STABLE AND RADIOGENIC ISOTOPES AS TRACERS FOR SOIL DEGRADATION

Inauguraldissertation

zur
Erlangung der Würde eines Doktors der Philosophie
vorgelegt der
Philosophisch-Naturwissenschaftlichen Fakultät
der Universität Basel

von

Monika Schaub
aus Basel (BS) und Rünenberg (BL)

Basel, 2008
Genehmigt von der Philosophisch-Naturwissenschaftlichen Fakultät
auf Antrag von

Prof. Dr. Christine Alewell
Fakultätsverantwortliche / Dissertationsleiterin

Dr. Rolf Siegwolf
Korreferent

Basel, den 11.11.2008

Prof. Dr. Eberhard Parlow
Dekan
SUMMARY

Soil erosion seriously threatens mountain slopes. Direct measurement of soil erosion in the field is difficult and needs long term recording. However, stable and radiogenic isotopes are potential tracers for soil erosion estimation and would enable a quick and easy estimation of soil erosion. Soil degradation of upland soils influences nutrient content and biogeochemistry of wetlands. Our hypothesis was that due to the fact that oxic upland soils with a predominantly assimilatory metabolism differ significantly from anoxic wetland soils and riparian zones with dissimilatory metabolism, stable isotopes of carbon, nitrogen and oxygen can be used as potential tracers for the erosion of soil material from upland to wetland soils.

Our main objective was to test different stable ($\delta^{13}$C, $\delta^{15}$N and $\delta^{18}$O) and radiogenic (Cs-137) isotopes on their suitability for soil erosion detection and especially for detection of early stage soil erosion in alpine environments. Transects in stable isotope dynamics were determined from upland soils (oxic environment and erosion source) to wetlands (anoxic environments and sink of erosion material) as they often occur in alpine environments. Cs-137 which is a common tracer for soil erosion in lowlands was adapted for application in high alpine environments. Cs-137 provides information about the spatial distribution and the extent of soil erosion in the investigation area and could be used as a control for stable isotope measurements. A NaI in-situ spectrometer was calibrated for Cs-137 determination at steep mountain slopes. Small scale heterogeneity in Cs-137 distribution in the field is averaged out by in-situ measurements which integrate over a distinct area. Calibration was done by comparing Cs-137 activities measured with GeLi detector in the laboratory and with NaI in-situ spectrometry at the same site. A close correlation between the two methods proved the validity of the in-situ measurements of the NaI detector system. No dependency of Cs-137 on pH, clay content and carbon content was found but in-situ data must be corrected on soil moisture. In-situ measurements with a NaI detector provide, thus, an easy to handle and quick method for soil erosion determination in remote mountain areas.

For the use of stable isotopes to detect soil erosion in a transect from uplands to wetlands the prerequisite of differing isotopic signatures for upland and wetland soils must be met. This is given for all tested elements. Carbon isotopic signature ($\delta^{13}$C) and SOC content have shown to be a promising tool to reflect short and long term soil erosion processes. A close correlation of $\delta^{13}$C and carbon content in uplands indicates that depth profiles of $\delta^{13}$C mainly reflect decomposition of SOC. Long term disturbance of an upland soil is indicated by decreasing correlation of $\delta^{13}$C and
SOC. Mixed signatures between typical upland and wetland $\delta^{13}$C values were measured for wetlands influenced by soil erosion indicating that soil input of upland soil material has happened recently. Similar mixed signatures were measured for $\delta^{15}$N at the site Seebodenalp indicating that $\delta^{15}$N can be used as a tracer for soil erosion. However, influence of farmyard manure on the stable isotope signature of wetland soils was identified as a factor changing $\delta^{15}$N signatures dramatically, so that erosion detection with $\delta^{15}$N was not possible in the Urseren Valley.

As oxygen is the most abundant element in soil, $\delta^{18}$O was tested analogue to $\delta^{13}$C as a tool for soil erosion detection. Soil $\delta^{18}$O measurements have not yet been done in the past, so that a pyrolysis temperature for the conversion of the sample in the TC/EA had to be determined first. A temperature of 1325 °C has shown to be suitable because at this temperature standard materials and soil samples yield a constant $\delta^{18}$O signature but quartz signature is still negligible. Soil $\delta^{18}$O signatures of uplands and wetlands were significantly different reflecting the proportion of organic and mineral constituents. First measurements at wetlands influenced by soil erosion indicate that $\delta^{18}$O might be used as erosion tracer parallel to $\delta^{13}$C. Cs-137 measurements in the Urseren Valley fully support $\delta^{13}$C erosion measurements and mostly $\delta^{18}$O results. This indicates that stable isotopes are indeed a suitable tool for tracking down soil erosion. Thus, both, qualitative and quantitative soil erosion information is available for single hillslopes. The combination of stable and radiogenic isotope data helps to better understand soil erosion processes and might enables developing an early warning system for soil erosion.
CHAPTER 1 _______________________________________________________________________1

Introduction.................................................................1
1.1. Isotopic tracers for soil erosion ....................................2
1.2. Stable isotope dynamics in uplands and wetlands ............3
1.3. Gamma spectrometry to track down soil degradation ......3
1.4. Aims of the project..................................................4

CHAPTER 2 _______________________________________________________________________7

Stable carbon isotopes as an indicator for soil degradation in an alpine environment (Urseren Valley, Switzerland).................................................................7

2.1. Summary......................................................................7
2.2. Introduction..............................................................8
2.3. Site description.........................................................10
2.4. Materials and Methods..............................................11
  2.4.1. Sample preparation ..............................................11
  2.4.2. Soil carbon content measurements ..........................12
  2.4.3. Stable isotope analysis ........................................12
  2.4.4. Cs-137 measurements .........................................13
  2.4.5. Statistics............................................................13
2.5. Results and discussion..............................................13
  2.5.1. Upland and wetland δ¹³C depth profiles .................13
  2.5.2. Differences between δ¹³C-values of upland and wetland soils ...15
  2.5.3. Influence of manure on δ¹³C signatures ..................15
  2.5.4. Short-term soil disturbance ..................................16
  2.5.5. Long-term soil disturbance .................................18
2.6. Conclusion.............................................................20
2.7. Acknowledgements..................................................20

CHAPTER 3 ______________________________________________________________________21

Determination of δ¹⁸O in soils: measuring conditions and a potential application 21

3.1. Abstract.....................................................................21
3.2. Introduction............................................................21
3.3. Analytical Procedure.................................................23
3.4. Site.............................................................................24
3.5. Results and Discussion..............................................24
  3.5.1. Determination of a suitable pyrolysis temperature for soil samples ..24
  3.5.2. δ¹⁸O of soil components........................................27
  3.5.3. δ¹⁸O of soils ........................................................27
  3.5.4. Use of δ¹⁸O as an indicator for soil erosion ...............29
3.6. Conclusions............................................................30
3.7. Acknowledgement....................................................30
<table>
<thead>
<tr>
<th><strong>PART I: A MEASUREMENT ROUTINE TO DETERMINE Cs-137 ACTIVITIES AT STEEP MOUNTAIN SLOPES</strong></th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1. Abstract</td>
<td>31</td>
</tr>
<tr>
<td>4.2. Introduction</td>
<td>31</td>
</tr>
<tr>
<td>4.3. Site</td>
<td>33</td>
</tr>
<tr>
<td>4.4. Analysis</td>
<td>33</td>
</tr>
<tr>
<td>4.4.1. Laboratory measurements</td>
<td>33</td>
</tr>
<tr>
<td>4.4.2. In-situ measurements</td>
<td>34</td>
</tr>
<tr>
<td>4.5. Method concepts, results &amp; discussion</td>
<td>35</td>
</tr>
<tr>
<td>4.5.1. Spatial heterogeneity of Cs-137</td>
<td>35</td>
</tr>
<tr>
<td>4.5.2. NaI detector calibration and boundary conditions</td>
<td>37</td>
</tr>
<tr>
<td>4.5.3. Sources of error</td>
<td>39</td>
</tr>
<tr>
<td>4.5.4. Dependency of Cs-137 on different soil parameters</td>
<td>39</td>
</tr>
<tr>
<td>4.5.5. Validation of the in-situ NaI measurements</td>
<td>41</td>
</tr>
<tr>
<td>4.6. Conclusion</td>
<td>42</td>
</tr>
<tr>
<td>4.7. Acknowledgements</td>
<td>43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>PART II: Cs-137 BASED EROSION RATE DETERMINATION OF A STEEP MOUNTAINOUS REGION</strong></th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8. Abstract</td>
<td>45</td>
</tr>
<tr>
<td>4.9. Introduction</td>
<td>46</td>
</tr>
<tr>
<td>4.10. Material and Methods</td>
<td>47</td>
</tr>
<tr>
<td>4.10.1. Study site</td>
<td>47</td>
</tr>
<tr>
<td>4.10.2. Erosion assessment with Cs-137</td>
<td>48</td>
</tr>
<tr>
<td>4.10.3. Erosion assessment with the USLE</td>
<td>48</td>
</tr>
<tr>
<td>4.11. Results and Discussion</td>
<td>50</td>
</tr>
<tr>
<td>4.11.1. Cs-137 measurements and erosion rates</td>
<td>50</td>
</tr>
<tr>
<td>4.11.2. Erosion assessment with the USLE</td>
<td>52</td>
</tr>
<tr>
<td>4.12. Conclusions</td>
<td>53</td>
</tr>
<tr>
<td>4.13. Acknowledgements</td>
<td>53</td>
</tr>
</tbody>
</table>

| **CHAPTER 4** | 31 |
| Methods to describe and predict soil erosion in mountain regions | 55 |
| 5.1. Abstract | 55 |
| 5.2. Introduction | 55 |
| 5.3. Site description | 57 |
| 5.4. Methods to quantify soil erosion over time | 59 |
| 5.5. Methods to describe early stage soil erosion | 61 |
| 5.6. New concepts for soil erosion modelling in mountain areas | 64 |
| 5.7. Conclusions | 66 |
| 5.8. Acknowledgement | 67 |

| **CHAPTER 5** | 55 |
| Methods to describe and predict soil erosion in mountain regions | 55 |
| 5.1. Abstract | 55 |
| 5.2. Introduction | 55 |
| 5.3. Site description | 57 |
| 5.4. Methods to quantify soil erosion over time | 59 |
| 5.5. Methods to describe early stage soil erosion | 61 |
| 5.6. New concepts for soil erosion modelling in mountain areas | 64 |
| 5.7. Conclusions | 66 |
| 5.8. Acknowledgement | 67 |

| **CHAPTER 6** | 69 |
| Final remarks & Outlook | 69 |
| 6.1. Methodological approach | 69 |
| 6.2. Erosion measurements | 69 |
| 6.3. Outlook | 70 |

| **BIBLIOGRAPHY** | 73 |

| **APPENDIX** | 83 |
| δ15N - Urseren Valley | 83 |
| δ13C/δ15N/δ34S - Seebodenalp | 85 |
LIST OF FIGURES

Figure 2-1. (a) Theoretically expected depth profiles at uplands (A) and undisturbed wetlands (C), and (b) theoretically expected influence of erosion on δ¹³C of wetlands disturbed by erosion (B). ............................................................9

Figure 2-2. Aerial photograph of the Urseren Valley in Southern Central Switzerland and location of the sites: (a) Spissen, (b) Bielen, (c) Laui, (d) Oberes Moos, (e) Höh, (f) Spiessenälpetli, and (g) Lutersee. ...............................................................10

Figure 2-3. Sites and sampled transects (lines): (a) Spissen, (b) Bielen, (c) Laui, (d) Oberes Moos, (f) Spiessenälpetli, and (g) Lutersee.......................................................12

Figure 2-4. Stable carbon isotope depth profiles for all upland transects, wetland transects in direct influence of upland sites (B) and wetland transects in reference position. Sampling points of one transect and mean line are displayed in the same chart ..............................................................................................................14

Figure 2-5. δ¹³C for two depth steps (0 – 12 cm and 12 – 24 cm). Boxplots indicate median (straight line), mean (dotted line), 10th-, 25th-, 75th- and 90th-percentile, and outliers (dots). ............................................................................................................16

Figure 2-6. δ¹³C for the vegetation cover at upland and wetland sites (left) and for unmanured and manured upland soils (right). Boxplots indicate median (straight line), mean (dotted line), 10th-, 25th-, 75th- and 90th-percentile, and outliers (dots). ........................................................................................................16

Figure 2-7. Cs-137 activities all hill slope transects from uplands to adjacent wetlands. Cs-137 activities are given relative to a reference value of 143.9 ± 5 Bq/kg. ..........17

Figure 2-8. Carbon content vs. δ¹³C for single transects for all uplands (A), wetlands in direct influence of upland sites (B) and reference wetlands (C). Sampling points of one transect are grouped in the same chart. .........................................................19

Figure 3-1. Dependency of signal intensity (left) and raw δ¹⁸O (right) on pyrolysis temperature for different standard materials and soil samples. .........................26

Figure 3-2. Stable oxygen isotope signature of phyllosilicates of Central Switzerland (repeated measurement of samples from the same rock sample), above ground vegetation from upland and wetland sites in the Urseren Valley and soil samples from sites in the Urseren Valley (A = upland, B = wetland with erosion influence, SB = sandy layer at position B, C = reference wetland unaffected by erosion). ........28

Figure 4-1. Aerial photograph of the Urseren Valley in Southern Central Switzerland and location of the sites (numbers), the altitudinal transect (dashed line) and the reference sites (crosses). ........................................................................................................34

Figure 4-2. NaI detector system with its components: (a) detector, (b) pole, (c) control unit, (d) battery and (e) interface to pocket PC.........................................................35
Figure 4-3. Altitudinal transect between 1500 and 2050 m a.s.l. with trendline (black). Dashed line represents the Cs-137 activity (146.5 Bq kg⁻¹) measured at reference sites. For cluster (a) influence of erosion is possible, cluster (b) is influenced by snow at the time of Cs-137 input.................................................................36

Figure 4-4. Spatial heterogeneity of the Cs-137 distribution at the calibration site.....37

Figure 4-5. (a) Cs-137 depth profile for an upland soil measured in the laboratory (GeLi detector). (b) Exponential decrease of the Cs-137 radiation measured at the surface with increasing burial depth of the point source (NaL detector). (c) Exponential decrease of the measured Cs-137 activity with increasing horizontal distance between the point source and the detector (NaL detector)..................38

Figure 4-6. Dependency of Cs-137 on (a) pH, (b) clay content, (c) carbon content and (d) soil moisture (3, 4, 5, 7, 9, 10 stand for different sampling sites)..........40

Figure 4-7. Comparison of Cs-137 activities determined by in-situ (NaL detector) and laboratory measurements (GeLi detector)..................................................................41

Figure 4-8. The Urseren Valley in Southern Switzerland and the location of the investigated sites with three grassland types: meadow (m), pasture without dwarf shrubs (pawo) and pasture with dwarf shrubs (paw)..........................................................48

Figure 4-9. Erosion rates due to Cs-137 based measurements (light grey) and calculations with the Universal Soil Loss Equation (dark grey). Cs-137 error bars (17 %) are due to manually analysis of gamma spectra. USLE error bars are gained by consideration of the uncertainty of single parameters........................................53

Figure 5-1. The Urseren Valley, Kanton Uri, Switzerland. View from west to east........58

Figure 5-2. Examples of landslides and sheet erosion on the (a) calcareous and (b) silicate schists of the south-facing slope of the Urseren Valley, Switzerland.........58

Figure 5-3. Landslide density histograms dependent on slope and geology. P = permocarbonic, Gr = Granite of the Aare massif, Gn = Gneiss of the Gotthard massif, A = "Altkristallin"(A), M= mesozoic-sediments (Labhart, 1999)......................60

Figure 5-4. Sub-images of aerial photographs in the Urseren Valley (Swisstopo, 2006)...............................................................................................................................................61

Figure 5-5. Fingerprint hypothesis of soil degradation: if soil erosion from upland A is influencing wetland B significantly, stable isotope signature of B should differ from undisturbed wetland C. ........................................................................................................62

Figure 5-6. Stable isotopes of carbon and nitrogen for the upland soils A (erosion source), wetlands B (erosion sink) and undisturbed wetlands C. Boxplots indicate medians, 10-, 25-, 75- and 90- percentiles. • = outliers.................................63

Figure 5-7. Water flow routing on vaulted area with (a) regular grids using the D8 algorithm and (b) irregular grid using the algorithm presented in Bänninger (2006)...........................................................................................................66
Table 2-1. Sampled sites in the Urseren Valley. .................................................................11
Table 3-1. Provenience of phyllosilicate samples. .............................................................25
Table 4-1. Cs-137 data of all sites for measurements with GeLi- and NaI detector.....42
Table 4-2. Measured and calculated parameters for the investigation sites in the Urseren Valley. The R factor is given with snow attenuation, cover rate was measured two times in 2007 (summer and autumn). The pH value was measured with 0.01 molar CaCl₂ with a relation of 1 (soil) to 2.5 (CaCl₂). K is kg·h·kg⁻¹·m⁻¹·s²·m⁻² and R kg·m·s⁻²·h⁻¹. .................................................................................................50
Table 4-3. Fractional vegetation cover of all plots in April and September 2007 (maximum standard deviation 5%)........................................................................................................50
Table 4-4. Cs-137 activity, soil density and resulting erosion rates. The Cs-137 reference value is about 145Bq·kg⁻¹. ..................................................................................................................51
CHAPTER 1

Introduction

The Alps represent one of the most sensitive ecosystems in Europe because of aggressive development in the recent past, large numbers of tourists and severe environmental damage enhanced by climate change. Degradation of soils seriously threatens the mountain environment and is of major concern to European governmental offices (EEA, 2000; Alpenkonvention, 2005). Soil erosion is not limited to the Alps, but is a problem of global scale for mountainous regions (Evans, 2006). Increasing temperatures and increasing heavy precipitation events in alpine ecosystems driven through climate change (Brunetti et al., 2006) enhance soil erosion risk (Fuhrer et al., 2006). Soil erosion activity results in a decreasing vegetation cover or, as an extreme, in bare soil. Once vegetation cover is disturbed soil loss through soil erosion occurs (e.g. Frankenberger & Eckert, 1994; Isselin-Nondedeu & Bédécarrats, 2007). Possible consequences of soil degradation are reduction in soil quality and biomass productivity, water contamination and eutrophication, and emission of trace gases to the atmosphere (Lal, 2001). In contrast to cultivated lowlands soil erosion damages are a more severe problem in mountain ecosystems. Due to the extreme topography and climate condition soil formation and revegetation take usually longer than in lowlands. Assuming a slow rate of soil formation soil erosion causes irreversible damages in the time scale of 50 to 100 years (Van der Knijff et al., 2000). Soil erosion is a highly event based process because erosion mostly occurs during snow melt or heavy rain storms. Tracking erosion via monitoring always requires high temporal resolution to capture peak events. Thus, classical techniques such as measuring nutrient concentrations in soil and runoff water, or estimating sedimentation rates in silt fences require a long period of continuous measurements to track soil degradation. New approaches for a better qualitative detection and quantification of soil degradation in alpine ecosystems are urgently needed in order to achieve a better conservation of soil resources (EEA, 2000).

