3	7.6	0.45	0.05	0.09	0.10	0.32
29	FÄL	6.4	66.8	10.9	55.9	9.1	50.7	6.7	0.2	9.7	0.45	0.00	0.29	0.05	0.21
30	SAL	5.2	71.0	21.4	49.6	17.8	85.1	7.7	0.5	9.1	0.52	0.00	0.29	0.03	0.15
31	GRO	2.7	48.8	22.1	26.7	18.4	45.5	41.2	0.6	7.9	0.79	0.01	0.03	0.15	0.02
32	ENG	2.0	68.6	44.7	23.9	37.3	149.2	4.6	0.5	2.5	0.29	0.00	0.59	0.04	0.08
33	SEB	21.8	185.6	1.2	184.4	1.0	14.8	8.7	0.2	3.4	0.42	0.00	0.15	0.15	0.27
34	TAN	6.8	96.1	0.5	95.6	0.4	6.5	7.0	0.3	4.8	0.70	0.02	0.18	0.00	0.10
35	MEL	2.8	29.7	1.2	28.4	1.0	5.8	9.0	0.5	6.2	0.72	0.01	0.19	0.02	0.06
36	SEW	6.7	59.5	0.4	59.1	0.3	4.0	3.9	0.1	8.5	0.24	0.00	0.00	0.70	0.06
37	BRT	5.1	84.1	41.6	42.5	34.7	139.0	9.2	0.1	4.2	0.83	0.05	0.00	0.10	0.01
38	TAY	7.2	106.3	46.5	59.9	38.7	164.0	3.1	0.1	4.8	0.35	0.01	0.21	0.25	0.17
39	NER	7.2	73.9	13.9	60.0	11.6	54.5	10.7	0.2	8.1	0.44	0.00	0.08	0.30	0.18
40	SÄG	2.4	53.8	37.9	15.9	31.6	123.1	8.0	1.0	5.7	0.41	0.00	0.40	0.02	0.17
41	WAN	2.8	26.4	0.2	26.1	0.2	7.0	8.4	0.2	5.9	0.03	0.00	0.84	0.00	0.13
42	BAN	3.3	35.5	6.7	28.8	5.6	26.4	15.5	0.7	5.2	0.32	0.00	0.58	0.02	0.07
43	IFF	1.4	44.4	34.0	10.4	28.3	115.1	8.1	0.4	5.1	0.18	0.00	0.73	0.00	0.09
44	FLU	2.2	35.2	18.1	17.1	15.1	56.4	8.0	0.6	5.6	0.08	0.00	0.92	0.00	0.00
45	LÄM	1.7	56.9	44.5	12.4	37.1	147.7	7.7	0.7	5.2	0.30	0.00	0.53	0.00	0.17
46	TRÜ	1.6	59.6	44.6	15.0	37.2	147.3	5.4	0.3	2.6	0.31	0.00	0.61	0.05	0.03
47	BAC	2.1	19.1	2.2	16.9	1.9	11.6	4.5	0.5	3.8	0.46	0.00	0.46	0.00	0.09
48	LUT	8.4	63.9	0.4	63.6	0.3	6.6	7.3	0.7	6.6	0.56	0.00	0.25	0.05	0.14
49	HAG	7.9	77.3	0.3	77.1	0.2	7.9	4.9	0.4	5.6	0.42	0.00	0.55	0.00	0.03
50	GRD	4.4	47.2	4.8	42.4	4.0	21.0	12.3	0.3	2.6	0.49	0.22	0.01	0.26	0.02
51	SCE	2.7	74.7	51.7	23.0	43.1	91.2	63.6	0.3	4.0	0.26	0.00	0.58	0.00	0.16
52	OBE	7.7	64.6	6.4	58.2	5.3	24.7	39.0	0.2	4.2	0.63	0.06	0.02	0.26	0.03
53	TÜR	6.1	102.7	59.0	43.7	49.1	192.1	11.7	0.2	3.3	0.58	0.15	0.00	0.25	0.02
54	SWL	4.1	80.3	48.4	31.9	40.3	153.6	16.2	0.5	3.0	0.27	0.00	0.57	0.01	0.15
55	BIC	3.5	91.4	56.8	34.6	47.3	167.1	39.3	0.1	3.3	0.28	0.03	0.00	0.69	0.00
56	EGE	13.9	158.6	34.2	124.3	28.5	137.4	5.5	0.1	1.7	0.00	0.00	0.03	0.80	0.17
57	DIT	12.5	165.4	60.7	104.8	50.5	205.4	2.3	0.2	1.4	0.69	0.06	0.03	0.21	0.00
58	INK	9.8	132.8	47.8	85.0	39.8	164.5	8.9	0.2	2.8	0.68	0.09	0.01	0.21	0.01
59	HAS	4.7	130.7	92.9	37.8	77.4	295.7	7.6	0.1	1.0	0.76	0.05	0.00	0.17	0.01
60	NUS	6.1	141.5	86.5	54.9	72.1	277.3	8.8	0.1	1.0	0.69	0.07	0.01	0.24	0.00
61	GAW	7.5	121.7	57.4	64.3	47.8	185.0	13.0	0.1	2.5	0.27	0.02	0.00	0.71	0.00
62	HÜN	7.7	145.1	68.0	77.1	56.7	225.4	6.6	0.1	1.8	0.82	0.09	0.01	0.06	0.02
63	ROU	10.2	169.6	60.6	109.0	50.5	206.4	5.1	0.1	2.2	0.40	0.10	0.00	0.50	0.00
64	ABB	23.1	218.3	24.4	193.9	20.4	88.0	6.4	0.1	2.5	0.50	0.10	0.00	0.40	0.00
65	MON	25.2	203.0	0.5	202.5	0.4	9.9	13.4	0.2	2.3	0.49	0.15	0.01	0.34	0.01
66	SEG	12.1	131.6	35.4	96.2	29.5	120.3	11.2	0.1	2.4	0.25	0.08	0.05	0.61	0.01
67	END	5.6	117.9	70.4	47.5	58.7	231.9	10.3	0.1	3.0	0.40	0.10	0.00	0.50	0.01
68	LIO	9.2	87.0	5.5	81.5	4.6	28.2	10.0	0.0	6.4	0.30	0.01	0.28	0.14	0.27