

# Initial Changes in Refilled Lysimeters Built with Metal Polluted Topsoil and Acidic or Calcareous Subsoils as Indicated by Changes in Drainage Water Composition

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**Abstract** Soil translocation for recultivation of soil removed from construction sites and for the preparation of refilled lysimeters inevitably involves disturbance of soil structure, and, if intermediate storage is included, also drying and rewetting of the soil. We report on an experiment with model forest ecosystems, where uncontaminated forest subsoils were covered with non-contaminated or freshly heavy metal (mainly Zn and Cu) contaminated topsoil in

large lysimeters. Monitoring of the chemical composition of the drainage water revealed two distinct soil conditioning phases. During an initial phase of about a year strongly elevated nitrate and sulfate concentrations occurred that were attributed to a mineralisation flush caused by the increased accessibility of mineralisable nitrogen and sulfur in destroyed aggregates. These effects were significantly larger in lysimeters with calcareous subsoil than in those with acidic subsoil. The second phase was characterised by a gradual decrease in dissolved organic carbon and sulfate concentrations, in particular in the acidic subsoil. This decrease may be attributed to the depletion of pools made accessible during aggregate destruction or the formation of new aggregates. These chemical changes had only little effects on the concentrations of copper and zinc in the drainage water. Based on our results, it can be concluded that large refilled lysimeters can be used for many purposes without risk of compromised results, if a conditioning phase of about 1 year with sufficiently moist soil conditions is respected. Nevertheless, gradual changes in soil chemical characteristics still occur after this initial phase. Implications for the recultivation of sites using relocated soils are discussed.

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Soil structure

## 1 Introduction

The recultivation of material removed from construction sites, waste deposits or open-cast mines involves the excavation of large amounts of soil material, its temporary storage and reuse in artificially built soils (Schmidt and Bannick 1996). The same is true, at a smaller scale, for experiments with refilled lysimeters, which provide a means to conduct factorially designed experiments with large plants or small ecosystems under controlled but relevant climate and soil conditions (Abrahamsen and Erstad 1995), bridging the gap between laboratory or greenhouse systems on one hand, and monolith lysimeters or the field on the other hand (Bergström and Stenström 1998).

Soil translocation inevitably involves disturbance or destruction of soil structures, and, if intermediate storage is included, also drying and rewetting of the soil (Zwölfer et al. 1991). Not taking into account the effects that this has on soil properties, can seriously compromise the results of studies performed with freshly reconstituted soil (Johnson et al. 1995). Here we focus on biologically mediated chemical processes in well aerated soil material rather than on the effects of compaction and waterlogging during intermediate storage on soil fertility. The latter aspect has been studied extensively and found its way into soil protection regulations and recommendations for practitioners (Zwölfer et al. 1991). A well known effect is a flush of nitrogen and carbon mineralization occurring upon rewetting of dried or sieved soil (Birch 1958). It leads to high nitrate and dissolved organic carbon (DOC) concentrations in soil solution. Highly elevated nitrate concentrations led to a negative growth response of pine seedlings to N fertilization in a pot experiment as opposed to a positive response in the field (Johnson et al. 1995). The effect is ascribed to a large amount of available C and N in dead microorganisms (Powelson 1980) or in liberated soil organic matter and ammonium in destroyed aggregates (Franzluebbers 1999; Ross and Hales 2003). The strong increase in nitrate concentrations upon aggregate destruction does not surprise considering the significant effects that rather small soil disturbances like footprints or formation of trenches can have on nitrogen mineralization rates (Miller et al. 1992; Ross and Hales 2003). There is agreement that this process is an initial one, and that the effects cease

with time. This is due to consumption and leaching of the liberated pool of easily mineralizable material (Ross and Hales 2003) and to the formation of new aggregates (Bergström and Stenström 1998). However, indications of how long elevated solute concentrations occur are rare, in particular for large refilled lysimeters. Johnson et al. (1995) observed nitrate concentrations in unfertilised pots going down from 1 mM to a few  $\mu\text{M}$  within 30 weeks. For a column experiment, Franzluebbers (1999) reported a ceasing of enhanced DOC concentrations after a conditioning phase of 10 days. Sogn and Abrahamsen (1998) observed enhanced leaching of sulfate in the first year after refilling lysimeters with forest soil material.

In a lysimeter experiment we studied the effects of subsoil type, irrigation pH and topsoil metal contamination on plant and soil parameters in model forest ecosystems. The lysimeters were filled with two different combinations of top and subsoils as substrates that were compatible with respect to texture, pH and soil organic matter (SOM) content. Results from the second phase of the experiment with rather stable soil conditions can be found elsewhere (Brunner et al. 2007; Frey et al. 2006; Hermle et al. 2006, 2007; Menon et al. 2005; Nowack et al. 2006; Rais 2005). Here, we report changes in drainage water composition as indicators of changes in the subsoil during the experiment.

## 2 Materials and Methods

### 2.1 Lysimeter Experiment

The model ecosystems were established in the open-top chamber (OTC) facility of the Swiss Federal Institute for Forest, Snow and Landscape Research, WSL, Birmensdorf, Switzerland (450 m a.s.l.). Each lysimeter was planted randomly with 14 trees (six *Picea abies* (L.) Karst. (3-year-old trees); four *Populus tremula* cuttings without roots; two *Salix viminalis* rooted cuttings; two *Betula pendula* rooted cuttings; all the rooted cuttings were 6 months old and planted before bud break) and understorey plants. Each of the 16 OTC contained two lysimeters. In the growing seasons (May through October), lysimeters in eight OTCs received irrigation with synthetic rain of pH 5.5 and those in the other eight synthetic rain of pH 3.5, and the roofs of the OTC closed automatically

during rain events to exclude natural precipitation. The ionic composition of the synthetic rain mimicked the 30 years mean of the local natural rain (70 NH<sub>4</sub>, 70 NO<sub>3</sub>, 3.2 PO<sub>4</sub>, 17 Cl, 3.1 SO<sub>4</sub>, 4.3 Na, 7.7 K, 5 Ca, 1.3 Mg, 0.15 Zn [ $\mu\text{mol/L}$ ]). The pH was adjusted with HCl. The amount of the irrigation was adjusted to keep the water potential above  $-300$  hPa. If this was achieved in the topsoil, potentials in the subsoil were generally above  $-50$  hPa, except during the first year, when subsoil potentials were mostly between  $-50$  and  $-250$  hPa. According to a comparison between tensiometer and TDR readings, a potential of  $-300$  hPa corresponded to a water content of 0.18, 0.16, and  $<0.19$  for the topsoil, the calcareous, and the acidic subsoil, respectively. A potential of  $-50$  hPa corresponded to a water content of 0.23, 0.22, and 0.3, respectively. During winter (November through April), the roofs remained open and the lysimeters received natural precipitation. Four additional lysimeters without OTC received natural precipitation throughout the year. Table 1 gives an overview of the amounts of irrigation and natural precipitation received by the lysimeters. More details on the lysimeter facility can be found in Landolt (2001) and Hermle et al. (2006).