Several projects concerning soil erosion in alpine areas are in work at the University of Basel. The aim of this project was to address the problem of soil degradation and nutrient export in the Alps in a qualitative way and to test methods which yield long term finger prints of soil degradation. Methods used range from determination of
gradients in stable isotopes of carbon (chapter 2 & 5), nitrogen (chapter 5), oxygen (chapter 3), sulphur (see appendix) and radiogenic isotopes (chapter 4) to minerals (see outlook). Soil degradation of upland soils influences nutrient content and biogeochemistry of riparian zones and wetlands in catchments significantly. Transects in stable isotope dynamics were determined from upland soils (oxic environment and erosion source) to wetlands (anoxic environments and sink of erosion material) and subsequently validated by Cs-137 measurements. The research focused on the upper Reuss watershed (Urseren Valley) where the degradation of soils has been shown to impact the valley slopes dramatically. Soil degradation in the Urseren Valley is caused by a combination of catchment characteristics (e.g. geology, soils, topography) as well as changes in climate and land use (Meusburger & Alewell, 2008)

1.1. Isotopic tracers for soil erosion

A promising tool to investigate element sources and sinks as well as processes in ecosystem biogeochemistry are isotope tracers (for overview see Kendall & McDonnell, 1998). Stable isotopes of sulphur have been shown to give a historic fingerprint of prevailing metabolism (aerobic or anaerobic) over time (Alewell & Novak, 2001). While the influence of soil erosion, weathering and sedimentation to wetlands and groundwater has been investigated with radioactive isotope tracers like Pb-210, Cs-137 or Be-7 (e.g. Albrecht, 1999; Walling et al., 1999; Matisoff et al., 2002; Zapata, 2003; Doering et al., 2006) to our knowledge so far nobody has tried to use stable isotopes of carbon, nitrogen and oxygen to track down soil erosion in transects from uplands to wetlands. While with the former elements the differences in source and sink isotopic signature can only point to direction and extent of erosion processes, the latter will also indicate impact on nutrient cycling, element kinetics and metabolism of the sites. In a review done by Amundson et al. (2003) it has been shown that $\delta^{15}N$ values of soils are dependent on soil age and soil slope. Soil age is correlated to the degree of steady state and the kinetics of N cycling. For soil slope it has been shown that steeply sloping soils have low residence times. Thus, Amundson et al. (2003) postulate that because soils are far from steady state they have lower $\delta^{15}N$ values that approach atmospheric input. However, Amundson et al. (2003) conclude that “there are presently no published data to test this hypothesis”. Apart from soil age and soil rejuvenation topographic position plays a key role in isotopic signature of elements, because dissimilatory reduction processes in wetland soils cause significant shifts in sulphur, nitrogen and oxygen isotopes (Krouse & Grinenko, 1991; Kendall, 1998; Mitchell et al., 1998; Wang et al., 1998). Thus, stable isotopes should be a suitable tool to follow the influence of erosion material from upland soils to wetland sites.
1.2. Stable isotope dynamics in uplands and wetlands

Upland soils, which are dominated by assimilatory reduction processes, can generally be expected to have distinctively different isotopes signatures than associated wetlands and water bodies. The latter has been shown for sulphur (Morgan, 1995; Alewell & Gehre, 1999; Alewell & Novak, 2001). For stable isotopes of sulphur, we know that organic material in wetlands is significantly lighter in $\delta^{34}S$ than in uplands because of the discrimination of $^{34}S$ during dissimilatory sulphate reduction (Alewell & Novak, 2001).

For carbon a difference between isotopic signature of upland and wetland sites can be expected because in the aerobic environment of the uplands oxidative processes dominate during decomposition of plant material. Due to isotopic fractionation during those processes residues are increasingly enriched in the heavier isotope ($^{13}C$) as the lighter ($^{12}C$) will preferentially be involved in chemical reactions (e.g. Kendall & Caldwell, 1998). In contrast wetland soils are characterized by anaerobic conditions. The lack of oxygen results in an incomplete decomposition of organic material which leads to preservation of organic material and, thus, a preservation of the original (plant) isotopic signature. Therefore, $\delta^{13}C$ of SOC in wetland soils can be supposed to be lighter than those of upland soils (see chapter 2 and 5).

For nitrogen isotopic discrimination against the heavy $^{15}N$ takes place both during decomposition of organic material in the oxic environment as well as during denitrification processes taking place under anaerobic conditions (Kendall, 1998). Thus, expected isotopic nitrogen signature of wetlands in comparison to uplands is ambiguous (see chapter 5 and appendix).

Oxygen isotopic signature of soil is the result of the mixture of organic and inorganic soil components making up the soil. Upland soils consist mainly of phyllosilicates and quartz with smaller fractions of organic matter (< 1 – 30 %) whereas wetland soils have by definition an organic matter content of at least 30 %. It can thus be expected that not only different soil components have diverse $\delta^{18}O$ values but that there is also a difference between upland and wetland soils (see chapter 3).

1.3. Gamma spectrometry to track down soil degradation

Cs-137, Pb-210 and Be-7 have been used before as tracers for soil erosion. Be-7 with its half life of 53.12 days is only suitable for measurement of recent erosion processes. Determination of both, Be-7 and Pb-210 needs a good spectral resolution and is not possible using our NaI detector. Among them Cs-137 is the most commonly used in erosion studies because it is relatively easy to measure, has a quite well defined date of input and with its half life of 30.17 years provides information about medium-term erosion (Ritchie & McHenry, 1990). Cs-137 is an artificial nuclide and has its origin either in bomb-testings in the 1960ies and 70ies or in the Chernobyl reactor accident in 1986. For Switzerland the biggest amount of Cs-137 was deposited after the Chernobyl reactor accident. Therefore, in the Urseren Valley the measurement of Cs-
137 concentrations can provide important information on the extent of soil erosion of
the last 20 years. After deposition Cs-137 is rapidly and tightly bound to the fine
particles in the soil, i.e. clay minerals and organic matter. Movement by chemical
and biological processes are strongly limited (Ritchie & McHenry, 1990). Redistribution
is mainly caused by physical processes where Cs-137 moves with soil particles (e.g.
Bonnett, 1990; Ritchie & McHenry, 1990). The vertical distribution of Cs-137 in
cultivated soils is influenced by the tillage practice which results in a more or less
homogeneous Cs-137 activity within the plough layer (Owens et al., 1996; He &
Walling, 2000; Ritchie & McCarty, 2003). In unploughed soils most of the Cs-137 is
accumulated at the top of the soil profile or few centimetres below and the content
decreases with depth (Ritchie & McHenry, 1990; Owens et al., 1996; Ritchie &
McCarty, 2003). Soil erosion and redistribution processes can therefore be tracked
down by the measurement of the Cs-137 activity. Various studies applied Cs-137 to
track down soil erosion, however mainly for agricultural areas in different parts of the
world (for overview see Wicherek & Bernard, 1995). It is possible to distinguish areas of
net soil loss from net deposition areas by analyzing the spatial distribution of Cs-137 in
the studied area (Ritchie & McHenry, 1990). However, applicability of the method
depends on the Cs-137 activity in the catchment as not all parts of Switzerland were
impacted with measurable amounts of Cs-137 after the Chernobyl reactor accident.
Cs-137 activity in the Urseren Valley is high enough for soil erosion measurements. Cs-
137 measurements are usually done either by analysing soil samples in the laboratory
or by in-situ measurements using a Ge or a NaI detector. Measurement time for in-situ
measurements is generally shorter due to the coverage of a representative sampling
area in the field in contrast to prepared small volume soil samples in the laboratory
(Beck et al., 1972). Because of the good resolution of peaks in spectra measured by
Ge detectors, these are usually favoured over the NaI detectors. However, the use of
a Ge detector in the field is difficult because Ge detector systems are usually
relatively heavy or not portable at all because of the Ge-crystal's need for cooling.
Thus, a NaI detector system was calibrated for Cs-137 measurements at steep
mountain slopes (chapter 4).

1.4. Aims of the project
This project aims to investigate the interaction between biogeochemical (isotope
displacement) and geomorphologic processes (soil erosion) of soil degradation in
the Alps. Simultaneously, this project shall give input to the development of new
techniques for detecting soil degradation in alpine regions. The main objective of this
project was to track down hot spots of soil erosion as well as to better understand
early stage soil erosion by determining gradients in stable and radiogenic isotopes
(and minerals; see outlook) from upland soils (erosion source) to wetland sites (sink for
eroded material).
Carbon and nitrogen are the most common elements in organic matter. Therefore, these elements were chosen for our stable isotope measurements. If the prerequisite of differing $\delta^{13}C$ and $\delta^{15}N$ signatures for uplands and wetlands is true, then $\delta^{13}C$ and/or $\delta^{15}N$ should be suitable for soil erosion measurements at the transect from uplands to wetlands. The suitability of $\delta^{13}C$ for soil erosion measurements is discussed in chapter 2 and 5; suitability of $\delta^{15}N$ is discussed in chapter 5.

As a constituent of both, organic and inorganic matter, oxygen is a key element for understanding soil dynamics. We aim to use stable oxygen isotopes of soil parallel to $\delta^{13}C$ for soil erosion detection. But, as there is no standard method available for soil $\delta^{18}O$ measurements using TC/EA we had to determine a suitable pyrolysis temperature at which standard materials and soils are pyrolysed completely. The methodical development as well as a first application for soil erosion measurements is presented in chapter 3.

Cs-137 can provide information about erosion intensity and extent in the investigation area of the last 20 years (time after the Chernobyl reactor accident in 1986). Further, Cs-137 data helps to interpret the stable isotope data. Measurement of Cs-137 by in-situ gamma spectrometry using a NaI detector was chosen. The aim of this part was to find a suitable measurement routine for measurement of Cs-137 in an alpine environment with great small scale heterogeneity of Cs-137 distribution (chapter 4). A field-portable NaI gamma spectrometer was used. In a continuative study the in-situ method was used for soil erosion quantification and determination of USLE management factor for steep alpine slopes.
Stable carbon isotopes as an indicator for soil degradation in an alpine environment (Urseren Valley, Switzerland)

2.1. Summary
Analyses of SOC content and stable carbon isotope signatures ($\delta^{13}$C) of soils were assessed for their suitability to detect early stage soil erosion. We investigated the soils in the alpine Urseren Valley (Southern Central Switzerland) which are highly impacted by soil erosion. Hill slope transects from uplands (cambisols) to adjacent wetlands (histosols and histic to mollic gleysols) differing in their intensity of visible soil erosion and reference wetlands without erosion influence were sampled. Carbon isotopic signature and SOC content of soil depth profiles were determined. A close correlation of $\delta^{13}$C and carbon content ($r > 0.80$) is found for upland soils not affected by soil erosion, indicating that depth profiles of $\delta^{13}$C of these upland soils mainly reflect decomposition of SOC. Long term disturbance of an upland soil is indicated by decreasing correlation of $\delta^{13}$C and SOC ($r \leq 0.80$) which goes parallel to increasing (visible) damage at the site. Early stage soil erosion in hill slope transects from uplands to adjacent wetlands is documented as an intermediate $\delta^{13}$C value (-27.5 ‰) for affected wetland soil horizons (0 – 12 cm) between upland (aerobic metabolism, relatively heavier $\delta^{13}$C of -26.6 ‰) and wetland isotopic signatures (anaerobic metabolism, relatively lighter $\delta^{13}$C of -28.6 ‰). Carbon isotopic signature and SOC content are found to be a sensitive indicator of short and long term soil erosion processes.
2.2. Introduction

Soil degradation is a major problem in mountainous regions. A key component for understanding soil degradation is soil organic carbon (SOC). SOC favourably affects soil quality; SOC complexes and soil aggregates stabilise the structure (e.g. Gregorich et al., 1994; Lal, 2004). As a result of soil erosion soil carbon pools in the source area might decrease (on-site effect) and carbon pools in the sink area are also affected (off-site effect). On-site effects are mostly described for farmlands where they are strongly linked to productivity loss caused by factors like worsening of soil structure and loss of soil organic matter (e.g. Lal, 2001). Soil aggregates can shield SOC from ambient influences. Due to soil erosion these aggregates are destroyed and SOC is mineralised or leached which results in a decrease of SOC content in the erosion source area; deposition of SOC in the sink area, on the other hand, may lead to enrichment in SOC (Lal, 2003). Production of CH$_4$, N$_2$O and NO$_x$ through methanogenesis and denitrification, respectively, increases as a consequence of SOC deposition under anaerobic conditions (Lal, 2003). However, carbon release through anaerobic decay in a wetland is much smaller compared to the loss of carbon by oxidation of organic carbon during dry periods (Staillard, 1998).

Detachment of soil particles and transport downhill is mostly caused by water influence through raindrop impact (Watung et al., 1996). Small colloid particles like SOC are the first to go into suspension and are hence preferentially exported by soil erosion (e.g. Watung et al., 1996; Lal, 2003; Polyakov & Lal, 2004; Bilgo et al., 2006). Identification and quantification of soil erosion using radiogenic isotopes as Cs-137 and Be-7 has been performed increasingly during the last decade (e.g. Walling et al., 1999; Matisoff et al., 2002; Zapata, 2003). In central Europe where Cs-137 mainly has its origin in the Chernobyl reactor accident, it is getting more and more difficult to apply Cs-137 for erosion studies because of the relatively low initial input and the continuous decay of Cs-137 (half-life time 30.2 years). A further disadvantage of the use of radiogenic isotopes is the relatively long measurement time of several hours for each individual sample depending on Cs-137 concentration. Therefore, for erosion tracking (even though not for quantitative applications) stable isotopes might be a good alternative. It has been shown before that stable carbon isotope signature can give information about the source area of suspended organic matter in rivers (e.g. Onstad et al., 2000; Masiello & Druffel, 2001) or runoff waters (e.g. Bellanger et al., 2004; Huon et al., 2006). Fox & Papanicolaou (2007) used $\delta^{13}$C and $\delta^{15}$N in combination with C/N ratios to describe single erosion events in a watershed. Turnbull et al. (2008) used $\delta^{13}$C as a tracer for soil erosion in a transition from C3 to C4 vegetation. However, to our knowledge, stable carbon isotopes have never been used before to track down soil erosion in hill slope transects from uplands (erosion source) to adjacent wetlands (erosion sink) with no transition from C3 to C4 vegetation as they often occur in alpine environments. Generally, distinctively different carbon isotope signatures can be expected for uplands and adjacent wetlands and water bodies because in the aerobic environment of the uplands oxidative processes dominate during decomposition of plant material. Due to
isotopic fractionation during those processes residues are increasingly enriched in the heavier carbon isotope (\(^{13}\text{C}\)) as the lighter \(^{12}\text{C}\) will preferentially be involved in chemical reactions (e.g. Kendall & Caldwell, 1998). In contrast, wetland soils are characterized by anoxic conditions. The lack of oxygen results in an incomplete decomposition of organic material by anaerobic bacteria. Carbon compounds are preserved to a higher degree and keep their original (plant) isotopic signature. Therefore, \(\delta^{13}\text{C}\) of SOC in wetland soils can be supposed to be lighter than those of upland soils.

The latter relationship between \(\delta^{13}\text{C}\) and decomposition of SOC might also be reflected in depth profiles. Increasing \(\delta^{13}\text{C}\) with depth is typical for upland soils and is usually related either to kinetic fractionation during decomposition of soil organic matter resulting in an enrichment of \(^{13}\text{C}\) in the residual material (Balesdent et al., 1993; Chen et al., 2002; Novak et al., 2003) or to soil age (Balesdent et al., 1993; Bird et al., 1994; Bellanger et al., 2004). The isotopic composition of atmospheric CO2 has decreased from \(\delta^{13}\text{C}\) values around -6.4 \(\permil\) at the end of the eighteenth century to values around -7.6 \(\permil\) in 1980 (Friedli et al., 1986). A further decrease to values around -8.1 \(\permil\) in 2002 was measured by Keeling et al. (2005). Here, we hypothesise that systematic differences between isotopic fingerprint of upland and wetland soils exist. For upland soils, we expect a clear increase of \(\delta^{13}\text{C}\) with depth due to decomposition processes taking place in the soil (Balesdent et al., 1993; Chen et al., 2002; Novak et al., 2003; Figure 2-1a). For an anaerobic environment in the wetland, where decomposition rates are small, a more or less constant \(\delta^{13}\text{C}\) with depth is expected (Novak et al., 1999; Figure 2-1a). Furthermore, the suitability of stable carbon isotope signatures to track down early stage erosion in transects from upland to wetland soils is tested. Therefore, we investigated the contribution of erosive upland soil material to the isotopic signature of wetland soils in the Urseren Valley (Canton Uri, Switzerland) where soil erosion is heavily impacting valley slopes. Our hypothesis here is that if upland (A) and reference wetland soils (C) differ in their \(\delta^{13}\text{C}\), \(\delta^{13}\text{C}\) of the wetland influenced by erosion (B) should have an intermediate isotopic signature, e.g. \(\delta^{13}\text{C}_A > \delta^{13}\text{C}_B > \delta^{13}\text{C}_C\) (Figure 2-1b).

**Figure 2-1.** (a) Theoretically expected depth profiles at uplands (A) and undisturbed wetlands (C), and (b) theoretically expected influence of erosion on \(\delta^{13}\text{C}\) of wetlands disturbed by erosion (B).
2.3. Site description

The study area is located in the southern part of Central Switzerland (Canton Uri) in the Urseren Valley (Figure 2-2). The bottom of the W-E extended mountain valley is approximately 1500 m a.s.l.. It is surrounded by mountain ranges of altitudes up to 2500 m a.s.l.. The mean annual rainfall is about 1400 mm and the mean annual air temperature is 4.3 °C (1986 – 2007; Source: MeteoSchweiz). The valley mainly consists of cultivated pastureland. Forested areas are limited to protection forests at slopes above villages. Land use is dominated by grazing and, in the lower reaches of the valley, by hay harvesting. Upland soils in the study area mainly consist of cambisols, podsols and stagnosols (WRB, 2006). Histosols and histic to mollic gleysols (WRB, 2006) are found in wetlands. All wetland soils have histic characteristics up to a minimal depth of 20 cm.

The valley is strongly affected by soil erosion. Extensive areas of the natural cover are disturbed especially on the southern slopes. The occurrence of variable intensities of surface erosion and landslides on comparable sites offers the required conditions to test our hypothesis. For a detailed description of the Urseren Valley see Meusburger & Alewell (2008).
Samples were collected at three erosive sites on the lower southern slopes (between 1500 and 1600 m a.s.l.) between the villages of Hospental and Realp: Spissen (affected by landslide erosion), Bielen (sheet erosion) and Laui (no visible erosion) (Table 2-1, Figure 2-3a-c). Additionally, four reference wetlands were sampled. Two of them (Oberes Moos and Höh) are located on the same altitudinal level as the erosive sites, while Spiessenälpetli is situated on 2340 m a.s.l. and Lutersee on 1990 m a.s.l. (Table 2-1, Figure 2-3d-g). The reference sites are not directly connected to hill slopes. Thus, input of upland soil material by water erosion is not possible. The site Spiessenälpetli is surrounded by debris and earlier rockfall events are documented in the soil profile as layers of almost pure granitic sand with carbon contents below 1 %. These layers were omitted for further analyses. Uplands were mainly sampled in vertical transects. Additionally, two horizontal transects were sampled at the sites Spissen and Bielen at an altitude level where most landslides tear off. All sites are grasslands with hay harvesting twice every summer. The plant cover mainly consists of Anthoxanthum odorata, Festuca s.d., Carex s.d., Dactylis glomerata, Poa alpina, Leontodon hispidulus, Trifolium montanum, Thymus serpyllum, Viola carnia ssp. carnia, Helictotrichon versicolor (uplands) and Agrostis capillaris, Anthoxanthum odorata, Alchemilla xanthochlora and A. pratense, Ranunculus acris and R. aconitifolius, Trifolium pretense ssp. pratense, Caltha palustris, Polygonum bistorta, Rumex alpinus, Chaerophyllum hirsutum villarsii (wetlands). In autumn 2005 all wetland sites, the upland of Laui and the vertical upland transects of Spissen were fertilised with farmyard manure.

### Table 2-1. Sampled sites in the Urseren Valley.

<table>
<thead>
<tr>
<th>site</th>
<th>altitude /m a.s.l.</th>
<th>type of erosion</th>
<th>landuse</th>
<th>fertilisation (2005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spissen</td>
<td>1530</td>
<td>landslide erosion</td>
<td>hay harvest</td>
<td>Y</td>
</tr>
<tr>
<td>Bielen</td>
<td>1530</td>
<td>sheet erosion</td>
<td>hay harvest</td>
<td>N</td>
</tr>
<tr>
<td>Laui</td>
<td>1550</td>
<td>no visible erosion</td>
<td>hay harvest</td>
<td>Y</td>
</tr>
<tr>
<td>Oberes Moos</td>
<td>1500</td>
<td>reference wetland</td>
<td>meadow</td>
<td>Y</td>
</tr>
<tr>
<td>Höh</td>
<td>1540</td>
<td>reference wetland</td>
<td>meadow</td>
<td>N</td>
</tr>
<tr>
<td>Spiessenälpetli</td>
<td>2340</td>
<td>reference wetland</td>
<td>no use</td>
<td>N</td>
</tr>
<tr>
<td>Lutersee</td>
<td>1990</td>
<td>reference wetland</td>
<td>no use</td>
<td>N</td>
</tr>
</tbody>
</table>

### 2.4. Materials and Methods

2.4.1. Sample preparation

Soil profiles were taken with a core sampler at five sampling points per transect (distance between sampling points was approximately 5 m in the uplands and 3 m in the wetlands; Figure 2-3). At each sampling point a soil core of 30 to 40 centimetres length was taken, which was divided into three to five subsamples each to obtain a
depth profile. In the laboratory the samples were stored at approximately 4 °C until further processing. Soil samples were 2 mm sieved, dried at 40 °C for three days and ground using a tungsten carbide swing grinder. Vegetation was sampled in summer 2006 by cutting the aboveground vegetation completely at three randomly selected subsites per site. After drying at 40 °C plant samples were ground in a tungsten carbide ball mill.

2.4.2. Soil carbon content measurements
Soils were tested for carbonate content with 10 % HCl. Over 85 % of the samples did not show any reaction. As the reaction of the remaining samples was very weak it is assumed that carbonate content is very small and total carbon content of samples approximate SOC content. Total carbon content was measured on a Leco CHN analyzer 1000, with measurement reproducibility better than 0.1 %.

2.4.3. Stable isotope analysis
As even small amounts of inorganic carbon can give significant errors in $\delta^{13}$C, inorganic carbon was removed prior to stable isotope analysis by acid fumigation following the method of Harris et al. (2001). Moistened subsamples were exposed to the exhalation of hydrochloric acid in an exsiccatior overnight. Afterwards the samples were dried at 40 °C and ground in a mortar before measuring stable isotopes. Stable carbon isotope analyses were accomplished using a continuous flow isotope ratio mass spectrometer ($\text{DELTA}^\text{plus}$ XP, Thermo, Bremen, Germany) coupled with a FLASH Elemental Analyzer 1112 (Thermo, Milan, Italy) combined with a CONFLO III Interface following standard processing techniques. Stable isotope ratios are reported as $\delta^{13}$C values [%o] relative to V-PDB defined in terms of NBS 19 =
1.95 ‰. The accuracy of the $^{13}$C/$^{12}$C ratio was monitored by analyses of the international standard NBS 22 and an inhouse standard INTC, which yielded values of $-29.73 \pm 0.06$ ‰ (1 SD, n = 62) and $-35.27 \pm 0.05$ ‰ (1 SD, n = 62), respectively, during the course of this study. The long term reproducibility for all standards is better than 0.1 ‰.

2.4.4. Cs-137 measurements

Cs-137 was estimated for all sites at four sampling points (three in the upland and one in the wetland) and at two reference sites with three replicates each. Soil samples of soil horizons 0 – 10 cm were packed into plastic containers (Semadeni25) and measured on a Li-drifted Ge detector (Princeton Gamma-Tech, Princeton, NJ, USA) at the Department of Physics and Astronomy, University of Basel for 8 hours. Cs-137 activities are shown as a deviation from a reference value ($143.9 \pm 5$ Bq/kg) which represents the Cs-137 activity of sites with no influence of soil erosion.

2.4.5. Statistics

Normal distribution of data was verified with a Kolmogorov-Smirnov test. Analysis of variance (ANOVA) was performed in order to test differences among groups. For all tests a level of significance of 0.01 was considered. In order to estimate the correlation between $\delta^{13}$C and C content, the Pearson correlation coefficient was calculated.

2.5. Results and discussion

2.5.1. Upland and wetland $\delta^{13}$C depth profiles

Upland soil $\delta^{13}$C signatures range from -25 to -27 ‰ in the uppermost soil horizon and from -21 to -27 ‰ for deeper soil horizons. Increasing $\delta^{13}$C values with depth were recorded for all upland soils with the exception of Spissen AA (Figure 2-4). Such depth profiles are typical for upland soils (Balesdent et al., 1993; Chen et al., 2002; Novak et al., 2003). While $\delta^{13}$C of the uplands at Spissen A and AAA increases by 3 ‰ the upland profiles at Bielen and Laui increase only slightly with depth (Figure 2-4). This might indicate that the latter soils are rather young because they have most likely been influenced by the erosive conditions in the catchment for a long time. For nitrogen, Amundson et al. (2003) describe a dependence of nitrogen isotopic signature on soil age and soil slope because steeply sloping soils have short residence times. Our results might indicate that, parallel to $\delta^{15}$N (Amundson et al., 2003), relatively light $\delta^{13}$C signatures with weak or no depth profiles can be expected for steeply sloping soils. (Please note that we could not use $\delta^{15}$N as a marker due the influence of organic manure on stable isotope signature. See below.)

The range of $\delta^{13}$C values for wetland soils is -24 to -29 ‰. None or slight $\delta^{13}$C depth profiles for undisturbed wetlands are obtained (Figure 2-4). The anoxic environment
Figure 2-4. Stable carbon isotope depth profiles for all upland transects (A), wetland transects in direct influence of upland sites (B) and wetland transects in reference position (C). Sampling points of one transect and mean line are displayed in the same chart.
of wetland soils conserves plant material and restricts the decay of organic matter. Anaerobic decay is a very slow process leading to storage of most of the carbon in the soil for a long time (Stallard, 1998). Hence, δ¹³C remains relatively unchanged as long as the wetland is not drained, which would stimulate aerobic decay. There is a significant difference in δ¹³C values (0 – 12 cm) between the wetlands Oberes Moos and Höh at around 1500 m a.s.l. and the wetlands Spiessenälpetli and Lutersee at around 2000 m a.s.l. (p < 0.01). Mean δ¹³C of the top 12 cm of Oberes Moos and Höh is -28.3 ± 0.6 ‰, while mean δ¹³C of Spiessenälpetli and Lutersee is -26.7 ± 0.5 ‰. Körner et al. (1988, 1991) also found considerably lighter δ¹³C values for C3-plants at low altitudes than at high altitudes. The heavier δ¹³C value on the higher altitudinal level can be explained by decreasing discrimination at lower temperatures and lower atmospheric pressure (Körner et al., 1988, 1991). As the source of soil organic matter is mainly the surface vegetation, the altitudinal decrease in δ¹³C is also documented in the soil, especially in wetlands where decay of organic matter is restricted. Such an altitudinal trend for δ¹³C of vegetation and soils has also been shown by Bird et al. (1994). Because of these differences in δ¹³C caused by altitudinal effects, the two wetlands Spiessenälpetli and Lutersee will not be used for the direct comparisons with δ¹³C of uplands at lower altitudes.

2.5.2. Differences between δ¹³C-values of upland and wetland soils
The isotopic signatures of the uppermost soil horizon (0 – 12 cm) of upland and reference wetland soils differ significantly (p < 0.01). Upland soils have a mean δ¹³C of -26.6 ± 0.6 ‰ while the reference wetlands at a similar altitude have a mean δ¹³C of -28.3 ± 0.6 ‰ (Figure 2-5). A significant difference in δ¹³C between upland and undisturbed wetland soils was also determined for the lower soil horizon (12 – 24 cm) with mean δ¹³C values of -25.7 ± 0.7 ‰ and -27.2 ± 0.7 ‰, respectively (p < 0.01; Figure 2-5). To a large extent, the carbon isotope signature of soil is determined by vegetation. Vegetation cover of upland and wetland soils are similar in their δ¹³C with values of δ¹³C of -28.2 ± 1.0 ‰ for upland sites and of -28.7 ± 0.4 ‰ for wetland sites (Figure 2-6). While carbon isotope signature of vegetation cover and wetland soil is very similar, the uppermost upland soil horizon (0 – 12 cm) is enriched in ¹³C by about 1 ‰ compared to δ¹³C of the vegetation. The latter is most likely due to fractionation during decomposition of organic matter.

2.5.3. Influence of manure on δ¹³C signatures
Isotopic signals may be influenced by animal manure or mineral fertiliser. Bol et al. (2005) show in a long term experiment that the application of animal manure results in an enrichment in nitrogen stable isotope composition, but no significant effect was observable for δ¹³C and δ³⁴S. Determination of the isotopic composition of animal manure, which was brought out in autumn 2005 in the investigation area, gives a mean δ¹³C value of -28.9 ± 0.4 ‰ and is, thus, very close to vegetation values (-28.2 ± 1.0 ‰ and -28.7 ± 0.4 ‰ for uplands and wetlands, respectively). Furthermore, a comparison of manured and unmanured upland soils shows no significant difference
in δ¹³C (p = 0.19; Figure 2-6). Thus, animal manure does not directly influence δ¹³C of the investigated soils. However, a strong influence of manure on δ¹⁵N values was documented at the same sites (Alewell et al., 2008).

Figure 2-5. δ¹³C for two depth steps (0 – 12 cm and 12 – 24 cm). Boxplots indicate median (straight line), mean (dotted line), 10th-, 25th-, 75th- and 90th-percentile, and outliers (dots).

Figure 2-6. δ¹³C for the vegetation cover at upland and wetland sites (left) and for unmanured and manured upland soils (right). Boxplots indicate median (straight line), mean (dotted line), 10th-, 25th-, 75th- and 90th-percentile, and outliers (dots).

2.5.4. Short-term soil disturbance

In order to detect increased and recent erosion, only the upper soil horizons were examined. As soil erosion is a surface process a change in δ¹³C within the top 12 cm of a wetland influenced by erosion can be expected. Carbon isotope signature of upper soil horizons of wetland soils influenced by erosion have intermediate δ¹³C values of -27.5 ± 0.5 ‰, i.e. between the δ¹³C of upland soils with -26.6 ± 0.6 ‰ and the reference wetland with -28.3 ± 0.6 ‰ (Figure 2-5). There is a significant difference between the reference wetlands and the wetlands influenced by erosion (p < 0.01). Stable carbon isotope signatures of lower horizons (12 – 24 cm) are corresponding in both wetland types (Figure 2-5). This confirms that the influence of erosion mainly affects the upper part of the soil profile. It can not be completely excluded that comparably higher oxidation rates at wetlands in position B are the cause of isotopic differences. But, field observations and carbon content data show that the two wetland types (B and C) have comparable conditions. Therefore, we assume that
the obtained mixed signature for the wetland influenced by erosion can be assigned to erosion input from the upland. The influence of erosion on a wetland can also be observed for the site Laui that does not show visible damage by soil erosion (Figure 2-3c, Figure 2-4). Measurements of Cs-137 confirm erosion processes at all sites. Output of soil material from the upland is represented by a lower Cs-137 activity in the upland compared to a reference site with no erosion (Figure 2-7). A clear negative deviation was found from the reference value of 146.4 ± 19.5 Bq/kg which gives evidence that since input of Cs-137 in 1986 (after Chernobyl reactor accident) soil loss through erosion processes took place. Parallel to output of soil material in the upland, input to the wetland is represented by Cs-137 activities of wetland sites exceeding the reference value (Figure 2-7). This indicates that stable isotopes are indeed a suitable and very sensitive tracer to detect soil degradation before visible damage is noticed. According to Lal (2003), eroded SOC is prone to mineralisation during the whole transport and redistribution process. Fractionation accompanying the decomposition of the eroded soil organic carbon increases shifts in δ^{13}C so that small amounts of upland soil can considerably influence wetland δ^{13}C.

[Figure 2-7. Cs-137 activities all hill slope transects from uplands to adjacent wetlands. Cs-137 activities are given relative to a reference value of 146.4 ± 19.5 Bq/kg.]

Theoretically, decreasing carbon content at the upland and increasing carbon content at the wetland can be expected. However, this is not confirmed by our data. As carbon content of wetlands is already high (from 17.6 ± 5.9 % in histic gleysols to 30.7 ± 7.4 % in histosols for soil horizons of 0 – 12 cm), additional input of minor amounts from the upland can not be detected. Furthermore, in the manured and nutrient rich uplands soil organic carbon is most likely produced rather fast,
which might obscures the carbon depletion due to soil erosion. Carbon content of upland soil horizons of 0 – 12 cm is 6.1 ± 1.5 % and does not differ significantly between sites with different erosion level. This range of carbon content in the Urseren Valley corresponds to the SOC content of 6.1 ± 3.3 % for soils (0 - 20 cm) of permanent grasslands above 1000 m a.s.l. reported in other studies (Leifeld et al., 2005).

Landslides are among short-term soil erosion types as they occur as an intensive sudden erosion event. Eroded soil material is deposited in the wetland where the event is documented as an overlying layer of upland soil material in the soil profile. This obvious influence of upland soil material on the wetland is clearly reflected in $\delta^{13}C$ as well as carbon content depth profiles. A layer of upland soil material is recorded as a kink in the $\delta^{13}C$ depth profile (see Spissen B and Bielen B, Figure 2-4, 0 – 4 cm). A similar kink is documented for carbon contents as a shift from high carbon content of the genuine wetland soil towards low carbon contents on top of the soil profile. As this layer is strongly depleted in carbon it can be assumed that its origin is a deeper mineral soil horizon.

2.5.5. Long-term soil disturbance

Correlation of upland $\delta^{13}C$ vs. C content indicates that $\delta^{13}C$ is strongly linked to soil carbon content and also suggests that isotopic fractionation accompanies SOC decomposition (Figure 2-8). A statistic dependence of $\delta^{13}C$ and C content is given for all upland transects. Correlation coefficients ($r$) between $\delta^{13}C$ and C content are over 0.80 for non-erosive upland soils ($r$: Spissen AAA = -0.89, Bielen AA = -0.93, Laui A = -0.97). All wetland soils have $|r|$ smaller than 0.80 ($r$: Spissen B = -0.75, Bielen B = -0.64, Laui B = -0.30, Oberes Moos C = -0.70, Höh C = -0.33, Spiessenälpetli C = -0.34, Lutersee C = 0.46)(Figure 2-8). The weaker correlation between $\delta^{13}C$ and C content at the wetlands Laui B, Höh C and Spiessenälpetli C is a result of the low decomposition rates of organic matter under anaerobic conditions. Hence, the relation of $\delta^{13}C$ to C content reflects the prevailing metabolism (aerobic/anaerobic) during soil formation.

A deviation from the strong correlation between $\delta^{13}C$ and C content of upland soils may be used as an indicator for enhanced soil degradation, i.e. carbon loss. Decreasing correlation coefficients ($r$) are paired with visual erosion damage at the sites (Figure 2-8). Transects from hill slopes with no visible erosion output have $|r|$ higher than 0.80 (Laui A = -0.97, Bielen AA = -0.93, Spissen AAA = -0.89) whereas sites prone to erosion have $|r|$ equal and smaller than 0.80 (Bielen A = -0.78, Spissen AA = -0.80, Spissen A = -0.57). The comparatively small $r$ of Spissen A ($r = -0.57$) supports the visually presumed grade of soil degradation at this site (Figure 2-3a), as samples were taken around a tear-off line of a landslide. Thus, enhanced leaching and erosion is very likely.