The lysimeters had a surface area of 3 m<sup>2</sup> and a depth of 1.5 m. They were filled as follows. A 50 cm drainage layer consisted of three sublayers of firedried quartz gravel with grain sizes of 5–8, 1.5–2.2, and 0.7–1.2 mm. It was composed of 99% SiO<sub>2</sub>, 0.4% Al<sub>2</sub>O<sub>3</sub>, 0.2% of Na<sub>2</sub>O+K<sub>2</sub>O, and 0.05% each of CaO+MgO, Fe<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, and was acid washed to remove impurities. Above the drainage packing there was an 80 cm layer of subsoil and a 15 cm layer of topsoil. The subsoil was either an acidic loamy sand from a Haplic Alisol near Eiken, Aargau, Switzerland, or a calcareous sandy loam originating from a Calcaric Fluvisol near Vogelsang-Brugg, Aargau, Switzerland. The topsoil was a slightly acidic loam from Birr, Aargau, Switzerland. The sequences of soil layers were representative of an acidic soil, in which the topsoil pH was raised by agricultural practice, and a calcareous soil with a decarbonated topsoil, respectively. Some physical and chemical characteristics of the soil materials are given in Table 2. For more data see Nowack et al. (2006). Before being filled into the lysimeters, the soils were stored near the experimental site, protected from precipitation (Brugg for 1 year, Eiken and Birr for less than 1 month). The subsoils

were filled in September 1999 to settle down during the following winter. The topsoil was mixed with a manure mixer and filled in January 2000. In March 2000, the roofs of the OTC were closed to allow the topsoil to dry, before end of April 2000 in half of the lysimeters the filter dust from a secondary non-ferrous metal smelter was worked into the topsoil layer. The filter dust increased the topsoils natural heavy metal (HM) contents (Table 2) to 640 mg/kg Cu, 3000 mg/kg Zn, 10 mg/kg Cd, and 90 mg/kg Pb. Finally, the vegetation was planted in May 2000. Unavoidably, this led to some structural disturbance in the topsoil. This, however, was the same in all treatments, and, thus, helped to balance a possible structural effect by the manual mixing of topsoil with dust in the heavy metal treatments. Irrigation started immediately after planting.

The combination of contaminated vs. uncontaminated topsoil, acidic vs. calcareous subsoil and irrigation with rain pH 5.5 vs. rain pH 3.5 resulted in eight different treatments that were replicated each four times, using a Latin square arrangement of the OTC with respect to irrigation and topsoil, while each OTC hosted one lysimeter with acidic subsoil and one lysimeter with calcareous subsoil. The additional treatments with natural precipitation (lysimeters outside OTC) were done only once.

## 2.2 Tensiometry, Sampling and Analysis of Drainage Water

In each OTC lysimeter, eight tensiometers were installed vertically, two each at 12.5, 37.5, 62.5 and 87.5 cm depths (middle of ceramic cups). Soil water potentials were recorded once a week during the growing season, using the method of Marthaler et al. (1983). No soil moisture data were recorded for the lysimeters receiving natural precipitation throughout the year.

Drainage water was collected in three polyethylene tanks each from the bottom of each lysimeter. The water collected from the three containers of the same lysimeter was pooled. Samples of the collected water were either analysed individually, or combined with the other samples of the same treatment for analysis. The volume of the drainage water was recorded consistently during the growing season, while this was not possible during the winter. For a given sampling, discharge in L m<sup>-2</sup> day<sup>-1</sup> was calculated by

**Table 1** Average daily rates of natural precipitation, irrigation, and drainage discharge, as well as average water potentials for different time periods; significant differences between acidic and calcareous subsoils are indicated next to the numbers, significant differences between irrigated and non-irrigated lysimeters in separate columns; \*\*\* $p < 0.0001$ , \*\* $p < 0.001$ , \* $p < 0.01$ , ( $*$ ) $p < 0.05$ , *ns* not significant

Time period	Natural precipitation [L m <sup>-2</sup> day <sup>-1</sup> ]	Irrigation [L m <sup>-2</sup> day <sup>-1</sup> ]	Water potential in irrigated lysimeters (mean±standard deviation)				Drainage water discharge						
			88 cm		38 cm		Irrigation (mean±standard deviation)		Natural precipitation (mean±standard deviation)		Irrigation vs. natural precipitation		
			Acidic subsoil [hpa]	Calcareous subsoil [hpa]	Acidic subsoil [hpa]	Calcareous subsoil [hpa]	Acidic subsoil [L m <sup>-2</sup> day <sup>-1</sup> ]	Calcareous subsoil [L m <sup>-2</sup> day <sup>-1</sup> ]	Acidic subsoil [L m <sup>-2</sup> day <sup>-1</sup> ]	Calcareous subsoil [L m <sup>-2</sup> day <sup>-1</sup> ]	Acidic subsoil	Calcareous subsoil	
1.10.1999–15.3.2000	2.80	2.802											
15.3.–22.5.2000	2.45	1											
22.5.–4.9.2000	4.69	3.14	-139±94	-95±61	-172±90	-132±64	0.17±0.12	0.20±0.17	0.76±0.13	0.69±0.17	*	(*)	
4.9.–8.11.2000	3.20	4.15	-18 <sup>3</sup>	-17 <sup>3</sup>	-27 <sup>3</sup>	-22 <sup>3</sup>	1.62±0.67	1.51±0.67	1.20±0.36	1.03±0.44	ns	ns	
8.11.2000–13.4.2001	3.18	3.182											
13.4.2001–18.7.2001	3.44	2.81	-66 ± 46(*)	-355 ± 212(*)	-47 ± 30	-141 ± 123	0.96 ± 1.28	0.31 ± 0.35	0.59 ± 0.45	0.50 ± 0.35	ns	ns	
18.7.2001–6.11.2001	3.62	5.5	-18±3*	-24±4*	-28±3*	-35±5*	2.28±1.44(*)	1.41±1.05	0.68±0.96	0.41±0.59	***	(*)	
6.11.2001–15.5.2002	2.36	2.362											
15.5.2002–2.7.2002	3.56	3.62	-33±12*	-113±115*	-145±118	-211±169	0.71±0.60	0.50±0.57	0.66±0.54	0.29±0.42	ns	ns	
2.7.2002–24.10.2002	4.92	5.59	-16±2	-35±21	-28±3**	-37±4**	2.05±0.72*	1.02±0.74*	0.77±1.06	0.58±0.96	**	ns	
24.10.2002–7.5.2003	2.60	2.602											
7.5.2003–18.9.2003	4.35	9.05	-17±3*	-32±22*	-35±18	-41±14	1.89±1.12	1.41±1.01	0.04±0.03	0.04±0.03	**	*	
18.9.2003–5.12.2003	2.67	2.672											