In summary, correlation between $\delta^{13}C$ and C content confirmed the visual impression of the erosion situation at single upland transects. However, $\delta^{13}C$ vs. carbon content
is not suitable to track down the incipiencies of soil erosion as the carbon content in the soil changes only slowly.

Figure 2-8. Carbon content vs. $\delta^{13}C$ for single transects for all uplands (A), wetlands in direct influence of upland sites (B) and reference wetlands (C). Sampling points of one transect are grouped in the same chart.

A striking visual similarity between $\delta^{13}C$ depth profile characteristics of upland and adjacent wetlands is found (Figure 2-4). In mountainous regions wetlands are often situated at the foot of a hill slope in direct connection to uplands. Downhill transport of minor amounts of soil material is a continuous process at hill slopes. The adaption of wetland $\delta^{13}C$ profile to upland characteristics may be caused by a continuous
longtime influence of the near upland. This can be due to long term soil erosion with very low rates or to leaching. As the whole soil profile is affected, long-term disturbance may be assigned to a time period of several hundreds of years.

2.6. Conclusion

Stable carbon isotopic signatures have shown to be a potential tool to detect soil erosion in transects from oxic upland soils to anoxic wetland soils when a significant difference in $\delta^{13}$C values of upland and wetlands unaffected by erosion is present. In this situation, $\delta^{13}$C signatures are a suitable tool to track down early stage soil erosion processes. In combination with the interpretation of $\delta^{13}$C vs. C content data a differentiation between short-term (only A-horizon affected) and long-term soil erosion (whole soil profile affected) is possible. Undisturbed uplands show a strong correlation of SOC and $\delta^{13}$C. A deviation from this strong correlation indicates long term disturbance of upland soils by erosion, which is confirmed by the visual impression of the erosion situation at single upland transects.

To conclude, $\delta^{13}$C generally seems to be a very sensitive tracer to track down both long term and recent erosion influence in wetlands. As a result of long lasting input of upland soil material, $\delta^{13}$C depth profiles of many wetlands in the Urseren Valley influenced by erosion had a striking similarity to adjacent uplands.

2.7. Acknowledgements

This work was financially supported by the Swiss National Science Foundation (SNF), project no. 200021-105579 and 200020-113331.

We would like to thank B. Seth for help with the stable isotope measurements and for the language editing of the manuscript and H. Strohm for carrying out the CHN-analyses.
Determination of $\delta^{18}$O in soils: measuring conditions and a potential application

Published in: Rapid Communications in Mass Spectrometry 23, 313-318, 2009
Authors: Schaub, M., Seth, B. & Alewell, C.
Environmental Geosciences, University of Basel

3.1. Abstract

Stable oxygen isotope signature ($\delta^{18}$O) of soil is expected to be the result of a mixture of the components within the soil with varying $\delta^{18}$O signatures. Thus, $\delta^{18}$O of soils should provide information about the soil's substrate, especially about the relative contribution of organic matter versus minerals. As there is no standard method available for measuring soil $\delta^{18}$O, the method for measurement of single components using High Temperature Conversion Elemental Analyzer (TC/EA) was adapted. We measured $\delta^{18}$O in standard materials (IAEA 601, IAEA 602, Merck Cellulose) and soils (organic and mineral soils) in order to determine a suitable pyrolysis temperature for soil analysis. We consider a pyrolysis temperature suitable when the yield of signal intensity (mass 28 per 100 μg) is at a maximum and acquired raw $\delta^{18}$O signature is constant for used standard materials and when the quartz signal from the soil is still negligible. After testing several substances within the temperature range of 1075 to 1375 °C we decided to use a pyrolysis temperature of 1325 °C for further measurements. For the Urseren Valley we have found a sequence of increasing $\delta^{18}$O signatures from phyllosilicates to upland soils, wetland soils and vegetation. Our measurements show that $\delta^{18}$O of upland soil samples differ significantly from wetland soil samples. The latter can be related to changing mixing ratio of mineral and organic constituents of the soil. For wetlands affected by soil erosion, we have found intermediate $\delta^{18}$O signatures which lie between typical signatures for upland and wetland sites and give evidence for input of upland soil material through erosion.

3.2. Introduction

Oxygen is the most frequent element in bedrocks and soils. It is a constituent of both, organic and inorganic matter. Nevertheless, the distribution and fractionation of
oxygen stable isotopes of soil material and the suitability of $\delta^{18}$O of soils as a tool to determine soil degradation have, to our knowledge, not yet been investigated in soil science. Even though isotopic signature of soil has not been studied yet single components have thoroughly been investigated independently but not in soils: Studies of $\delta^{18}$O of clay minerals or carbonates have been used to determine basic conditions under which the minerals formed, which mainly finds application in climate reconstruction and/or palaeothermometry studies (e.g. Savin & Epstein, 1970a; Savin & Epstein, 1970b; Delgado & Reyes, 1996). Stable isotopes of organic matter, especially cellulose, are, as well, used in palaeoclimatological studies (for an overview see Barbour, 2007).

It can be assumed that $\delta^{18}$O values of clay minerals in soil represent in part their initial signature and in part an adaptation of the $\delta^{18}$O composition during post-formational metamorphism (Savin & Epstein, 1970; Sheppard & Gilg, 1996). Although oxygen isotope exchange takes place even at low temperatures (hydrothermal conditions), the clay mineral largely keeps the original $\delta^{18}$O signature as long as recrystallization does not occur (Sheppard & Gilg, 1996). Doser et al. (1998) found only little change in $\delta^{18}$O for a weathering sequence from illite to kaolinite. O’Neil & Kharaka (1976) show in an experiment with kaolinite, illite and montmorillonite that oxygen exchange in the water-clay system is minor up to temperatures of 350 °C (except kaolinite at 350 °C). Consequently, weathering of phyllosilicates during soil formation should not be accompanied by significant fractionation processes and $\delta^{18}$O values of phyllosilicates in the soil should be more or less similar to $\delta^{18}$O of phyllosilicates in the source rock.

Upland and wetland soils differ in their metabolism and constituents. Upland soils consist mainly of phyllosilicates and quartz with smaller fractions of organic matter (< – 30 %) whereas wetland soils have by definition an organic matter content of at least 30 %. It can thus be expected that not only different soil components have diverse $\delta^{18}$O values but that we also find a difference between upland and wetland soils. Difference in soil $\delta^{18}$O is thought to be mainly due to changing mixing ratio of organic and inorganic substances making up the soil. Additionally to the soil $\delta^{18}$O measurements, we measured phyllosilicates from bedrock and vegetation samples from the investigation area separately in order to estimate their contribution to the soil $\delta^{18}$O.

As a potential application of $\delta^{18}$O measurements in soils we tried to trace soil erosion. Input of upland soil material to wetlands through soil erosion could be detected with stable carbon isotopes as a mixed isotopic signature which lies between the $\delta^{13}$C values for upland and unaffected wetland soils (Alewell et al., 2008). Parallel to carbon, oxygen should be suitable for erosion detection in wetlands if the precondition of differing upland and wetland isotopic signatures is given. If soil erosion takes place in a transect from upland soils to wetlands, then the input of upland soil material to the wetland results in a mixed signature which lies between the $\delta^{18}$O of the erosion material (upland soil) and the $\delta^{18}$O of unaffected wetlands.
For δ¹⁸O measurement of different components different pyrolysis temperatures have been used in the past. A temperature of 1080 °C was used for measurement of cellulose and sucrose (Werner et al., 1996; Saurer et al., 1998) as well as for measurements of whole spruce needles (Jaggi et al., 2003). However, Webb & Longstaffe (2006) measured cellulose using a temperature of 1300 °C. Leuenberger & Filot (2007) suggest a temperature above 1450 °C for pure organic samples like cellulose and sucrose in order to avoid CO₂ and H₂O production as a by-product in the reactor. Kornexl et al. (1999) used a temperature of 1400 °C for measuring various organic and inorganic standard materials. A study about BaSO₄ measurements was accomplished at 1400 – 1420 °C (Boschetti & Iacumin, 2005). No knowledge exists for soil, i.e. mixtures of organic matter and siliceous minerals (clay minerals, mica, feldspar, quartz). It was the aim of this study to find a method to measure δ¹⁸O in soil. A suitable measurement temperature for soils had yet to be determined. Determination of δ¹⁸O of upland and wetland soils should give evidence if the resulting δ¹⁸O signature is the result of a pure mixing of δ¹⁸O of single components or if considerable isotopic fractionation takes place during soil formation. A further aim was to scrutinise whether δ¹⁸O is suitable to be used as a tracer to track down changes in soil composition by soil erosion influence.

3.3. Analytical Procedure

Oxygen isotope signatures were measured as CO with a High Temperature Conversion Elemental Analyzer (TC/EA, Thermo Finnigan, Bremen, Germany) equipped with a Zero Blank Autosampler (Costech Analytical Technologies, Valencia, CA, USA) and combined with a CONFLO III Interface and a Delta plus XP mass spectrometer (Thermo Finnigan, Bremen, Germany). The pyrolysis furnace consists of an outer ceramic tube and an inner glassy carbon tube with a 4 cm graphite tube on its top. The inner glassy carbon tube is filled with glassy carbon granulate up to a level just below the hot zone of the furnace. On top of the glassy carbon granulate in the hottest zone of the furnace a graphite crucible collects the ashes and molten silver capsules. The He-flow carrying the gas to the gas chromatograph (GC, 75 °C) was 110 ml/min. Samples were wrapped in silver capsules. ¹⁸O/¹⁶O isotope ratios are reported as δ¹⁸O values (‰) relative to V-SMOW. Accuracy of isotope ratio is monitored by analysis of international standards IAEA 601 and IAEA 602 (both benzoic acid). The δ¹⁸O values of these standards at different pyrolysis temperatures are discussed below. Signal intensity as monitored by the yield of mass 28 (C¹²O₁⁶) per 100 μg against temperature gives information about the efficiency of pyrolysis. Raw δ¹⁸O (‰) is the uncorrected machine output measured against a laboratory reference gas. Raw δ¹⁸O against temperature provides information about potential fractionation accompanying pyrolysis.

Soil samples (0 – 10 cm) were taken with a core sampler (6 cm of diameter) at upland and wetland sites in the Urseren Valley. After sampling they were stored at
24

approximately 4 °C until further processing. Soil samples were 2 mm sieved, dried at 40 °C for three days and ground using a tungsten carbide swing grinder (Siebtechnik GmbH, Mülheim-Ruhr, Germany). Carbonate was removed prior to measurement by acid fumigation (Harris et al., 2001) in order to eliminate the influence of carbonates on δ18O (note that carbonate of primary or secondary origin can have a large heterogeneity in soils and can thus obscure results and data interpretation). Phyllosilicate sheets were carefully removed from bedrock surfaces using a sharp blade and subsequently homogenised in a mortar. Vegetation was sampled at all sites in summer 2006 by cutting the aboveground vegetation completely at three randomly selected subsites per site. After drying at 40 °C plant samples were ground in a tungsten carbide ball mill (Retsch, Haan, Germany).

3.4. Site
The study area is located in the southern part of Central Switzerland (Canton Uri) in the Urseren Valley. The bottom of the W-E extended mountain valley is approximately 1500 m above sea level. It is surrounded by mountain ranges of altitudes up to 3200 m above sea level. The valley is strongly affected by soil erosion. For a more detailed description of the catchment see Meusburger & Alewell (2008). The soil's substrates are rocks from a geological contact between Aar massif and Gotthard massif. These units are partly overlaid by moraine material. The most abundant bedrock material is a white mica-rich gneiss. This could be confirmed by the detection of phyllosilicates (muscovite/illite) in the soil by X-ray diffraction (using a Siemens D5000 diffractometer, Bruker AXS, Madison, WI, USA). Upland soils in the study area mainly consist of cambisols, podsols and stagnosols (WRB, 2006). Wetland soils are represented by histosols and histic to mollic gleysols (WRB, 2006). All wetland soils have histic characteristics up to a minimal depth of 20 cm. The plant cover mainly consists of alpine grasses and herbs. Provenance of the phyllosilicate samples are rocks from the Aar-, Gotthard- and Tavetsch-intermediate-massif region (see Table 3-1).

3.5. Results and Discussion

3.5.1. Determination of a suitable pyrolysis temperature for soil samples
The ideal pyrolysis temperature was determined by repeated measurement of standard materials (IAEA 601, IAEA 602, Merck cellulose) and soil samples (mineral and organic soil) in 50 °C steps between 1075 and 1375 °C. With increasing temperature the signal intensity increases for the standard materials IAEA 601 and 602 (Figure 3-1a + b). There is also an increase of raw δ18O up to a temperature of 1325 °C above which raw δ18O remains relatively constant (Figure 3-1a + b). Because of this temperature dependency we decided the ideal measuring temperature for
the benzoic acid standards to be at a minimum temperature of 1325 °C. Merck cellulose shows a similar dependency of signal intensity on temperature reaching a steady state above 1325 °C but has a rather constant raw $\delta^{18}$O signature around -3 ‰ over the whole temperature range (Figure 3-1c). Leuenberger & Filot (2007), in contrary, measured an increase of 3 ‰ between 1125 °C and 1450 °C for Merck cellulose. Soils (both organic and mineral soils) have a steady increase of signal intensity (yield of mass 28 per 100 μg) with increasing temperature (Figure 3-1d + e). Especially for mineral soils only minor amounts of the sample are pyrolysed at low temperatures. Raw $\delta^{18}$O values remain constant at temperatures above 1225 °C for mineral soils and above 1325 °C for organic soils (Figure 3-1d + e).

Table 3-1. Provenance of phyllosilicate samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>source rock</th>
<th>unit</th>
<th>sample location</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>gneiss</td>
<td>Aar massif</td>
<td>Hospental</td>
</tr>
<tr>
<td>M2</td>
<td>quartz porphyry</td>
<td>Aar massif (Perm?)</td>
<td>Realp</td>
</tr>
<tr>
<td>M3</td>
<td>muscovite gneiss</td>
<td>Tavetsch intermediate massif</td>
<td>Disentis</td>
</tr>
<tr>
<td>M4</td>
<td>sericite schist</td>
<td>Gotthard massif (Mesozoic cover)</td>
<td>Andermatt</td>
</tr>
<tr>
<td>M5</td>
<td>lime phyllite</td>
<td>Gotthard massif (Mesozoic cover)</td>
<td>Andermatt</td>
</tr>
</tbody>
</table>

Other studies working with organic material (e.g. cellulose, sucrose) used a pyrolysis temperature of 1080 °C (Werner et al., 1996; Saurer et al., 1998; Jaggi et al., 2003). Our results show that this temperature is too low for soil samples consisting of both, organic and inorganic matter. We, thus, decided to use a temperature of 1325 °C for measurements of soil because at this temperature mineral as well as organic soils are pyrolysed sufficiently and yield in constant raw $\delta^{18}$O (Figure 3-1). Generally a bigger variability in raw $\delta^{18}$O values was achieved for measurements at lower temperatures (Figure 3-1). This might be due to incomplete and/or selective pyrolysis of components. Besides the temperature dependency of the international standards IAEA 601 and 602 at temperatures below 1325 °C, the better reproducibility of measurements of all tested substances at higher temperatures supports the preference of a pyrolysis temperature at 1325 °C. At that temperature mineral and organic soils have reached a stable raw $\delta^{18}$O signature and signal of quartz is negligible (see below). Leuenberger & Filot (2007) conclude that only at temperatures above 1450 °C a total conversion of pure organic samples like cellulose and sucrose is achieved. However, despite the fact that our system setup is comparable our results are contrary. All tested substances reach constant raw $\delta^{18}$O values by a temperature of 1325 °C which gives evidence that a complete reaction of the material takes place.
Figure 3-1. Dependency of signal intensity (left) and raw $\delta^{18}O$ (right) on pyrolysis temperature for different standard materials and soil samples. Raw $\delta^{18}O$ values are uncorrected machine outputs measured against a laboratory reference gas.
There is no standard material available for soil measurements. Benzoic acid was used because its characteristics with rising temperature are comparable to soils (Figure 3-1). Thus, the accuracy of isotope ratios was monitored by analysis of IAEA 601 and IAEA 602 (both benzoic acid) giving $\delta^{18}O$ values of 23.20 ± 0.24 ‰ (1 SD, n = 129) and 71.38 ± 0.56 ‰ (1 SD, n = 116), respectively, during the course of this study using a pyrolysis temperature of 1325 °C. Long term reproducibility for $\delta^{18}O$ data at 1325 °C is generally better than 0.6 ‰.

3.5.2. $\delta^{18}O$ of soil components

The main components of the soils in the Urseren Valley are organic matter (determined with a LECO CHN-1000 Elemental Analyser, St. Joseph, MI, USA), phyllosilicates (white mica) and quartz (determined with a Siemens D5000 X-ray diffractometer, Bruker AXS, Madison, WI, USA). Quartz was measured for the whole temperature sequence between 1075 and 1375 °C. Contribution of quartz to the soil $\delta^{18}O$ signature is negligible as signal intensity is below 50 mV for the whole tested temperature range (data not shown). Such small signal intensities can not be extracted from background noise and consequently determination of quartz $\delta^{18}O$ is not possible. From literature $\delta^{18}O$ values of quartz from all over the world range between 0 and 15 ‰ (Taylor & Sheppard, 1986) and is thus within the range of the phyllosilicates of the investigated sites (Figure 3-2). Vegetation has the most positive $\delta^{18}O$ value which is 22.6 ± 2.0 ‰ for uplands and 21.0 ± 1.5 ‰ for wetlands. Vegetation signatures differ significantly from all measured phyllosilicate samples (P < 0.05; Figure 3-2). Stable oxygen isotopes of phyllosilicates from the Aar-massif and the Tavetsch intermediate massif are similar and lie between -13 and -9 ‰. The phyllosilicates from the Mesozoic cover (Table 3-1) of the Gotthard-massif have $\delta^{18}O$ values between -1 and 7 ‰. The bad reproducibility of phyllosilicate samples might be due to difficulties in homogenisation of samples consisting of phyllosilicates. The similarity of $\delta^{18}O$ values of micas from the same geologic unit might be the result of similar conditions during formation and/or reequilibration during metamorphosis which affected oxygen in silicate structure as well as oxygen in interlayers. Differences in $\delta^{18}O$ between mica from the massifs and mica from the Mesozoic cover might be explained by different formation conditions of sedimentary and igneous rocks and additionally may also reflect differences in metamorphosis conditions.