<sup>1</sup> OTC closed.

<sup>2</sup> OTC received natural precipitation.

<sup>3</sup> Only one sampling.

dividing the volume first by the area of a lysimeter and then by the number of days since the last sampling.

Individual or pooled drainage water samples were filtered (0.45µm), and analysed for pH (potentiometrically, electrode: Radiometer pHC4000-8), electrical conductivity (cell: Radiometer XE170), DOC (elemental analyser, Shimadzu TOC-V), inorganic anions (ion chromatography, Dionex DX-120) and total element concentrations (inductively coupled plasma mass spectrometry, Perkin Elmer ELAN 6000).

### 2.3 Soil Respiration

Soil respiration was measured in all lysimeters in August 2000, June 2001, and August 2001. In June and August 2002 and 2003, soil respiration was measured only in the irrigated lysimeters. The measurements were taken from pre-installed soil collars with a diameter of 10.2 cm and a depth of 4.5 cm. Four soil collars were installed in each lysimeter, avoiding placements close to a tree or at the edge of the lysimeter, and were kept free of

**Table 2** Selected physical and chemical characteristics of the soil materials used to build the lysimeter soils (from Nowack et al. 2006); measurements were taken from dried and sieved composite samples at the beginning of the experiment

	Topsoil	Acidic subsoil	Calcareous subsoil
Texture [% sand; silt; clay] <sup>1</sup>	36; 49; 15	87; 8; 5	74; 16; 10
pH (0.01 M CaCl <sub>2</sub> ) <sup>2</sup>	6.4	4.2	7.4
C <sub>inorg</sub> [g/kg] <sup>3</sup>	<1	<1	21
C <sub>org</sub> [g/kg] <sup>3</sup>	15.1	3.2	11.2
N <sub>tot</sub> [g/kg] <sup>3</sup>	1.5	<0.3	0.6
CEC [mmol <sub>c</sub> /kg] <sup>3</sup>	102	31	134
Base saturation [%] <sup>3</sup>	99.9	35.9	99.9
Cu <sub>tot</sub> [mg/kg] <sup>3</sup>	28	7.4	14
Zn <sub>tot</sub> [mg/kg] <sup>3</sup>	97	39	58
Cd <sub>tot</sub> [mg/kg] <sup>3</sup>	0.1	<0.2	0.2
Pb <sub>tot</sub> [mg/kg] <sup>3</sup>	37	13	19

<sup>1</sup> Laboratory precision  $\pm 0.5\%$ .

<sup>2</sup> Laboratory precision  $\pm 0.02$ .

<sup>3</sup> Laboratory precision  $\pm 10\%$ .

mosses and germinating plants. At a given measurement series, CO<sub>2</sub> efflux from each collar was measured once, using a Li-6400 portable photosynthesis system (Li-Cor Inc., Lincoln, Nebraska) fitted directly with a 6400-09 soil CO<sub>2</sub> flux chamber. The total system volume was 991 cm<sup>3</sup>. Mixing in the chamber headspace was achieved with the gas analyzer mixing fan and the associated manifold. Efflux of CO<sub>2</sub> from the soil was computed based on the rate of CO<sub>2</sub> increase in the chamber headspace between -10 ppm and +10 ppm from the actual ambient CO<sub>2</sub> concentration (Healy et al. 1996). For each measurement, soil temperature was recorded using a probe with a precision of  $\pm 1.5^\circ\text{C}$ .

### 3 Results

#### 3.1 Drainage Discharge and Soil Moisture in the Irrigated OTC Lysimeters

In the first summer, drainage discharge was very low until September (Table 1) with water potentials in the topsoil and both subsoils varying between -40 and -250 hPa. In September the water potential at all soil depths rose to about -20 hPa and large amounts of drainage discharge were collected (Table 1). In 2001, until mid of July, irrigation was not sufficient leading to small amounts of drainage and water potentials down to -550, -130, and -250 hPa in the calcareous subsoils, acidic subsoils, and topsoils, respectively

(data not shown). After this period, large amounts of drainage discharge were obtained. Water potentials in the subsoil were between -20 and -50 hPa with little temporal variation, and in the topsoil they varied between -25 and -100 hPa. Both average drainage discharge and water potentials were significantly larger in the acidic than in the calcareous subsoil (Table 1). In 2002 and 2003, water potentials varied between -15 and -40 hPa in the subsoils and between -50 and -300 hPa in the topsoils most of the time. The exception was a purposely induced drought period in June 2002 with water potentials going shortly down to -550, -350, and -750 hPa in the calcareous subsoil, acidic subsoil and topsoil, respectively (data not shown). Drainage discharge was large (Table 1) except for the induced drought period. In both years, soil moisture in the lower part of the subsoil was higher in the acidic subsoil than in the calcareous subsoil (Table 1). In 2002, this was also the case for the drainage discharge.

#### 3.2 Drainage Discharge and Soil Moisture in the Lysimeters Receiving Natural Precipitation

Weather conditions during the first and second summer allowed the lysimeters with natural precipitation to remain sufficiently moist throughout the growing season to allow collection of drainage water. From May through August 2000, there was even more drainage from these lysimeters than from the irrigated lysimeters (Table 1). However, there was

almost no drainage discharge in August and September 2002 and during the entire warm summer 2003. In 2001, 2002 and 2003, discharge from the lysimeters with natural precipitation was significantly lower than in the corresponding irrigated lysimeters except for the calcareous subsoil in 2002 (Table 1).