3.5.3. $\delta^{18}O$ of soils

Significantly different $\delta^{18}O$ values were measured for uplands and wetlands not affected by erosion (P < 0.05; Figure 3-2). While upper horizons (0 – 10 cm) of upland soils have a mean $\delta^{18}O$ between 5 and 15 ‰, $\delta^{18}O$ signatures of reference wetland soils vary between 15 and 20 ‰ (Figure 3-2). The oxygen isotope signatures of both soil types are influenced by the organic matter and mineral components (except carbonate) which are the main sources of soil material. As expected, wetland soils are rather similar to the $\delta^{18}O$ of their vegetation cover which reflects the big portion...
Figure 3-2. Stable oxygen isotope signature of phyllosilicates of Central Switzerland (repeated measurement of samples from the same rock sample), above ground vegetation from upland and wetland sites in the Urseren Valley and soil samples from sites in the Urseren Valley (A = upland, B = wetland with erosion influence, SB = sandy layer at position B, C = reference wetland unaffected by erosion).
of organic matter. $\delta^{18}$O signature of upland soils is shifted towards less positive values indicating the influence of mineral components. Soils $\delta^{18}$O seems to be the result of pure mixing of components with differing $\delta^{18}$O signatures. Our results give no indication of major isotopic fractionation during decomposition of organic matter. Calculating the mixing ratio for organic soil with a fraction of 80% of organic matter ($\delta^{18}$O = 21.0 ± 1.5‰) and 20% of mineral components (mean $\delta^{18}$O of phyllosilicates from the Gotthard massif = 1.8 ± 2.0‰) the calculated mixing signature for wetland soils is 17.2 ± 1.6‰ which is in the range of measured $\delta^{18}$O signatures for reference wetlands.

While uplands at the sites Spissen and Bielen have similar $\delta^{18}$O values with a mean around 12‰, the upland at Laui is shifted to more positive values (Figure 3-2). Organic carbon content is comparable for all upland sites (6.1 ± 1.5%). Hence, the heavier $\delta^{18}$O value is obviously not the result of a higher content in organic matter for Laui compared to Spissen and Bielen. Possibly the site Laui has developed from another substrate with a differing $\delta^{18}$O signature (e.g. moraine material). This might indicate the sensitivity of $\delta^{18}$O to the soil's bedrock material.

### 3.5.4. Use of $\delta^{18}$O as an indicator for soil erosion

Transects from upland to wetland soils at hill slopes with varying soil erosion intensity were compared. Additionally, $\delta^{18}$O of wetlands with soil erosion material input were compared to $\delta^{18}$O of reference wetlands not affected by soil erosion. The occurrence of erosion was verified in previous studies by analysis of $\delta^{13}$C and Cs-137 profiles (Alewell et al., 2008). Soil samples were taken from the lower part of the hillslope which is affected by erosion, both, in the uplands (assigned as A) and in the wetlands below (assigned as B). Only the top 10 cm of the soil profiles were analysed because soil erosion and redistribution mostly affects the uppermost soil layer. A difference in isotopic signatures of upland and reference wetland soils (assigned as C) is a prerequisite for the use of $\delta^{18}$O as a tracer for soil erosion. This is given for soils in the Urseren Valley (Figure 3-2). Consequently, intermediate $\delta^{18}$O values for wetland soils adjacent to an upland are due to mixing of soil erosion material with the organic wetland soil (Figure 3-2). A significant shift towards upland soil signatures was determined for the wetlands (B) at the sites Spissen and Bielen (P < 0.05), where erosion is also visually documented as a sediment layer covering parts of the wetland ($S_B$, Figure 3-2). The sediment layers probably originate from upland subsoil layers and were relocated by former landslide events. Theses sandy layers are low in organic carbon content (2.9 ± 1.1%). Thus, at both sites layers of sedimented soil material have even lighter $\delta^{18}$O signatures than their source upland. The latter reflects the higher content of mineral components with lower $\delta^{18}$O signatures in the sediment layers.

Intermediate $\delta^{18}$O signatures for the wetlands (B) at Spissen and Bielen confirm $\delta^{13}$C data which also show input of upland soil material to these wetlands (Alewell et al., 2008). $\delta^{18}$O signature of the wetland (B) influenced by soil erosion at Laui is similar to $\delta^{18}$O of the reference wetlands (C). There are indications for a significant input of
upland soil material to this wetland by $\delta^{13}\text{C}$ (Alewell et al., 2008) which is inconsistent with $\delta^{18}\text{O}$ data. This inconsistency at site Laui might be due to the small difference between $\delta^{18}\text{O}$ signatures of uplands and wetlands which might obscure input of erosion material.

3.6. Conclusions

A pyrolysis temperature of 1325 °C is considered as suitable for $\delta^{18}\text{O}$ measurements of soil samples. At that temperature pyrolysis of standard materials (IAEA 601, IAEA 602, Merck-cellulose) and soil samples is complete and a constant raw $\delta^{18}\text{O}$ signature is reached. The reproducibility of standard materials, soil components and soil samples was better than 0.6 ‰. A gradient towards increasing $\delta^{18}\text{O}$ in isotopic signatures from phyllosilicates of bedrock samples to upland and wetland soils to vegetation was found for the Urseren Valley indicating that soil $\delta^{18}\text{O}$ signature is the result of mixing of components with varying $\delta^{18}\text{O}$ signatures. Distinctly different $\delta^{18}\text{O}$ values were measured for upland and wetland soils as a result of differences in the mixing ratio between organic matter and mineral constituents of these soils. We therefore consider $\delta^{18}\text{O}$ to have potential as a suitable tracer for soil erosion in transects from upland to wetland soils. However, soil erosion detection with $\delta^{18}\text{O}$ needs to be verified at hillslope transects with known erosion rates. Further, determination of gradients from bedrock material to soils and vegetation at other sites with difference in geology, climate, altitude and vegetation might help to acquire an even broader understanding of $\delta^{18}\text{O}$ of soils and to transfer the method to other catchments.

3.7. Acknowledgement

This work was financially supported by the Swiss National Science Foundation (SNF), project no. 200021-105579 and 200020-113331. We would like to thank M. Saurer and R. Siegwolf for discussion of the results.
Part I: A measurement routine to determine Cs-137 activities at steep mountain slopes

Submitted to: Soil Use & Management
Authors: Schaub, M., Konz, N., Meusburger, K. and Alewell, C.
Environmental Geosciences, University of Basel

4.1. Abstract
Cs-137 is a common tracer for soil erosion. So far, in-situ measurements in steep alpine environments have not often been done. Most studies work in arable lands and with Ge detectors. However, the NaI detector system is a good priced, easy to handle field application. A comparison of laboratory measurements (GeLi detector) and in-situ measurements (NaI detector) of Cs-137 gamma radiation has been done for an alpine catchment (Urseren Valley, Switzerland). The aim of this study was to calibrate the in-situ NaI detector system for application at steep alpine slopes. Replicate samples from an altitudinal transect through the Urseren Valley, measured in the laboratory with a GeLi detector, showed a big variability in Cs-137 activities. These extreme differences are smoothed out by in-situ measurements giving an average Cs-137 for one site. Dependency of Cs-137 on pH, clay content, carbon content and soil moisture was tested in order to check if data interpretation must consider dependencies. There was no dependency of Cs-137 on pH, clay content and carbon content. However, in-situ data must be corrected on soil moisture. Close correlation was found for Cs-137 activities estimated with both, in-situ (NaI detector) and laboratory (GeLi detector) methods which proves the validity of the in-situ measurements with our NaI detector system. This paper describes the calibration of the NaI detector system for field application in the case of elevated Cs-137 activities originating from Chernobyl fallout. See Konz et al. (submitted) for an application to an erosion study.

4.2. Introduction
The measurement of Cs-137 concentrations can provide important information on the extent of soil erosion in areas of elevated Cs-137 concentration, which can be
either due to nuclear weapon testing or the Chernobyl reactor accident in 1986. After deposition Cs-137 is rapidly and tightly bound to the fine particles in the soil. Movement by chemical and biological processes is strongly limited (Ritchie & McHenry, 1990). Redistribution is mainly caused by physical processes where Cs-137 moves with soil particles (e.g. Bonnett, 1990; Ritchie & McHenry, 1990). The vertical distribution of Cs-137 in cultivated soils is influenced by the tillage practice which results in a more or less homogenous Cs-137 activity within the plough layer (Schimmack et al., 1994; Owens et al., 1996; He & Walling, 2000; Ritchie & McCarty, 2003). In unploughed soils most of the Cs-137 is accumulated at the top of the soil profile or few centimetres below and the content decreases with depth (Ritchie & McHenry, 1990; Owens et al., 1996; Ritchie & McCarty, 2003). Thus, it is possible to distinguish areas of net soil loss from net deposition areas by analyzing the spatial distribution of Cs-137 in the studied area (for an overview see Ritchie & McHenry, 1990). Erosion studies often assume that Cs-137 distribution is homogenous for a catchment (e.g. Walling & Quine, 1991; Wu & Tiessen, 2002; Schoorl et al., 2004; Heckrath et al., 2005). However, a possible heterogeneity in Cs-137 has to be considered in sampling design.

There are only few studies about Cs-137 in alpine regions (e.g. Hofmann et al., 1995; Albers et al., 1998; Agnesod et al., 2001) mainly analysing soil samples in the laboratory. Albers et al. (1998) studied the distribution of Cs-137 in alpine soils and plants in the German Kalkalpen. They found that 10 years after input through Chernobyl reactor accident most of the Cs-137 was still stored in the top 5 cm of the soil profile and uptake by plants was limited. Advantages and disadvantages of field and laboratory applications of gamma detectors have already been discussed in detail (e.g. Beck et al., 1972; Miller & Shebell, 1993; He & Walling, 2000). Measurement time for in-situ measurements is generally shorter due to the coverage of a representative sampling area in the field in contrast to prepared soil samples in the laboratory (Beck et al., 1972). Comparability of in-situ and laboratory measurements could be shown before, but mainly for Ge detectors and/or on cultivated fields with low heterogeneity (Haugen, 1992; Agnesod et al., 2001; Tyler et al., 2001). Because of the good resolution of peaks in gamma spectra measured with Ge detectors, these are usually favoured over the NaI detectors whose spectra often show interference of neighbouring peaks. However, for application in a mountain environment with difficult accessibility and steep slopes of up to 45 ° priorities must be set different than for good accessible areas or for arable lowland sites. Ge detector systems are usually relatively heavy or not portable at all because of the Ge-crystal's need for cooling. In contrast to Ge detector systems NaI detectors have the advantage that they are good priced and easy to handle. The aim of this study was to find a measurement routine with a NaI detector which is rather quick and can be handled by one person in the field and which still achieves accurate results.

With the objective of finding a suitable measurement routine to describe eroded and uneroded hill slopes in mountain regions an application-oriented method to give a quick overview of Cs-137 distribution in the field had to be developed. Comparison
of soil sample measurements in the laboratory (GeLi detector) and in-situ measurements in the field (NaI detector) was done in order to calibrate the field device. GeLi measurements of soil samples in the laboratory were also done in order to check dependency of Cs-137 content on soil parameters.

4.3. Site

The study area is located in the southern part of Central Switzerland (Canton Uri) in the Urseren Valley (Figure 4-1). The bottom of the W-E extended mountain valley is approximately 1450 m a.s.l.. It is surrounded by mountain ranges of altitudes up to 3200 m a.s.l.. The mean annual rainfall is 1516 mm (1986 – 2007, Source: MeteoSwiss) and the mean annual air temperature is 4.3 °C (1986 – 2007, Source: MeteoSwiss). The valley mainly consists of cultivated grasslands. Forested areas are limited to protection forests at slopes above villages. Land use is dominated by grazing and, in the lower reaches of the valley, by hay harvesting. The valley is strongly affected by soil erosion. Vegetation cover is disturbed especially on the southern slopes. Soils in the study area mainly consist of podsols and cambisols often with stagnic properties (WRB, 2006). For a detailed description of the Urseren Valley see Meusburger & Alewell (2008).

Sampling took place at 12 sites at the south exposed slope (Figure 4-1). Sites represent hillslope sections of about 20 m slope length. Mean slope angle of these hillslopes is 36°. Soil samples were taken for GeLi laboratory measurements and every site was measured three times with in-situ NaI spectrometry. Additionally, an altitudinal transect between 1500 and 2050 m a.s.l. and two reference sites with high vegetation cover at sheltered positions behind geomorphologic barriers near the valley bottom (1470 m a.s.l.) were sampled (Figure 4-1). The reference sites represent an original Cs-137 activity without erosion influence.

4.4. Analysis

4.4.1. Laboratory measurements

For laboratory measurements soil samples of a depth of 10 cm were taken as most of the Cs-137 is stored in this section (e.g. Schimmack et al., 1989; Owens et al., 1996; Schoorl et al., 2004). Five to nine samples were taken at each hillslope section. Samples were collected during summer seasons 2006 and 2007 using a core sampler of 72 mm of diameter. Soil samples were dried at 40 °C, passed through a 2 mm sieve and finally ground using a tungsten carbide swing grinder. The ground soil samples were filled into 25 ml sample containers (6.5 cm diameter; Semadeni25) and measured for 8 hours. Measurements were done with a Li-drifted Ge detector (GeLi; Princeton Gamma-Tech, Princeton, NJ, USA) at the Department for Physics and Astronomy, University of Basel. In order to reduce the amount of radiation from
background sources in the environment the samples were shielded by lead during measurement. Cs-137 activity concentrations were determined using the InterWinner 5 gamma spectroscopy software (Ortec, Oak Ridge, TN, USA). The energy calibration of the GeLi detector was done using a Eu-152 source. For efficiency calibration three samples enriched with known activities of U-238, Th-232 and K-40 were used. These calibration samples were of the same geometry and a comparable density as our analysed soil samples. The resulting measurement uncertainty on Cs-137 peak area is lower than 15%.

Figure 4-1. Aerial photograph of the Urseren Valley in Southern Central Switzerland and location of the sites (numbers), the altitudinal transect (dashed line) and the reference sites (crosses).

4.4.2. In-situ measurements

For field measurements a 2 x 2 inch NaI-scintillation detector (Sarad, Dresden, Germany) was used. The field equipment consists of a detector, a pole, a control unit, a battery and a pocket PC (Figure 4-2). The detector was mounted perpendicular to the ground on a height of 25 cm. Usually detectors are mounted 1 m above floor which means that the yield area has, as a rule of thumb, a radius of 10 m. For a comparable result the yield area should be flat and should not have irregularities (Laedermann et al., 1998; He & Walling, 2000). As this can not be fulfilled
for such a large area at any site in a mountain region, we decided to use a detector height of 25 cm. The area of yield according to this detector height was determined (see below). For all in-situ measurements Cs-137 concentration was determined for one hour. Every hillslope section was measured three times. Spectra evaluation was done with a software provided by H. Surbeck, University of Neuchâtel/Switzerland. Peak area is specified by a gauss function over the region of interest (ROI). The background is separated from the peak area by a straight line between the beginning and end point of the ROI. The ROI was set to include the three interfering peaks Tl-208 at 583.2 keV, Bi-214 at 609.3 keV and Cs-137 at 661.7 keV. This multiplet was deconvolved in order to get peak areas of single peaks. All measured Cs-137 activities refer to 2007.

**Figure 4-2.** NaI detector system with its components: (a) detector, (b) pole, (c) control unit, (d) battery and (e) interface to pocket PC.

### 4.5. Method concepts, results & discussion

#### 4.5.1. Spatial heterogeneity of Cs-137

We tested the homogeneity of Cs-137 distribution in the field by measuring an altitudinal transect from 1500 m a.s.l. to 2050 m a.s.l. on a south exposed hillslope through the valley (Figure 4-1). Samples were taken at sites with high vegetation cover and no visible erosion. Cs-137 activities of samples vary between 47 and 363 Bq·kg⁻¹ (Figure 4-3). On single altitudinal levels a big difference in Cs-137 activity was measured for replicate samples within 1 m². Generally, the wide variation of Cs-137 concentration in a limited area gives evidence that either Cs-137 was not evenly deposited and/or not bound homogeneously to soil particles at its input or secondary processes like erosion and accumulation lead to the high small scale heterogeneity of Cs-137. The problem of inhomogeneity in Cs-137 distribution has
been named in other studies, but mostly relating to a larger scale (e.g. Clark & Smith, 1988; Albers et al., 1998; Kaste et al., 2006; Machart et al., 2007). According to Machart et al. (2007) the distribution of the radionuclide in the cloud as well as inhomogeneous rainfall intensity can be the cause for inhomogeneous spatial distribution of Cs-137 in the field. Inhomogeneity in Cs-137 distribution may also be due to runoff connected to the rainfall event depositing the Cs-137 (Albers et al., 1998). The higher altitudes were still snow-covered at the time of Cs-137 deposition (Source: MeteoSwiss). Therefore, snow melt processes must be accounted as a reason for heterogeneous distribution of Cs-137, also on a small scale (Haugen, 1992). Heterogeneity in Cs-137 activities for replicate samples at higher altitudes above 1800 m a.s.l. is particularly striking. There are two interpretations possible: (i) a linear trend line through all data points shows an increase of Cs-137 with altitude or (ii) extreme outliers at 1850, 1950 and 2050 m a.s.l. are excluded which results in a homogeneous distribution of Cs-137 over 1800 m a.s.l.. The linear trend through the data points is supported by other studies who have found a dependency of Cs-137 on altitude (McGee et al., 1992; Arapis & Karandinos, 2004). However, interference with snow cover (Haugen, 1992) as an explanation for outliers in higher altitudinal levels is very likely. The remaining data from an altitude above 1800 m a.s.l. is similar to the reference value (146.4 ± 19.5 Bq·kg⁻¹) determined near the valley bottom (Figure 4-3). Even though no erosion damage is visible in the grasslands today, the lower activities measured at sites below 1800 m a.s.l. give evidence for soil loss through erosion. This interpretation can be supported by the correspondence of lower Cs-137 activities with more intensive land use practice below 1800 m a.s.l.. With the available data we can neither definitively reject nor confirm the existence of an altitudinal trend. However, small scale heterogeneity in Cs-137 distribution gets obvious from replicate samples taken at the same altitudinal level.

![Figure 4-3. Altitudinal transect between 1500 and 2050 m a.s.l. with trendline (black). Dashed line represents the Cs-137 activity (146.4 Bq·kg⁻¹) measured at reference sites. For cluster (a) influence of erosion is possible, cluster (b) is influenced by snow at the time of Cs-137 input.](image-url)
4.5.2. NaI detector calibration and boundary conditions

Cs-137 peak area obtained from measurements with the NaI detector has to be converted to Bq·kg⁻¹. This was done by comparison of an in-situ measurement using NaI detector to laboratory measurements using GeLi detector at the same site. Measurements from the altitudinal transect have shown large differences in their Cs-137 content in replicate samples of the same sites (Figure 4-3). Therefore, small-scale heterogeneity of Cs-137 concentration was analysed for NaI system calibration by laboratory measurement (GeLi detector) of 9 samples (0 - 10 cm depth) distributed over a circular area with 3 m of diameter (Figure 4-4). Mean Cs-137 concentration amounts 58.8 ± 8.2 Bq·kg⁻¹ with a maximum at 68.2 Bq·kg⁻¹ and a minimum at 42.0 Bq·kg⁻¹. The mean value of these 9 single measurements (GeLi) was used as a calibration value with which the factor for the conversion of the Cs-137 peak area (counts) determined from in-situ measurement (NaI) to Bq·kg⁻¹ was estimated. This factor allows the conversion from peak area in counts to Bq·kg⁻¹ for all further in-situ measurements at comparable soils in the Urseren Valley.

![Figure 4-4. Spatial heterogeneity of the Cs-137 distribution at the calibration site.](image)

In order to estimate the soil volume which is representative for the Cs-137 measured in the field, depth and spatial yield of the detector (NaI detector) as well as Cs-137 distribution in soil depth were determined. Depth distribution of Cs-137 was measured at a subdivided soil core (0 – 5 cm, 5 – 10 cm, 10 – 15 cm, 15 – 20 cm) by laboratory measurements (GeLi detector). Cs-137 activity is decreases exponentially with depth (Figure 4-5a). This is a typical distribution for unploughed soils (Ritchie & McHenry, 1990; Owens et al., 1996; Ritchie & McCarty, 2003). Over 70 % of the total Cs-137 inventory of the soil originates from the top 10 cm of the soil column (Figure 4-5a).
is in accordance with Schimmack & Schultz (2006) who studied the migration of Cs-137 deposited after the Chernobyl reactor accident in a grassland for 15 years.

Contribution of radiation from the depth was estimated by repeated measurement of a buried Cs-137 point source (7.6 kBq 08/2007) in steps of 2 cm between 0 and 20 cm soil depth by in-situ measurement with the NaI detector mounted 25 cm

**Figure 4-5.** (a) Cs-137 depth profile for an upland soil measured in the laboratory (GeLi detector). (b) Exponential decrease of the Cs-137 radiation measured at the surface with increasing burial depth of the point source (NaI detector). (c) Exponential decrease of the measured Cs-137 activity with increasing horizontal distance between the point source and the detector (NaI detector).
above the surface. The radiation contributing to the total measured Cs-137 activity decreases exponentially with depth (Figure 4-5b). Most of the activity comes from the top 10 cm of the soil. Radiation from below 18 cm has a minor influence on the measured surface activity. Setting the Cs-137 content of the soil off against the depth yield of the detector, the contribution of the top 10 cm of the soil column amounts to 90.3 %.

The coverage of the detector (NaI) was estimated in the field by repeated measurement of a Cs-137 point source (15.8 kBq 08/2007) with increasing horizontal distance from the detector which was mounted on 25 cm above ground. The distance was increased in 0.5 m steps. For increasing horizontal distance of the point source from the detector Cs-137 activity decreases exponentially (Figure 4-5c). Under the assumption of a homogenous distribution, 90 % of the measured Cs-137 activity origin from a circular area with a radius of 1 m around the detector (3.1 m²).

4.5.3. Sources of error

Determination of the Cs-137 peak position in the spectrum obtained by NaI measurement is subjective. Small changes in start and end position of the region of interest (ROI) leads to a big variability in peak area. This error on peak area was determined by using the mean standard deviation of peak areas of 20 test spectra evaluated by eight persons independently. Uncertainty on peak area of every single measurement amounts to 17.3 %.

Knowledge about contribution of pre-Chernobyl Cs-137 is important for quantitative estimation of erosion rates because date of input is crucial. For qualitative consideration of Cs-137 distribution in a catchment this is negligible. Contribution of pre-Chernobyl Cs-137 originating from above ground nuclear weapon tests in the 1950’s and 1960’s is not clear for total Cs-137 activities measured at the site Urseren Valley as only little data is available. Riesen et al. (1999) measured samples collected in 1986 before the Chernobyl reactor accident from 12 forested sites distributed over Switzerland. Cs-137 activities of the top soil layers (0 – 5 cm) lie between 2 and 58 Bq·kg⁻¹ (Riesen et al., 1999). Consequently, after decay with a half-life of 30.17 years, in 2007 only 1 – 35 Bq·kg⁻¹ are left, which means that the maximum contribution of pre-Chernobyl Cs-137 might amount to 20 % at reference sites.

Additionally, vertical migration must be considered. From literature migration values between 0.03 and 1.30 cm·a⁻¹ are known (Schimmack et al., 1989; Arapis & Karandinos, 2004; Schuller et al., 2004; Schimmack & Schultz, 2006; Ajayi et al., 2007). However, our measurements show that in the Urseren Valley most part of the Cs-137 is still stored in the top 10 cm of the soil profile. Thus, only moderate migration of Cs-137 occurred.

4.5.4. Dependency of Cs-137 on different soil parameters

Cs-137 content of the soil was tested for dependency on pH, clay content, soil moisture and organic carbon content in order to check if Cs-137 must be corrected on these soil parameters (Figure 4-6). It must be kept in mind that variations in Cs-137,
especially between different sites, may also be due to heterogeneity in Cs-137 distribution in the field as shown above. There are two groups of soil differing in pH, one with a pH between 4 and 5 and the other one with a pH around 7 (Figure 4-6a). There is no dependency of Cs-137 content on pH, neither for the whole dataset nor within the single groups. This is in accordance with Livens & Loveland (1988) who state that immobile conditions of Cs-137 relate to a pH range between 4 and 7.

Figure 4-6. Dependency of Cs-137 on (a) pH, (b) clay content,(c) carbon content and (d) soil moisture (3, 4, 5, 7, 9, 10 stand for different sampling sites).

A negative correlation between clay content and Cs-137 content was calculated (Figure 4-6b). However, the calculated correlation is due to different sites forming different clusters. Niesiobedzka (2000) found a positive dependency of Cs-137 on clay content for soils with very low clay contents under 3%. Since we do not see a correlation of Cs-137 and clay content within sites, we do not see evidence for a dependency. No dependency of Cs-137 on organic carbon content was found (Figure 4-6c). Dependency of Cs-137 on soil moisture was estimated by repeated measurement of a soil sample at different moisture levels with the NaI detector in the laboratory. The sample was sealed in a plastic bag during measurement time to keep moisture constant. Soil moisture shows an influence on the measured Cs-137 activity (Figure 4-6d). Therefore, soil moisture was measured parallel to in-situ measurements in order to correct data with soil moisture using an EC-5 soil moisture sensor (DecagonDevices, Pullman, WA, USA). Measured soil moisture in the field at
the time of in-situ measurements varies from 5 to 12 %, which represents a shielding of gamma radiation between 3 and 7 %.

4.5.5. Validation of the in-situ NaI measurements

In-situ and laboratory determination of Cs-137 activity were compared in order to check the validity of the calibration of the NaI detector system. The mean value of all soil samples (0 – 10 cm) of one site measured in the laboratory (GeLi detector) was checked against the mean value of the in-situ measurements (NaI detector) at the same sites (Table 4-1, Figure 4-7). A good correspondence of Cs-137 activities determined by in-situ NaI measurements and laboratory GeLi measurements was found ($R^2 = 0.86$). In Figure 4-7 standard deviations for both, laboratory measurements with GeLi detector and in-situ measurement with NaI detector are given. Note that the big variation of Cs-137 activities for single sites is due to spatial heterogeneity in Cs-137 distribution (see above). The latter is especially true for laboratory measurements (GeLi detector). In-situ measurements generally have a smaller standard deviation because the detector integrates over a measurement area of 3.1 m$^2$ (Table 4-1, Figure 4-7). The close correlation between in-situ and laboratory measurements shows that both methods give good average Cs-137 activities for single hillslopes. Our results are supported by Haugen (1992) and Tyler et al. (2001) who have found similar correspondences for cultivated fields. Despite the fact that our estimations do not include an exact calculation of the basic conditions concerning Cs-137 flux and detector response (e.g. Beck et al., 1972; Miller & Shebell, 1993) the achieved results with low calculating effort are equal to laboratory measurements (GeLi detector) of several soil samples. NaI in-situ measurements provide a quick and easy to apply possibility to determine Cs-137 inventories.

![Figure 4-7. Comparison of Cs-137 activities determined by in-situ (NaI detector) and laboratory measurements (GeLi detector).](image)
Spatial distribution of Cs-137 in grasslands is much more variable than in cultivated lands where Cs-137 is mechanically homogenised by ploughing. Therefore, interpretation of in-situ data of alpine grasslands is subject to errors relating to the spatial heterogeneity. Our data shows that Cs-137 varies greatly over a small scale. Consequently, either the number of soil samples per site must be increased or in-situ measurements which smooth irregularities out must be done in order to achieve a representative Cs-137 activity of a site. Collecting big amounts of samples in the field does not seem adapted to the case of sensitive mountain soils seriously affected by soil erosion. Especially in regions where soil restoration takes hundreds of years, non-destructive in-situ measurements should be favoured.

In-situ measurements with our NaI detector enable a determination of a mean Cs-137 activity of a single hillslope section and at the same time an estimation of the erosion state in a steep alpine catchment characterised by elevated Cs-137 activities originating from Chernobyl fallout. Application of the method is subject of Konz et al. (submitted).

**Table 4-1.** Cs-137 data of all sites for measurements with GeLi- and NaI detector.

<table>
<thead>
<tr>
<th>site</th>
<th>GeLi Mean (Bq·kg⁻¹)</th>
<th>s.d. (Bq·kg⁻¹)</th>
<th>Min. (Bq·kg⁻¹)</th>
<th>Max. (Bq·kg⁻¹)</th>
<th>NaI Mean (Bq·kg⁻¹)</th>
<th>s.d. (Bq·kg⁻¹)</th>
<th>Min. (Bq·kg⁻¹)</th>
<th>Max. (Bq·kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>73.9</td>
<td>31.5</td>
<td>42.7</td>
<td>134.0</td>
<td>73.3</td>
<td>0.9</td>
<td>72.2</td>
<td>73.8</td>
</tr>
<tr>
<td>2</td>
<td>134.8</td>
<td>59.4</td>
<td>68.6</td>
<td>266.0</td>
<td>148.0</td>
<td>3.1</td>
<td>144.4</td>
<td>150.5</td>
</tr>
<tr>
<td>3</td>
<td>104.0</td>
<td>48.5</td>
<td>52.6</td>
<td>177.8</td>
<td>108.2</td>
<td>12.0</td>
<td>95.3</td>
<td>119.0</td>
</tr>
<tr>
<td>4</td>
<td>91.9</td>
<td>24.9</td>
<td>59.59</td>
<td>144.5</td>
<td>75.8</td>
<td>23.2</td>
<td>56.2</td>
<td>105.9</td>
</tr>
<tr>
<td>5</td>
<td>92.2</td>
<td>24.3</td>
<td>48.83</td>
<td>132.5</td>
<td>99.1</td>
<td>28.5</td>
<td>70.4</td>
<td>135.2</td>
</tr>
<tr>
<td>6</td>
<td>113.8</td>
<td>24.9</td>
<td>76.8</td>
<td>131.2</td>
<td>118.6</td>
<td>14.1</td>
<td>103.0</td>
<td>130.5</td>
</tr>
<tr>
<td>7</td>
<td>133.6</td>
<td>67.4</td>
<td>53.9</td>
<td>260.9</td>
<td>128.3</td>
<td>32.8</td>
<td>104.9</td>
<td>165.8</td>
</tr>
<tr>
<td>8</td>
<td>110.8</td>
<td>49.8</td>
<td>49.6</td>
<td>160.3</td>
<td>131.7</td>
<td>23.8</td>
<td>113.7</td>
<td>158.6</td>
</tr>
<tr>
<td>9</td>
<td>66.0</td>
<td>16.4</td>
<td>40.55</td>
<td>84.95</td>
<td>63.6</td>
<td>10.9</td>
<td>52.5</td>
<td>63.8</td>
</tr>
<tr>
<td>10</td>
<td>63.7</td>
<td>19.3</td>
<td>37.7</td>
<td>91.4</td>
<td>64.4</td>
<td>4.6</td>
<td>59.2</td>
<td>68.2</td>
</tr>
<tr>
<td>11</td>
<td>86.2</td>
<td>25.5</td>
<td>55.3</td>
<td>112.5</td>
<td>84.1</td>
<td>12.6</td>
<td>70.0</td>
<td>94.5</td>
</tr>
<tr>
<td>12</td>
<td>70.7</td>
<td>29.3</td>
<td>41.0</td>
<td>127.8</td>
<td>90.1</td>
<td>12.2</td>
<td>82.6</td>
<td>104.1</td>
</tr>
</tbody>
</table>

**4.6. Conclusion**

Cs-137 distribution in the Alps is very heterogeneous especially on a small scale. The Cs-137 activity is averaged spatially by in-situ measurements. Our NaI detector mounted 25 cm above ground integrates over a measurement area of 3.1 m². No dependency of Cs-137 on pH, carbon content and clay content was found, but in-situ measurements must be corrected on soil moisture. The NaI detector which is a quick and easy to apply method was successfully applied to an alpine grassland with strong heterogeneity in Cs-137 distribution. In alpine areas the steep terrain
hampers the use of Ge detectors in the field, hence NaI detector system offers a good alternative. Further, in-situ measurements are non-destructive which is important particularly at sites strongly affected by soil erosion. The use of NaI detectors in the field is a valid and rather quick alternative for extensive soil sampling series.

4.7. Acknowledgements
This work was financially supported by the Swiss National Science Foundation (SNF), project no. 200020-113331.
We would like to thank H. Surbeck (University of Neuchâtel) for help with spectra evaluation and provision of software and samples for detector calibration and S. Estier (Federal Office of Public Health FOPH) for helpful discussion.
Part II: Cs-137 based erosion rate determination of a steep mountainous region

Submitted to: Journal of Plant Nutrition and Soil Science
Authors: Konz, N.¹, Schaub, M.¹, Prasuhn, V.² and Alewell, C.¹
¹ Environmental Geosciences, University of Basel
² Agroscope Reckenholz-Tänikon

4.8. Abstract

Data on quantification of sheet erosion rates in alpine grasslands and their dependency on land use remain scarce but are urgently needed to estimate soil degradation. We determined soil erosion rates based on the Cs-137 method with in-situ measurements. This method integrates the erosion over the last 22 years (time after the Chernobyl accident). The gained erosion rates were compared with erosion rates that we determined with the Universal Soil Loss Equation (USLE). The comparison was done in order to verify the validity of USLE in steep mountainous grassland systems. Three different land use types were investigated: hayfields, pasture with dwarf shrubs and pasture without dwarf shrubs. Our test plots are situated in the Urseren Valley (Central Switzerland) with a mean slope steepness of 37 °. Mean annual soil erosion rates determined with Cs-137 of the investigated sites ranged between 4.7 t·ha⁻¹·a⁻¹ for pastures with dwarf shrubs to > 20 t·ha⁻¹·a⁻¹ at hayfields and pastures without dwarf shrubs and are thus 10 to 20 times higher compared to previous measurements in alpine regions. Our measurements integrated over the last 22 years, including extreme rainfall events as well as winter processes; whereas previous studies mostly reported erosion rates based on summer time, short term irrigation experiments. Our results indicated that land use has a considerable influence on soil erosion rates. Erosion rates based on the USLE are in the same order of magnitude as Cs-137 based results. However, the uncertainty of the USLE results due to the steep slopes can not be estimated that makes it quite difficult to estimate the relative standard deviation. If the high erosion rates determined in our study for the Urseren Valley are confirmed for other alpine regions, soil conservation strategies need to be reconsidered.
4.9. Introduction

Soil erosion in the Alps is a well recognised problem, identified as a priority for action within the soil protocol to the Alpine Convention (Alpenkonvention, 2005). Steep slopes, extreme climate as well as restricted agricultural land use characterise the Alpine environment. Main drivers for soil erosion are topography, soil type, land cover and rainfall patterns. Additionally, snow processes like snow melt or avalanches enhance erosion in alpine regions. A comprehensive assessment of soil erosion on the Alps is still missing (ClimChAlps, 2008). Mapping and quantification of soil erosion under different land use conditions has been studied in numerous projects for agricultural soils in lowlands or low mountain ranges (Morgan, 1985; Walling et al., 1999; Melville & Morgan, 2001; Leser et al., 2002; Matisoff et al., 2002; Tamene & Vlek, 2007) as well as in laboratory experiments (Boubakari & Morgan, 1999). However, only few studies exist on soil erosion measurement and quantification under natural precipitation regimes in alpine environments (Felix & Johannes, 1995; Schlunegger et al., 2002; Descroix & Mathys, 2003; Isselin-Nondedeu & Bédécarrats, 2007). Hence, more data on soil erosion in alpine regions is needed. While the term soil erosion includes sheet-, rill- and gully erosion, we focus on sheet erosion because rill and gully erosion are not important processes in our region.