### 3.3 Chemical Composition of Drainage Water

The chemical data of the drainage water samples from the different sampling dates were subjected to a multivariate analysis of variance (MANOVA) to test the influence of subsoil type, irrigation vs. natural precipitation, irrigation type, and topsoil contamination (comparing lysimeters with and without metal dust added to the topsoil). This showed that the chemical composition of the drainage water differed mainly between acidic and calcareous subsoil, and, in the first year in addition between irrigated and non-irrigated lysimeters (Table 3). Only pH was influenced by irrigation pH and somewhat by topsoil contamination. Therefore, irrespective of topsoil contamination or irrigation pH, data were pooled for a given subsoil and watering treatment (artificial irrigation vs. natural precipitation) (Figs. 1, 2 and 3).

Below calcareous subsoil, the electrical conductivity as well as the concentrations of nitrate and sulfate were higher during an initial phase of 9, 12 and 10 months, respectively, than during the later stages of the experiment (Fig. 1). These effects were smaller for the lysimeters receiving only natural precipitation (Fig. 1). Below acidic subsoil, conductivity and nitrate concentrations were elevated during an initial phase of 6 months with significantly smaller conductivity values for lysimeters receiving only natural precipitation.

During the second phase, below calcareous subsoil, electrical conductivity exhibited a regular sea-

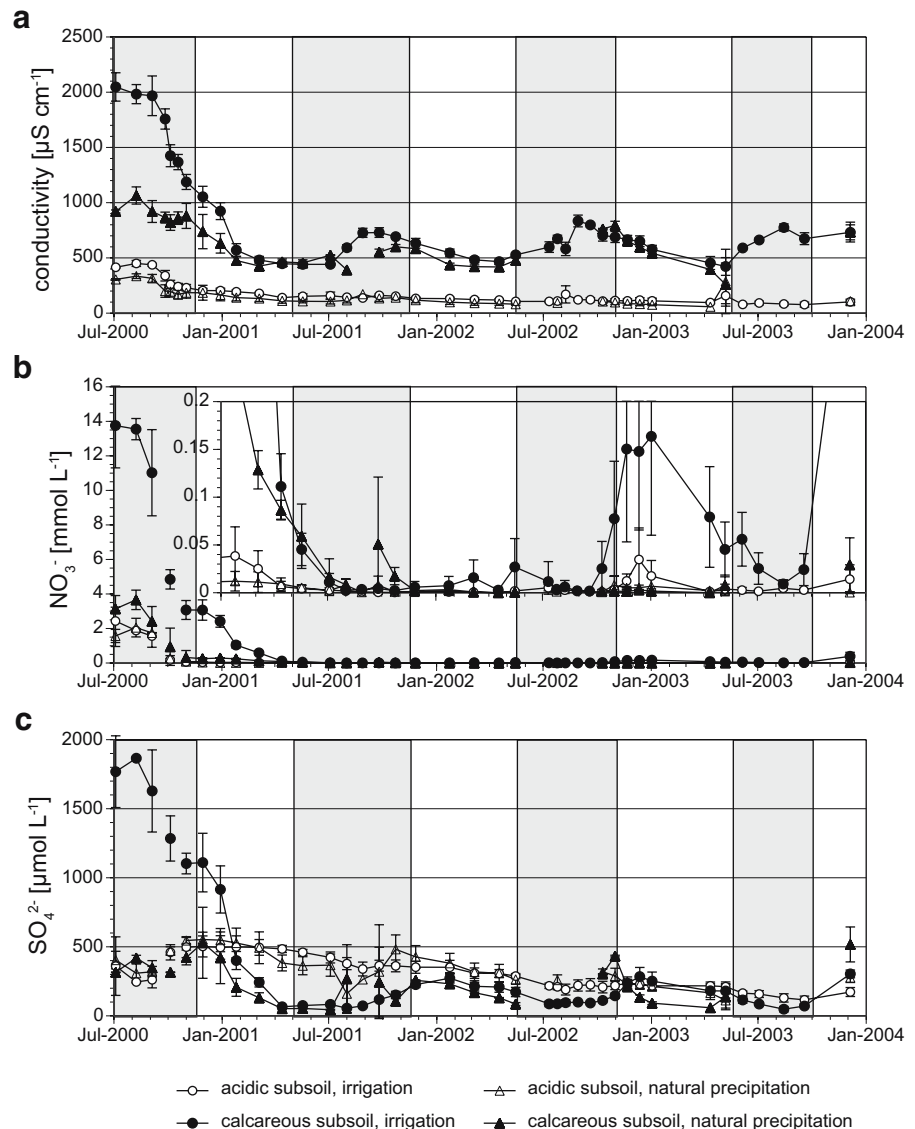
sonal variability with maxima in October, which was the same in irrigated and non-irrigated lysimeters. Below acidic subsoil, conductivity decreased slightly and constantly. This change was significant only for the irrigated lysimeters however (Table 4). In contrast to constantly low nitrate concentrations during the second phase of the experiment below acidic subsoil and calcareous subsoil in non-irrigated lysimeters, nitrate below the irrigated lysimeters with calcareous subsoil remained low for one and a half years, but exhibited small seasonal increases in winter 2002/2003 and in winter 2003/2004 (Fig. 1b, inset). The latter were responsible for a small increasing trend (Table 4). From the second year on the sulfate concentrations exhibited a seasonal variation with maxima in early winter below calcareous subsoil in both irrigated and non-irrigated lysimeters. Below irrigated and non-irrigated lysimeters with acidic subsoil, sulfate decreased over the entire observation period (Fig. 1c; Table 4).