Numerous models have been developed and used to quantify and predict soil erosion. The Universal soil loss equation USLE (Wischmeier & Smith, 1978) is one of the most used models to identify erosion risk areas and to select conservation methods in agricultural lowlands for long term average erosion (e.g. Kuss & Morgan, 1984; Auerswald et al., 2003). Erosion rates are calculated as

\[ A = C \times R \times K \times L \times S \times P \]  

where \( A \) is the average annual soil loss (kg·m\(^{-2}\)·a\(^{-1}\)) erosion, \( R \) is the rainfall-runoff factor (kg·m·s\(^{-2}\)·h\(^{-1}\)), \( K \) is the soil erodibility factor and gives the soil’s tendency to erode (kg·h·kg\(^{-1}\)·m\(^{-1}\)·s\(^{-2}\)·m\(^{-2}\)), \( L \times S \) is the topography factor combining slope length and slope steepness (dimensionless), \( P \) is the support practice factor (dimensionless) and \( C \) is the management factor (dimensionless). \( C \) factors are well defined for crop rotations (e.g. Gabriels et al., 2003). For most rotation systems the \( C \)-factors were between 0.28 and 0.38 (e.g. winter wheat). High \( C \)-factor values were obtained by maize (\( C = 0.47 \)) and potato (\( C = 0.51 \)). In contrast to the relatively well determined \( C \)-factors of arable land, roughly estimated uniform values are used for grassland, forest and fallow. Wischmeier and Smith (1978) suggest a \( C \) factor of 4·10\(^{-3}\) for established hayfields with a mean annual hay production of 6.7 t·ha\(^{-1}\) and a fractional vegetation cover of >95 %, and 3·10\(^{-3}\) for permanent pastures. The values are increasing with decreasing fractional vegetation cover. Van der Knijff et al. (2000) used a \( C \) factor of 1·10\(^{-3}\) for the soil erosion risk assessment in Europe for woodlands and pastures and 5·10\(^{-3}\) for hayfields. Auerswald & Schmidt (1986) and Gündra et al. (1995) used \( C \) factors of 4·10\(^{-3}\) for grass- and woodlands for the Bavarian (south east Germany) erosion hazard maps and for south west Germany,
respectively. Prasuhn et al. (2007) used a C factor of $3 \times 10^{-3}$ for woodland and grassland for the Swiss erosion hazard map.

The determination of long-term soil erosion rates and patterns of soil redistribution on cultivated land via Cs-137 is seen as an established method (e.g. Ritchie & McHenry, 1990; Walling & Quine, 1990; He & Walling, 2000). The use of Cs-137 measurements to quantify soil redistribution rates is commonly based upon a comparison of Cs-137 inventories for individual sampling points to the local reference inventory. When Cs-137 reaches the soil surface by wet deposition, it is tightly adsorbed to fine soil particles. The subsequent lateral redistribution of adsorbed Cs-137 is associated with soil erosion (Sawhney, 1972). Erosion is indicated by lower Cs-137 values, while sedimentation is indicated by higher Cs-137 inventories compared to the reference site (Walling & Quine, 1990; Walling & He, 1999; Walling et al., 1999).

Cs-137 based erosion rates (A in the USLE) were compared to results of the USLE in order to assess the validity of the model for steep alpine grasslands. The Cs-137 amounts were determined with in-situ NaI (Sodium-Iodide) gamma detector measurements. The advantages of such in-situ measurements in alpine areas are discussed by Schaub et al. (submitted).

4.10. Material and Methods

4.10.1. Study site

The study area is located in Central Switzerland (Canton Uri) in the Urseren Valley (Figure 4-8). The investigated sub-catchment has an area of about 30 km$^2$. The elevation of the W-E extended mountain valley ranges from 1450 to 3200 m a.s.l. Mean annual rainfall from 1986 to 2007 was 1516 mm and mean air temperature was 4.3 °C. The valley is snow covered from November to April with the maximum snow height in March (Ambuehl, 1961) and a mean annual snowfall between 1986 and 2008 of 448 mm (Source: MeteoSwiss). Runoff is usually dominated by snowmelt in May and June. Land use in the valley is hayfield near the valley bottom and pasture further upslope. Dominant soil types of the investigation site - classified after WRB (2006) - are podsol and cambisol, often with stagnic properties. For a detailed description of the Urseren Valley see Meusburger & Alewell (Meusburger & Alewell, 2008).

All investigated plots are situated on the south-facing slopes between 1550 and 1800 m a.s.l. (Figure 4-8). Three different grassland types were investigated with three replicates: hayfield (hf), pasture with dwarf shrubs (pawo) and pasture without dwarf shrubs (paw). The angle of the plots is between 35 ° - 39 °. Soil texture at all 9 plots was classified as loamy silt (Table 4-2). Dominant plant species in the hayfields are Trifolium pratense ssp. Partense, Festuca sd, Thymus serpyllum and Agrostis capillaries. Pasture with dwarf shrubs are dominated by Calluna vulgaris, Vaccinium myrtillus, festuca violacea, Agrostis capillaries and Thymus serpyllum. Main species of pastures without dwarf shrubs are Gluebalaria cordifolia, Festuca sd and Thymus serpyllum.
4.10.2. Erosion assessment with Cs-137

We used a NaI scintillation detector with a 2 x 2 inch crystal to measure Cs-137 distribution in the field. For the one hour measurements the gamma spectrometer was placed perpendicular to the ground at a height of 25 cm. The Cs-137 measurements were done in summer and autumn 2007 with three replicates at each plot. Additionally, two reference sites near the valley bottom unaffected by erosion were measured with the same procedure.

Boundary conditions, measurement procedures and details about reference sites are described in Schaub et al. (submitted). The measurement error of the Cs-137 peak area is 17.3% since the determination of the Cs-137 peak position in the spectrum is subjective. Small changes in start and end position of the peak leads to a big variability in peak area. This error on peak area was determined by using the mean standard deviation of peak areas of 20 test spectra evaluated by eight persons independently. Acquisition and processing of the spectra was done with software provided by H. Surbeck, University of Neuchâtel (Schaub et al., submitted).

4.10.3. Erosion assessment with the USLE

The Universal Soil Loss Equation (USLE) is one of the models that are frequently used world wide to appraise erosion rates for different land use types. One of the reasons is that the data requirement is low. As there is no special model for steep alpine regions, we tested the USLE for applicability in steep alpine regions. For our study, all factors of USLE were either determined from field data or taken from literature values.
R was calculated from daily precipitation data of the local meteorological station of MeteoSwiss (Table 4-2). There are different algorithms to estimate the rainfall-runoff factor R for the USLE. All of them are region-specific, for example Lal (1976) for Western Africa, Wischmeier & Smith (1978) for northern America, Renard & Freimund (1994) for Asia, USA and Africa and Rogler & Schwertmann (1981) for southern Germany. We used the algorithm of Rogler & Schwertmann (equation 2) for the determination of the R factor in the Urseren Valley because of the comparable geographical location and meteorological similarity. Rogler and Schwertmann (1981) calculate R as:

\[ R = 0.083 \times N \times (1 - (0.0264 \times \text{height} - 2.0663)/100) - 1.77 \]  

(2)

where \( R \) is the rainfall-runoff factor (kg·m·s\(^{-2}\)·h\(^{-1}\)) and N the average annual rainfall (mm). We determined the erodibility factor \( K \) after the German soil mapping instruction (Sponagel et al., 2005) from the soil texture, using the grain size analyses data of the top 10 cm profile. Uncertainty of \( K \) is determined by error of grain size analyses which is ± 4.4 %.

\( L \) and \( S \) are topographic factors typically combined into \( L \times S \) factor. \( L \) scales the distance of upstream flow accumulation at any field location to the length of the standard USLE plot used for experimental erosion measurements (22.13 m). \( S \) scales the steepness at the field site relative to the slope of the experimental USLE plots (9 %; 5.1 °) and was calculated after Renard et al. (1997) for this investigation as it is valid for slopes between 22 % (12.4 °) and 56 % (29.3 °):

\[ L = \left( \frac{\lambda}{22.13} \right)^m \]  

(3)

with

\[ m = \frac{\beta}{(1 + \beta)} \]

\[ \beta = \frac{(\sin \theta / 0.0896)}{[3 \times (\sin \theta)^0.8 + 0.56]} \]

for \( \theta \geq 5.14° \)

\[ S = 16.8 \times \sin \theta - 0.5 \]  

(4)

where \( L \) is the slope length factor (dimensionless), \( \lambda \) is the real slope length (m), \( m \) the slope length exponent (dimensionless), \( \beta \) the susceptibility to rill erosion (dimensionless), \( \theta \) slope gradient (°) and \( S \) the slope factor (dimensionless).

The support and practice factor \( P \) was set to 1 for all investigated plots (Table 4-2) since alpine grasslands have no parallel contour lines which have been suggested to be considered in \( P \) (Wischmeier & Smith, 1978; Foster & Highfill, 1983). \( S \) factors for more than 29.3 ° were not collected so far.

The support and practice factor \( P \) was set to 1 for all investigated plots (Table 4-2) since alpine grasslands have no parallel contour lines which have been suggested to be considered in \( P \) (Wischmeier & Smith, 1978; Foster & Highfill, 1983). The cover and management factor \( C \) was set 3·10\(^{-3}\) according to literature data (Wischmeier & Smith, 1978; Auerswald & Schmidt, 1986; Van der Knijff et al., 2000; Prasuhn et al., 2007).
Table 4-2. Measured and calculated parameters for the investigation sites in the Urseren Valley. Relative standard deviation (*n = 10 soil samples) of grain size analyses is 10 %. Relative standard deviation of the C factor is 33 %. The pH value was measured with 0.01 molar CaCl₂ with a relation of 1 (soil) to 2.5 (CaCl₂). K is kg·h·kg⁻¹·m⁻¹·s⁻²·m⁻² and R kg·m·s⁻²·h⁻¹.

<table>
<thead>
<tr>
<th>grassland type</th>
<th>m1</th>
<th>m2</th>
<th>m3</th>
<th>pawo1</th>
<th>pawo2</th>
<th>pawo3</th>
<th>paw1</th>
<th>paw2</th>
<th>paw3</th>
</tr>
</thead>
<tbody>
<tr>
<td>slope (°)</td>
<td>39.0</td>
<td>38.0</td>
<td>35.0</td>
<td>38.0</td>
<td>38.0</td>
<td>35.0</td>
<td>38.0</td>
<td>37.5</td>
<td>35.0</td>
</tr>
<tr>
<td>sand (%)</td>
<td>40.2</td>
<td>23.8</td>
<td>39.3</td>
<td>37.9</td>
<td>36.6</td>
<td>39.4</td>
<td>49.8</td>
<td>25.7</td>
<td>44.9</td>
</tr>
<tr>
<td>silt (%)</td>
<td>47.3</td>
<td>58.8</td>
<td>43.8</td>
<td>50.5</td>
<td>47.1</td>
<td>45.6</td>
<td>37.6</td>
<td>63.5</td>
<td>40.9</td>
</tr>
<tr>
<td>clay*</td>
<td>12.5</td>
<td>17.3</td>
<td>16.9</td>
<td>11.6</td>
<td>16.4</td>
<td>15.0</td>
<td>12.5</td>
<td>10.8</td>
<td>14.2</td>
</tr>
<tr>
<td>pH</td>
<td>5.0</td>
<td>4.4</td>
<td>4.5</td>
<td>7.1</td>
<td>7.3</td>
<td>4.6</td>
<td>4.3</td>
<td>4.4</td>
<td>4.5</td>
</tr>
<tr>
<td>R</td>
<td>178.7</td>
<td>178.7</td>
<td>178.7</td>
<td>178.7</td>
<td>178.7</td>
<td>178.7</td>
<td>178.7</td>
<td>178.7</td>
<td>178.7</td>
</tr>
<tr>
<td>K</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>P</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>S</td>
<td>10.1</td>
<td>9.8</td>
<td>9.0</td>
<td>9.8</td>
<td>9.8</td>
<td>8.5</td>
<td>9.8</td>
<td>9.7</td>
<td>9.1</td>
</tr>
<tr>
<td>L</td>
<td>2.2</td>
<td>0.9</td>
<td>2.3</td>
<td>1.2</td>
<td>1.4</td>
<td>1.8</td>
<td>1.4</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>C</td>
<td>3·10⁻³</td>
<td>3·10⁻³</td>
<td>3·10⁻³</td>
<td>3·10⁻³</td>
<td>3·10⁻³</td>
<td>3·10⁻³</td>
<td>3·10⁻³</td>
<td>3·10⁻³</td>
<td>3·10⁻³</td>
</tr>
</tbody>
</table>

4.11. Results and Discussion

4.11.1. Cs-137 measurements and erosion rates

Mean Cs-137 activity was 91 Bq·kg⁻¹ (RSD ± 24.3 %) for hayfields, 94 Bq·kg⁻¹ (RSD ± 9.0 %) for pasture without dwarf shrubs and 121 Bq·kg⁻¹ (RSD ± 15.05 %) for pasture with dwarf shrubs (Table 4-3). The reference sites in the Urseren Valley had a mean Cs-137 activity of 146.4 Bq·kg⁻¹ (RSD ± 13.3 %). The Cs-137 activity of each single plot was calculated by multiplication with the appropriate bulk density. For our sites a mean soil bulk density of 1195 kg·m⁻³ (RSD ± 13.7 %) was determined for the upper soil layer (0 – 10 cm) (Table 4-3). As over 90 % of the Cs-137 at our sites measured by in-situ spectrometry originates from the top 10 cm of the soil profile (Schaub et al., submitted), the estimated Cs-137 activities refer to this soil layer with a mass of 119.5 kg·m⁻² (RSD ± 13.7 %). Deviations of the measured Cs-137 activity from reference site values give a quantitative estimation for soil loss or gain through erosion. The total erosion estimated by Cs-137 measurements includes the cumulative erosion since 1986 (time after deposition of radioisotopes due to the Chernobyl reactor accident). Cs-137 input from atomic bomb tests in the early sixties had minor impacts on the Urseren Valley (Schaub et al., submitted). Therefore, a mean annual soil erosion rate can be estimated for the latter time period 1986 – 2007.

Average soil erosion rates of hayfields, pastures without dwarf shrubs and pastures with dwarf shrubs were 19.3, 18.3 and 7.1 t·ha⁻¹·a⁻¹ (Table 4-3). The similar values of hayfields and pastures without dwarf shrubs seem surprising, considering the larger visible degradation on pasture without dwarf shrubs as compared to hayfields. However, the variability of the hayfields (Table 4-3) is high and might be explained by
different fertilisation levels as well as different avalanche impact during winter time. The high value of hayfield hf1 (Table 4-3, Figure 4-9) could be due to fertilisation in late autumn just before snowfall. Decomposition of organic manure on the soil had not been completed or not even started before snowfall. Release of ammonia from dung with its detrimental effects in vegetation (Krupa, 2003) under the snow might explain the decreased vegetation cover after the winter. This has been observed during surveys in spring 2007 (Table 4-4). The latter results in high erosion susceptibility. A second reason for the high variability of erosion rates in hayfields might be the avalanche frequency which is high on the hayfield hf3 (Ambuehl, 1961). High avalanche frequency might cause higher erosion rates during winter time and early spring. In contrast, hayfield hf2, which is neither influenced by intensive manuring nor by avalanches, has low erosion rates. Hayfield hf2 and pasture with dwarf shrubs paw1 had similar erosion rates even though the fractional vegetation cover was significantly lower in pastures (77 % paw1) than in hayfields (92 % m2) (Table 4-4). The latter might be due to increased sedimentation by dwarf shrubs which stabilize the soil and act as physical barriers, thus reducing transport of soil particles downslope.

Table 4-3. Cs-137 activity, soil density and resulting erosion rates. The Cs-137 reference value is about 145 Bq·kg\(^{-1}\). Soil density is determined for the first 10 cm (*n = 3 soil samples*).

<table>
<thead>
<tr>
<th>grassland type</th>
<th>meadow</th>
<th>pasture without dwarf shrubs</th>
<th>pasture with dwarf shrubs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m1</td>
<td>m2</td>
<td>m3</td>
</tr>
<tr>
<td>Cs-137 [Bq·kg(^{-1})] (RSD %)</td>
<td>73.9 (1.3)</td>
<td>118.6 (2.4)</td>
<td>79.8 (11.1)</td>
</tr>
<tr>
<td>soil density* [kg·m(^{-3})]</td>
<td>1066</td>
<td>1044</td>
<td>1041</td>
</tr>
<tr>
<td>erosion rate [t·ha(^{-1}·a(^{-1})] (s.d. %)</td>
<td>25.4 (4.8)</td>
<td>9.4 (7.8)</td>
<td>23.3 (16.9)</td>
</tr>
</tbody>
</table>

Mean annual erosion rates of pastures without dwarf shrubs were almost three times higher than erosion rates on pastures with dwarf shrubs. Thus, dwarf shrubs seem to reduce sheet erosion considerably.

Overall, mean annual soil erosion rates up to 25 t·ha\(^{-1}·a\(^{-1}\) are high in comparison to published data and seem to be even higher than for many lowland arable regions. The measured values are 10 to 20 times higher than previous measurements in alpine grasslands (Bunza, 1989; Frankenberg & Eckert, 1994; Felix & Johannes, 1995; Hewitt, 1996; Mathys et al., 2005; Zuazo et al., 2006; Isselin-Nondedeu & Bédécarrats, 2007; McBroom et al., 2008). The previously low measured rates of erosion in alpine regions have been determined during summer time and are mostly results from short term irrigation experiments. In contrast, our measured erosion rates based on Cs-137 inventories included extreme events and winter processes of 22 years. Thus, snow
and avalanche activity is included and the likelihood to capture extreme events is much higher with our approach than with short term measurements and/or irrigation experiments. Therefore, the previous published general statement that erosion rates are low on alpine grasslands (e.g. Felix & Johannes, 1995; Mathys et al., 2005; Prasuhn et al., 2007) cannot be confirmed with our results. Furthermore, our high erosion rates up to > 25 t·ha\(^{-1}\)·a\(^{-1}\) are congruent with the high visible damages at the sites. The visible damages cannot not be compared with visible damages in arable field, where large gullies are visible. Moreover, large areas with low fractional vegetation cover and incoherent soil that is spread over large areas are visible. Due to air photographs of the last 20 years it can be excluded that our high erosion rates gained by Cs-137 based measurements arise from land slides.