Dissolved organic carbon (DOC) concentrations were somewhat elevated during the first year below calcareous subsoil (Fig. 2a). Later, the DOC concentrations below calcareous subsoil adopted a seasonal variation with maxima in late summer on top of a trend to decrease (Table 4). Below acidic subsoil, DOC concentrations decreased continuously during the entire experiment without distinctive initial phase and without seasonal fluctuations. The pH below calcareous subsoil was approximately 8 for the first 5 months and varied between 8.2 and 8.7 thereafter (Fig. 2b), with no difference between irrigated and non-irrigated lysimeters. The pH for irrigated lysimeters with acidic subsoil was also approximately 8 for the first 5 months, followed by a drop to seasonally varying values between 6 and 7.5 with maxima in summer. The drainage water below non-irrigated lysimeters with acidic subsoil showed a seasonal

**Table 3** Results of MANOVA for the drainage water samples of all sampling dates ( $n=40$ )/sampling dates of the first year (4.7.2000–18.5.2001;  $n=13$ ); \*\*\* $p < 0.0001$ , \*\* $p < 0.001$ , \* $p < 0.01$ , ns not significant

	Subsoil type	Irrigation vs. natural precipitation	Irrigation type	Topsoil contamination
Conductivity	***/**	ns/**	ns/ns	ns/ns
NO <sub>3</sub>	***/**	ns/ns	ns/ns	ns/ns
SO <sub>4</sub>	ns/**	ns/*	ns/ns	ns/ns
DOC	***/**	ns/ns	ns/ns	ns/ns
pH	***/**	***/**	***/ns	*/ns
Cu	***/**	*/ns	ns/ns	ns/ns
Zn	***/**	ns/ns	ns/ns	ns/ns

**Fig. 1** Electrical conductivity (a), nitrate (b), and sulfate concentrations (c) in the drainage water. Shown are mean values with standard deviations for irrigated lysimeters ( $n=4$  for pooled samples per treatment) and lysimeters receiving natural precipitation throughout ( $n=2$  for individual samples per treatment); the grey parts indicate the time period with irrigation

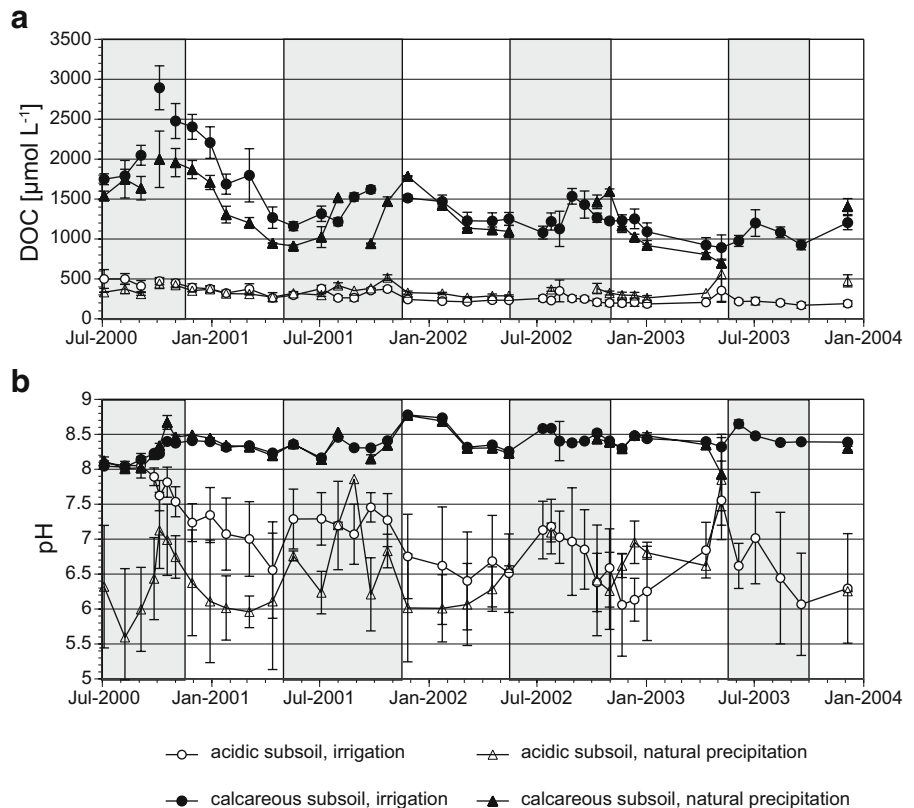


variation throughout the experiment with no distinct initial phase.

Copper concentrations were generally larger below calcareous subsoil than below acidic subsoil. Below calcareous subsoil, Cu varied similar to DOC (Fig. 3a, Table 4), and there was a good correlation between logarithmic concentrations of Cu and DOC ( $R^2=0.58$ ;  $p<0.0001$ ). Below acidic subsoil, Cu concentrations increased gradually during the first year and remained constant for the rest of the experiment. The increase during the first year was negatively correlated with pH (logarithmic concentrations;  $R^2=0.33$ ;  $p=0.003$ ).

Zinc concentrations below calcareous subsoil showed a seasonal variation during the entire experiment with maxima in summer (Fig. 3b). The logarithmic Zn concentrations were correlated mainly with pH (negative correlation;  $R^2=0.23$ ;  $p<0.0001$ ) and logarithmic conductivity ( $R^2=0.13$ ;  $p=0.003$ ). Zinc below acidic subsoil was correlated mainly with sulfate (logarithmic concentrations;  $R^2=0.36$ ;  $p<0.0001$ ). An initial phase of about 3 months was characterized by elevated Zn concentrations below non-irrigated and distinctly low concentrations below irrigated lysimeters. Later, Zn concentrations below

**Fig. 2** Dissolved organic carbon concentrations (a), and pH (b) in the drainage water. Shown are mean values with standard deviations for irrigated lysimeters ( $n=4$  for pooled samples per treatment) and lysimeters receiving natural precipitation throughout ( $n=2$  for individual samples per treatment); the grey parts indicate the time period with irrigation



acidic subsoil decreased more or less continuously (Fig. 3b, Table 4).

### 3.4 Soil Respiration

Figure 4 shows soil respiration measurements taken in August of each year. In the first year, respiration was significantly larger from the lysimeters receiving natural precipitation than from the irrigated lysimeters, in 2001 this was the case only for the lysimeters with acidic subsoil. Mostly, there were no significant differences between the respiration from lysimeters with calcareous and acidic subsoils. The exception was 2001, when respiration from the irrigated lysimeters with calcareous subsoil was larger than from the irrigated lysimeters with acidic subsoil, while it was the other way around for the non-irrigated lysimeters. Average respiration from the irrigated lysimeters correlated quite well with the average soil moisture in August in the topsoil:  $q\text{CO}_2$  [ $\mu\text{mol m}^{-2} \text{s}^{-1}$ ] $=8.2+0.023 \times h$  [hpa] ( $R^2=0.58$ ;  $p=0.029$ ). Correlations with water potentials in the

subsoil were worse with  $R^2=0.16$  at 38 cm depth and  $R^2=0.10$  at 88 cm depth.

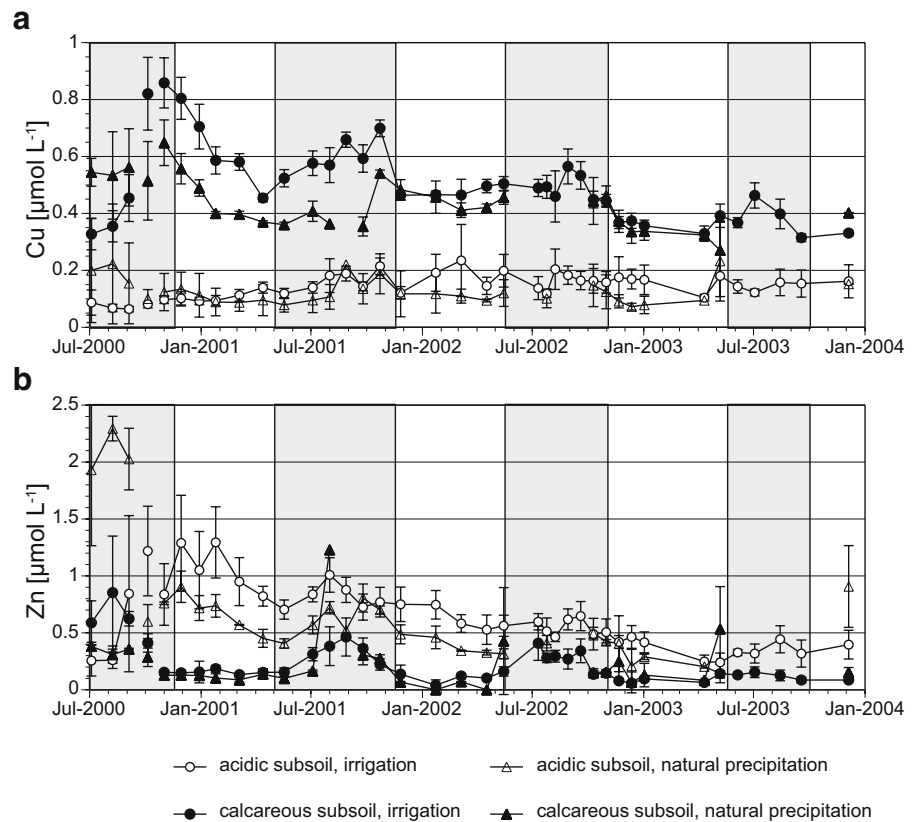
## 4 Discussion

### 4.1 Comparison Between Irrigated and Non-irrigated Lysimeters; Soil Moisture in the Irrigated Lysimeters

The initial electrical conductivity values below both subsoils and the initial nitrate and sulfate concentrations below calcareous subsoils were much less elevated in the drainage water of the lysimeters receiving natural precipitation throughout the year than in those receiving artificial irrigation during the growing season. This may be explained by the different moisture and temperature regime during the last phase of installation and the first growing season. The lysimeters in the OTC received no water at all for 2 months during the establishment of the contamination in the topsoil, whereas, at the same time, the lysimeters outside the OTC were exposed to natural



**Fig. 3** Copper (a), and zinc concentrations (b) in the drainage water. Shown are mean values with standard deviations for irrigated lysimeters ( $n=4$  for pooled samples per treatment) and lysimeters receiving natural precipitation throughout ( $n=2$  for individual samples per treatment); the grey parts indicate the time period with irrigation



precipitation of  $2.45 \text{ L m}^{-2} \text{ day}^{-1}$  (Table 1). In addition, there was more natural precipitation than irrigation during the first part of the growing season 2000 (Table 1). This marked difference in soil moisture regime between irrigated and non-irrigated lysimeters for about half a year very likely also explains why during the first phase of the experiment high pH values of about 8 below acidic subsoil were

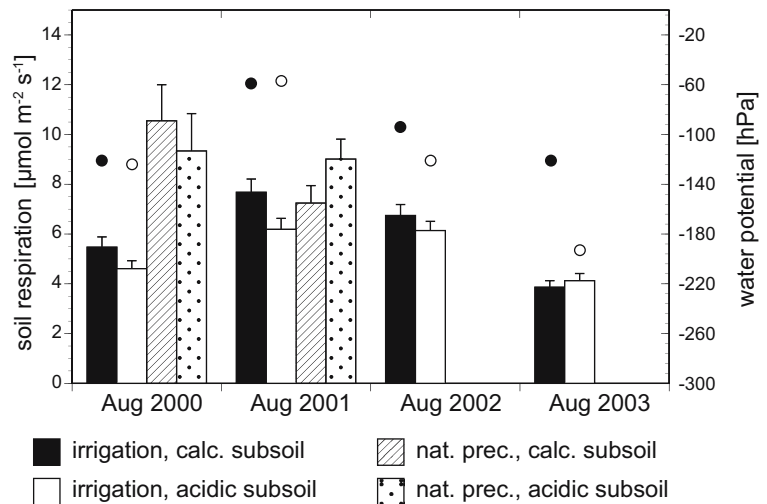
observed only below the irrigated lysimeters. These high pH values indicate the occurrence of carbonate impurities in the quartz drainage packing that were dissolved after passage of sufficient drainage water.

The generally drier conditions in the irrigated lysimeters with calcareous subsoils than with acidic subsoils during the growing seasons 2001, 2002, and 2003 can be attributed to the larger water consumption

**Table 4** Change in drainage water composition between July 2001 and July 2003; \*\*\* $p < 0.0001$ , \*\* $p < 0.001$ , \* $p < 0.01$ , ( $*$ ) $p < 0.05$ , *ns* not significant

	Acidic subsoil, irrigation	Acidic subsoil, natural precipitation	Calcareous subsoil, irrigation	Calcareous subsoil, natural precipitation
conductivity [ $\mu\text{S cm}^{-1} \text{ year}^{-1}$ ]	-24*	-1	-7	+6
$\text{NO}_3$ [ $\mu\text{mol L}^{-1} \text{ year}^{-1}$ ]	+4	+0.4	+45*	-10
$\text{SO}_4$ [ $\mu\text{mol L}^{-1} \text{ year}^{-1}$ ]	-116***	-92(*)	+19	-9
DOC [ $\mu\text{mol L}^{-1} \text{ year}^{-1}$ ]	-45(*)	-2	-213**	-227
pH [ $\text{year}^{-1}$ ]	-0.22	+0.18	+0.04	-0.06
Cu [ $\mu\text{mol L}^{-1} \text{ year}^{-1}$ ]	-0.02	-0.01	-0.12***	-0.06(*)
Zn [ $\mu\text{mol L}^{-1} \text{ year}^{-1}$ ]	-0.31***	-0.25***	-0.11(*)	-0.12

**Fig. 4** Soil respiration (*columns*) and average water potential in the topsoil (*bubbles*) measured in August; *filled* and *empty bubbles* refer to lysimeters with calcareous and acidic subsoil, respectively



by the plants associated with the larger biomass production (Menon et al. 2005; Hermle et al. 2006).

#### 4.2 Drainage Water Chemistry Below Irrigated Lysimeters, General Considerations

A bromide tracer experiment with the calcareous subsoil, carried out in an earlier study, revealed that a small part of water moved in larger pores at a velocity of about  $25 \text{ mm day}^{-1}$ , while the main part drained at velocities between 3 and  $10 \text{ mm day}^{-1}$  (Sonnleitner et al. 2003). From this it can be concluded that the chemical composition of the drainage water can be assumed to be determined mainly by equilibrium with the deeper subsoil. Considering the similar texture of the two subsoils, the same can be assumed for the drainage water leaving the acidic subsoil.

Nowack et al. (2006) showed, based on the analysis of soil solution samples collected during the last 2 years of the experiment using tension lysimeters, that the addition of the HM dust had led to elevated concentrations of Cu, Zn, Cd and Pb in the topsoil (10 cm depth), but not in the subsoil solution (40 and 70 cm depth). Effects of the topsoil contamination were therefore restricted mainly to the topsoil and are not discussed in the following.

Based on electrical conductivity as a sum parameter representing ionic strength, we can distinguish two phases: an initial phase with rapid chemical changes during about 9 months, and a second phase characterized by gradual chemical changes overlaid by seasonal variations. The generally higher electrical

conductivity below the calcareous subsoils can be attributed to the dissolution of carbonates. The seasonal increase of conductivity below calcareous subsoils in autumn indicates mineralisation of soil organic matter (SOM). This is probably much stronger below calcareous subsoils than below acidic subsoils because of the higher SOM content and higher pH of the calcareous subsoils.

#### 4.3 Nitrate in the Drainage Water Below Irrigated Lysimeters

The initial flush of nitrate can be ascribed to the mineralisation of organic nitrogen (followed by nitrification) exposed to microbial decomposition after the disruption of soil structure in the course of soil relocation and rewetting of the soil at the onset of the experiment (Birch 1958). Concentrations were up to 100 times and 20 times higher than the combined input of ammonium and nitrate by irrigation ( $140 \mu\text{mol L}^{-1}$ ) below calcareous and acidic subsoil, respectively. Below the calcareous subsoil, the nitrification during the initial phase was so strong that the related proton production probably exceeded the buffering capacity of the soil and was therefore responsible for the slightly lower pH value during the initial phase. The difference between the calcareous and acidic subsoil can be ascribed to the marked difference in total N and soil organic carbon content between the two subsoils and the less favorable conditions for microorganisms resulting from the lower pH and nutrient contents in the acidic subsoil

(Table 2). The concentration of 12 mmol L<sup>-1</sup> nitrate below the calcareous subsoil is similar to the increase of the initial nitrate concentration in soil solution during a pot experiment caused by fertilising a homogenized agricultural topsoil (weakly acidic clay loam) with 100 µg/g ammonium (Johnson et al. 1995). The latter study was carried out at 25°C, i.e. at a somewhat higher temperature than during our experiment. With an irrigation to ensure a constant free drainage, the elevated initial nitrate concentrations came down to about 500 µmol L<sup>-1</sup> within 8 months. In a column study with homogenized material from an acidic sandy loam from a forest topsoil rich in soil organic carbon and total N (2.4%) at a temperature of 10°C, Ross and Hales (2003) observed initial nitrate concentrations of about 5 mmol L<sup>-1</sup>. With a regular weekly irrigation of 25 mm, i.e. similar as the average irrigation in our experiment during the first summer, nitrate concentrations decreased much more slowly than in the one of Johnson et al. (1995). After 2 years, nitrate concentrations were still at about 1.5 mmol L<sup>-1</sup>. The comparison with these earlier studies suggests, that the intensity of the initial nitrification flush depends both on the SOM content and the temperature, while the rate at which the elevated nitrate concentrations decrease is determined by the rate of irrigation and possibly by the temperature.

The seasonal maxima of nitrate in the drainage water below calcareous subsoils in the third and fourth winter roughly correspond to the total nitrogen input during these periods, during which there was no uptake by plants and microorganisms. The lack of this maximum in the second winter indicates a strong depletion of available nitrogen during the initial mineralisation burst. In the same line of argumentation, the much smaller increase in leached nitrate during the second, third and fourth winter below acidic subsoils than below calcareous subsoils suggests, that, despite its relatively low intensity, the initial nitrification flush in the acidic subsoil had led to a strong depletion of available nitrogen.

#### 4.4 Sulfate in the Drainage Water Below Irrigated Lysimeters

In contrast to nitrate, sulfate concentrations were orders of magnitude higher than input concentrations (3 µmol L<sup>-1</sup>) over the entire observation period

independently of the type of subsoil. In line with the hypothesized nitrogen mineralization above, the elevated sulfate concentrations below the calcareous subsoil during the initial phase can be attributed to mineralisation of SOM that became exposed by disruption of soil structure as a result of soil relocation. The winter maxima of sulfate leaching below calcareous subsoils during the second phase of the experiment paralleled the seasonality of DOC, and thus can be explained also by mineralisation of organic sulfur. The high sulfate concentrations below the acidic subsoils can be attributed either to mineralisation of organic sulfur, or to leaching of sulfate previously accumulated in the soils at their original site. All soils were taken from suburban areas in Switzerland that were subjected to high sulfate depositions during the nineteen seventies and eighties, as were most such areas in central Europe (Ferrier et al. 2001). Leaching of sulfate, that was accumulated during the time period of high atmospheric input of sulfur, has been observed widely for acidic forest soils (Alewell and Matzner 1993). The rather rapid continuous decrease of the sulfate concentrations below acidic subsoil during the second phase of our experiment could have resulted from depletion of the mobilisable sulfate pool, or from the formation of new aggregates protecting adsorbed sulfate or organic sulfur.

#### 4.5 Dissolved Organic Carbon in the Drainage Water Below Irrigated Lysimeters

Both the generally much higher DOC concentrations below calcareous subsoil than below acidic subsoil, and the more pronounced seasonal variations below the calcareous subsoils can be attributed, firstly, to the much higher organic carbon content of the calcareous subsoil, and secondly to the probably less favorable conditions for microorganisms in the acidic subsoil because of the lower pH.

The seasonal variation of DOC below calcareous subsoil corresponds to the expected patterns in the activity of SOM degrading microorganisms, which are stimulated by plant growth and high temperatures with maximum activity in late summer. The decrease in DOC in the drainage water during winter on one hand reflects reduced microbial activity, and, on the other hand, retarded leaching of DOC produced during the time of maximum microbial activity. Water

flux as the governing force is less likely, since the highest DOC concentrations in autumn coincide with large water flux, and the lowest DOC concentrations at the beginning of the growing season with dry soil conditions. This is supported by the small effect of irrigation rate on DOC leaching from the subsoil in a column experiment using the same topsoil and subsoil as in our lysimeter experiment (Zhao et al. 2007) and by the mainly negative correlations between DOC concentrations and water flux observed by Strand et al. (2002). Considering the initial nitrogen mineralization flush, the somewhat enhanced DOC concentrations below calcareous subsoil in the first autumn can be ascribed to SOM mobilisation due to structural disruption during soil relocation (Birch 1958; Franzluebbers 1999). The gradual decrease of DOC over the entire experiment in both subsoils could be explained by a decrease of the rate of SOM degradation with time due to the formation of new aggregates, and/or by a gradual depletion of the SOM pool during the experiment. Indeed, the  $C_{\text{org}}$  content of the calcareous subsoil decreased somewhat from  $11.2 \text{ g kg}^{-1}$  at the beginning (Table 2) to  $9.7 \text{ g kg}^{-1}$  at the end of the experiment. Apart from the mineralisation burst during the first phase of the experiment, this depletion can be explained by the lack of fresh carbon input by litter fall. The aboveground biomass of poplar, willow and the understorey plants was harvested every year in September (Hermle et al. 2006).

#### 4.6 Soil Respiration

The better correlation of soil respiration with soil moisture in the topsoil than with the one in the subsoil, and the lack of a clear dependence of respiration on the type of subsoil, suggests that this parameter is mainly governed by topsoil parameters. This is in good agreement with the larger root density in the topsoils than in the subsoils (Menon et al. 2005) indicating a higher microbial activity in the topsoil. Nevertheless, one could have expected that an enhanced  $\text{CO}_2$  production during the initial mineralisation burst would have led to strongly elevated soil respiration, in particular from lysimeters with calcareous subsoil. The fact, that this was not observed in August 2000, can be explained with earlier findings that respective  $\text{CO}_2$  flushes, in contrast to increased nitrate production, subside a few days after rewetting (Franzluebbers 1999).

In addition, based on the correlation of respiration with soil moisture in the topsoil, the higher respiration from lysimeters receiving natural precipitation in August 2000 supports the assumption of higher soil moisture in these lysimeters than in the irrigated lysimeters.

#### 4.7 Trace Metals in the Drainage Water Below Irrigated Lysimeters

Since there was no influence of the HM contamination in the topsoil on the drainage water chemistry, the metal concentrations in the drainage water reflect the solubility of lithogenic HM in the subsoil. Overall, the chemical changes induced by aggregate destruction and/or drying and rewetting had only little consequences on the HM concentrations in the drainage water. The good correlation of Cu concentrations below calcareous subsoil with DOC (Rais 2005) and the generally higher Cu concentrations below calcareous than acidic subsoil, indicate strong complexation of Cu with dissolved organic matter, which is in agreement with the well known high affinity between Cu and DOC (McBride 1994). The positive correlation between Zn and electrical conductivity below calcareous subsoil, and the correlation between Zn and sulfate below acidic subsoil suggest an influence of cation exchange. Higher ionic strength means higher concentration of cations competing with Zn in the solution for cation exchange sites on the soil surface. Unfortunately, the concentrations of major cations, in particular Ca and Mg, were not measured. The occurrence of low Cu and Zn concentrations during the first months below irrigated lysimeters with acidic subsoil may have been caused by the precipitation of leached metals in the drainage layer due to carbonate impurities. However, the strongly elevated initial Zn concentrations below the non-irrigated lysimeters with acidic subsoil, for which pH values indicated no such artefact, suggest that the solubility of this metal was somehow related to the disturbance of soil structure.

## 5 Conclusions

Our study with refilled lysimeters revealed two distinct soil conditioning phases that can be related to structural disturbance of the soil material during

relocation. During an initial phase, the nitrogen and sulfur chemistry of a soil can be seriously affected by a mineralisation flush upon rewetting the dried soil which is enhanced by increased accessibility of mineralisable nitrogen and sulfur in destroyed aggregates. With respect to nitrogen, this corroborates previous findings. In our study, the effects were significantly larger in the lysimeters with calcareous subsoil than in those with acidic subsoil. This very likely can be attributed to the higher content in SOM and the higher pH of the calcareous subsoil. The second phase was characterised by a gradual decrease in DOC and sulfate, in particular in the acidic subsoil. This decrease may partly be attributed to depletion of pools made accessible previously during aggregate destruction, or to the formation of new aggregates.

Based on our results, it can be concluded that large refilled lysimeters can be used for many purposes without risk of compromised results, if a conditioning phase of about 1 year with sufficiently moist soil conditions is respected. Nevertheless, gradual changes in soil chemical characteristics still occur after this initial phase. Our results have implications also for the recultivation of sites using relocated soils. Nitrate flushes occurring after soil restoration may negatively affect the quality of water resources. Desiccation of stored soil should be avoided to minimise the extent of the mineralisation flush during recultivation. Temporary soil deposits are often kept dry to avoid degradation due to waterlogging (Zwölfer et al. 1991).

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