<table>
<thead>
<tr>
<th>Table 4-4. Fractional vegetation cover of all plots in April and September 2007 (RSD 5 %, n = 3 times of vegetation cover determination of each plot).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>April</td>
</tr>
<tr>
<td>September</td>
</tr>
</tbody>
</table>

4.11.2. Erosion assessment with the USLE

Results of the USLE are in a similar order of magnitude compared to Cs-137 based erosion rates if uncertainty of methods is considered (Figure 4-9). Pastures without dwarf shrubs are in a similar range compared with Cs-137 based erosion rates. Erosion rates of hayfields 1 and 3 are underestimated by the USLE, whereas pastures with dwarf shrubs are overestimated by the model. The reason for the underestimation of the two hayfields might be the influence of manuring in late autumn and avalanches during winter time as discussed above. This might cause higher erosion rates that are not considered within the USLE. Because dwarf shrubs have a reducing effect to sheet erosion, the overestimation of the USLE erosion rates for pastures with dwarf shrubs might be explained. This reducing effect could be considered by adapting the C factor. The C factor is not accurately explained for different grasslands. Generally, the uncertainty of the C and the L x S factors is high. The range of the C factor is 2·10\(^{-3}\) to 4·10\(^{-3}\) (Auerswald & Schmidt, 1986; Van der Knijff et al., 2000; Prasuhn et al., 2007). The uncertainty of the L x S factor is more complicated to consider since the investigated slopes are not within the valid range. Hence, we expected the maximum deviation of the C-factor that results in a relative standard deviation (RSD) of +43 % to -53 %. The relative standard deviation due to the L x S factor can not be estimated. Consequently, the results of the Universal Soil Loss Equation have an uncertainty that can not be declared. Generally, applying the USLE to steep alpine regions seems not to be possible and should be avoided.
4.12. Conclusions

We determined mean annual soil erosion rates of steep alpine slopes of 5 – 21 t·ha\(^{-1}\)·a\(^{-1}\) which are about 10-20 times higher than previously reported. Our erosion rates were based on Cs-137 measurements and thus included winter processes as well as extreme rainfall events over the last 22 years. These high rates of erosion are concordant with the high visible soil degradation in the Urseren Valley and explain the low recover rates of degraded alpine sites. Erosion rates that are calculated with the Universal Soil Loss Equation are in the same order of magnitude and comparable to Cs-137 based erosion rates. However, the uncertainty of the results is not known since the slope steepness is not within the valid range and therefore not empirically ensured. Furthermore, slopes that might be affected by avalanches should not be calculated with the USLE as these processes are not defined. For the future it would be helpful to adapt C factors for alpine grasslands with different plant species as well as S factors for slopes steepness > 56 % (29.3 °). Hence, estimation of land use influence on erosion rates are known and soil conservation strategies can be designed for the future.

4.13. Acknowledgements

This work was financially supported by the State Secretariat for Education and Research (SER), in the framework of the European COST action no. 634: "On- and Off-site Environmental Impacts of Runoff and Erosion". The authors thank H. Surbeck from...
the University of Neuchâtel, Switzerland for the supply of gamma-analysis software to analyse the NaI spectra and S. Estier from the Federal Office of Public Health (FOPH) for her valuable support and discussion.
Methods to describe and predict soil erosion in mountain regions

Published in: Landscape & Urban Planning 88, 46-53, 2008
Authors: Alewell, C., Meusburger, K., Brodbeck, M. & Bänninger, D.
Environmental Geosciences, University of Basel

5.1. Abstract
Suitable methods to describe and predict soil degradation in mountain areas with low accessibility, steep topography and extreme climate are urgently needed for suitable planning processes in Alpine regions under global change regime. Aerial photograph mapping has been proven to be a valuable tool to survey landslide development over time. However, landslides < 10 m² as well as sheet erosion were difficult to detect. Thus, the beginning of potentially heavy soil degradation can not be tracked down with aerial photographs.

As an early warning system for soil degradation we analyzed gradients of carbon and nitrogen stable isotopes from upland (erosion source) to wetland soils (erosion sink). Oxic upland soils and anoxic wetlands differ in their isotopic signature, because aerobic and anaerobic metabolism yields in differing isotopic fingerprints of soils. Gradients of δ¹⁵N and δ¹³C in soils reflected erosion of material. However, if soils were fertilized with manure δ¹⁵N profiles were obscured.

To quantify soil erosion, we noted that existing soil erosion models are mostly not suitable for mountain regions. In a first step we developed a new modelling concept with a special algorithm for spatial discretization with irregular grids. The latter ensures three dimensional water flow routing which is controlled by topography and not by the underlying algorithm. Regarding quantification of soil erosion an improvement and validation of existing modelling approaches or development of new models is urgently needed.

5.2. Introduction
Mountain systems all over the world are unique in their ecology, economy and cultural diversity. However, the extreme topography and climate result in high
instability, fragility and sensitivity of these ecosystems (Gellrich & Zimmermann, 2007). Simultaneously, most mountain environments have been exploited by human society to a maximum (Lasanta et al., 2006) with serious degradation since the Middle Ages (Höchtl et al., 2005). Economic, societal and environmental changes are often an immediate threat to mountain systems and careful planning is needed (Höchtl et al., 2005; Lasanta et al., 2006). Transformation rates in the Swiss Alps are very diverse and the spatial and contextual specifics have to be considered (Schneeberger et al., 2007). Thus, methods to describe and predict ecosystem stability in mountain systems are urgently needed (Garcia-Ruiz et al., 1996; Lasanta et al., 2006). One inherent parameter of ecological stability is the status of soils in the ecosystems which affects ecosystem services like slope stability, water budgets (drinking water reservoirs as well as flood prevention), vegetation productivity, ecosystem biodiversity and nutrient production. First priority of most planning processes in Alpine grassland or arable systems is to reduce soil erosion risk (Garcia-Ruiz et al., 1996). Soil degradation is driven by environmental conditions as well as land management practices (Meusburger & Alewell, 2008). In the near future, soil degradation might be significantly increased by the combined effects of global climate and land use change (Beniston, 2006; Fuhrer et al., 2006). With the projection of further warming the duration of snow cover will be shortened by up to 100 days with earlier snowmelt in spring dependent on region and altitude (Jasper et al., 2004; Beniston, 2006; Horton et al., 2006). In Europe, raising snowline, intensified precipitation during the winter as well as strong leaching effects with no or sparse vegetation cover in late fall and early spring will result in an increase in erosion especially in the northern (mainly north-western) Alps (Fuhrer et al., 2006). Nevertheless, increased erosion is also likely in the southern Alps where extreme droughts will be followed by rain events of increased intensity (Schmidli & Frei, 2005; Brunetti et al., 2006).

In addition to changes connected with global climate change, European mountain systems have been confronted with a substantial change in land use management during the last decades (Lasanta et al., 2006; Gellrich & Zimmermann, 2007; Schneeberger et al., 2007). Since the late 19th century the forested area is increasing because reforestation was promoted for flood protection and erosion control or because of the abandonment of agricultural sites (BFS, 2001; Descroix & Mathys, 2003; Piégay et al., 2004; Lasanta et al., 2006; Tasser et al., 2007). Simultaneously, remaining farm land is managed with increased intensity (Meusburger & Alewell, 2008). In the Swiss High Alps, livestock size has increased from 200'000 to 420'000 sheep during the last 40 years (Troxler et al., 2004). Furthermore, permanent shepherding of cattle and sheep has mostly been abandoned since 1950 and replaced by uncontrolled grazing. The latter resulted in a significantly higher grazing intensity at high alpine meadows (Troxler et al., 2004). Thus, destabilising effects on soils can be expected by changes in animal farming practice. In contrast, studies in the Mediterranean mountains like the Spanish Pyrenees state a re-vegetation of lower and medium slopes with shrubs due to land abandonment (Lasanta et al., 2006). Planning tools were developed in these areas to support vegetation clearing
to maintain a productive landscape and revitalize the economy. However, the latter was accompanied by an increase in soil erosion risk (Lasanta et al., 2006). Regarding land use change, it is not yet clear whether we can expect a reduced erosion risk due to reforestation or erosion risk increases due to land use intensification of remaining pastures. Generally, the combined effects of climate and land use change are predicted to increase future soil erosion in Alpine regions (OCC/ProClim-, 2007). Modelled estimations of sediment delivery to the river Rhine from alpine regions resulted in more than a 200 % increase by the year 2100 (Asselman et al., 2003). Because of the high degree of uncertainty connected to estimating soil erosion in mountainous regions, the demand for methods to describe and predict erosion of alpine soils from small to large scale has been put forward (Asselman et al., 2003). This need for method development suitable for Alpine systems has already been proposed 15 years ago (Lange, 1994) and planning tools have been developed in the mean time (Lange, 1994; Höchtl et al., 2005; Lasanta et al., 2006; Schneeberger et al., 2007). However, we still lack methods to describe and predict change of alpine ecosystem stability and degradation.

Here, we present an interdisciplinary approach of the combination of new methods to describe and predict soil degradation of mountainous soils qualitatively and quantitatively with special emphasis on tools for inaccessible or difficult to access regions with low infrastructure. We chose the Urseren Valley (Canton Uri, Switzerland) as our study area, where the relevance of farming and the numbers of farmers gradually decreased during the last decades and "the traditional principles of land use are dissolving" (Kaegi, 1973).

5.3. Site description

The catchment of the Furkareuss (80 km², 1400 - 2500 m a.s.l.) is located in the Urseren Valley (Canton Uri, Switzerland; Figure 5-1). The valley corresponds to a fault line that separates the gneiss massif of the Gotthard system to the south from the granite massif and the pre-existing basement (named “Altkristallin by Labhart, 1999) of the Aare system in the north. Intermediate layers consist of Permocarbonic and Mesozoic sediments (Labhart, 1999). The Mesozoic sequences include rauhwacke (Triassic), sandy marble and sandy-schistous marble, calcareous quartzite (Lias), dark clayey schist and quartz schist (Dogger), marble (Callovian-Oxfordian), coprolite and dark schist (Malm) (Wyss, 1986). The whole sequence was deformed at compressive conditions during the Tertiary (for a detailed discussion of the geology of the region see Wyss, 1986). Weathering of the calcareous material produced clay-rich soils that are prone to landslides and weathering of the silicate schist yields silty soils prone to sheet erosion (Figure 5-2). On the valley slopes, quaternary moraines and scree deposits are very common and consist mainly of siliceous loamy gravel material.
Dominant soil types of the catchment classified after WRB (2006) are Podsols, Podzocambisols and Cambisols, partly with stagnic properties. Above 2000 m a.s.l. and on steep valley slopes, Leptosols are common (with rendzic Leptosols on the calcareous substrate). At the valley bottom, clayey gleyic Luvisols and Gleysols developed.

The valley is characterized by a high mountain climate with a mean air temperature of 3.1 °C. Mean annual rainfall at the meteorological station in Andermatt of MeteoSchweiz located at the outlet of the valley (8° 35' / 46° 38'; 1442 m a.s.l.) is about 1400 mm with maximum in October and minimum in February. The valley is typically snow covered for 5 – 6 month (from November to April) with maximum snow depth in March. Runoff is usually dominated by snowmelt in May and June, with maximum in June. Summer and early autumn floods represent an important contribution to the flow regime (BAFU, 2007).

The four main land cover types are (i) alpine grasslands and dwarf-shrubs (64 %), (ii) scree (16 %), (iii) shrubs (7 %) and (iv) bare rock at higher elevations (11 %) (Meusburger & Alewell, 2008). Urban areas and forests cover less then 1 % of the valley (70 % of the forest was cultivated for avalanche protection above the villages). Natural vegetation is strongly influenced by anthropogenic land use due to

Land use in the Urseren Valley is dominated by pasturing. The property of the land is divided between the Korporation Urseren and private owners. The alp areas belonging to the Korporation Urseren are traditionally used as summer pastures. The private land serves as hay meadows to feed the cattle during the winter month.

5.4. Methods to quantify soil erosion over time

Environmental characteristics of ecosystems are one inherent driver of soil erosion and mass movement (Carrara et al., 1991; Guzzetti et al., 1999). To assess the contribution of catchment characteristics to soil degradation in the Urseren Valley, landslide densities for variable catchment characteristics were calculated (Suezen & Doyuran, 2004). Landslide densities are calculated according to:

\[
D_i = \frac{SX_i}{X_i} \times 100 \times \sum_{k=1}^{n} \frac{X_{i=k}}{SX_{i=k}}
\]

in which \(D_i\) = landslide density for a variable class, \(SX_i\) = number of pixels with landslides within a variable class, \(X_i\) = number of pixels within a variable class and \(n\) = number of variable classes. To ease the comparability between landslide densities of different classes a normalisation with the sum of landslide densities for all classes was done.

To assess the development over time within the Urseren Valley, we used aerial photograph interpretation. A geographic information system (ArcDesktop 9.1, ESRI, Zürich, Switzerland) was used to collect, superimpose and analyse the spatial data layers. Landslides were mapped by visually vectorising the affected area from aerial photographs. Photographs of 1959 and 2004 were selected from a serial of aerial photographs that are available at Swisstopo (BA071108) with a scale of at least 1:12'000. In order to allow for the local comparison of the individual landslides between different years the photographs were georeferenced and orthorectified using the ENVI software package (Version 4.0) with the help of ground control points, the DEM and the camera calibration protocol supplied by Swisstopo (BA071108).

Field verification was done in spring 2005 to check the inventory map produced by aerial photograph interpretation (comparison of photos from autumn 2004). During these field surveys, 8 landslides were investigated in more detail to assess the accuracy of the GIS mapping method. The areas of those 8 landslides determined during the field survey were compared with the corresponding areas achieved by photo interpretation. The latter resulted in an error of ± 10 %. 
There is no doubt that the instable geology of the south facing slopes in the Urseren Valley, as well as the steepness of the slopes, is significantly influencing slope instability (Figure 5-3a). Erosion peaked at slopes of $35 - 40^\circ$ (note that the lower rates of erosion with slopes $> 45^\circ$ are most likely due to thin soil development and low land use pressure). Furthermore, instable bedrock of the Mesozoic layer was connected to high erosion rates in the catchment (Figure 5-3b) and hydrology plays a crucial role because subsurface and return flow within the Mesozoic schists seems to trigger landslides (Meusburger & Alewell, 2008). However, if environmental characteristics like geology, geomorphology and/or hydrology would be the only or the main driving factors of soil erosion, we would not expect a trend over time. Thus, determining soil erosion over time is not only crucial for assessing the development of ecosystem stability but can also help us with the analysis of cause–effect relationships which is important for planning processes in fragile systems like Alpine grasslands.

Aerial photographs of the Urseren Valley demonstrate that we have a strong increase of landslides and sheet erosion over the last 45 years (Figure 5-4). The aerial extent of the smallest landslide observable in the catchment in the 1959 photograph is approximately 10 m² and the largest landslide is about 7000 m². Landslides with a minimum area of 25 m² can be accurately digitized from aerial photographs. In 2004, 383 landslides ($> 25$ m²) with an area of 9.42 ha and a mean size of 250 m² were mapped (for a typical landslide see Figure 5-2). The eroded area in the catchment increased between 1959 and 2004 by 92%. The causes of this increase are mostly an effect of land use change (increase in intensity as well as change in management practice) but might also be triggered by climate change (Meusburger & Alewell, 2008). One effect of the latter is the dramatic increase of intensity of three day rain events from 200 mm in the seventies to 270 mm today. Prolonged rain events over more than 3 days are known to decrease soil stability and trigger landslide activity. One disadvantage of erosion mapping with aerial photographs is that the beginning of erosion (e.g., landslides $< 10$ m², initial forms of sheet erosion) can not be detected and accurate mapping is only possible with landslides $\geq 25$ m². The latter is crucial,
because the extreme climate and topography in mountain regions sets the pre-
conditions for self-energizing events: once erosion has started and stability of the
slopes decreased, destabilization of slopes will accelerate. Thus, in mountain systems
it is crucial to develop methods to detect the first signs of erosion or even detect
erosion before it is visibly seen. The strong increase in slope instabilities in the last
decades stresses the need for an early warning system of soil erosion and an
implementation of these tools into planning processes.

Figure 5-4. Sub-images of aerial photographs in the Urseren Valley (Swisstopo, 2006).

5.5. Methods to describe early stage soil erosion

The influence of soil erosion, weathering and sedimentation to wetlands and
groundwater has often been investigated with radioactive isotope tracers like $^{137}$Cs
or $^7$Be (for an overview see Walling et al., 1999; Matisoff et al., 2002; Zapata, 2003).
Both tracers are deposited from the atmosphere and a soil inventory of these
isotopes that is less than the reference value (soil without erosion) is assumed to
indicate erosion whereas an inventory greater than the reference value provides
evidence of deposition. The assumed prerequisites are homogenous distribution
within the catchment and strong bounding of the tracer to soil particles. The first
assumption is not always given and might cause problems in data interpretation. The
half-life time of $^7$Be is 54 days, thus $^7$Be is only suitable for short term investigations.
With the half-life time of $^{137}$Cs (30.2 years) longer term investigations are possible;
however, the latest source for atmospheric $^{137}$Cs fallout has been the Chernobyl
accident in 1986. Thus, for regions with low $^{137}$Cs deposition time for using $^{137}$Cs as
erosion tracer is already running out.

A new tool to detect soil erosion has to be developed. Stable carbon isotopes ($^{13}$C)
have been used to track down changes in geomorphology coupled to changes
from C3 to C4 vegetation (Buck & Monger, 1999; Gibbs et al., 2001). Papanicolaou et
al. (2003) used stable carbon and nitrogen signature to track down the origin (forest
versus crops soils) of river sediments within catchments. They found differences
between sediments from irrigated versus unirrigated crop soils but not between forest
and crop soils (Papanicolaou et al., 2003). In a review done by Amundson et al.
(2003) it has been shown that $\delta^{15}$N values of soils are dependent on soil age and soil
slope. Soil age is correlated to the degree of steady state and the kinetics of N cycling. For soil slope it has been shown that steeply sloping soils have low residence times. Thus, Amundson et al. (2003) postulated that because steeply sloping soils are far from steady state they have lower δ¹⁵N values that approach atmospheric input. In addition to soil age and soil rejuvenation topographic position plays indirectly a key role in isotopic signature of elements, because dissimilatory reduction processes in lowland or wetland anaerobic soils cause significant shifts in carbon, nitrogen and sulphur isotopes (Krouse & Grinenko, 1991; Kendall, 1998; Wang et al., 1998). The latter is most likely due to the lower energy efficiency of dissimilatory processes and the slower reduction rates. Low reduction rates are known to cause a greater discrimination of the heavier isotopes and thus a greater fractionation between isotope ratios of substrate and product (Krouse & Grinenko, 1991). Stable sulphur isotopes have been shown to give a historic fingerprint of prevailing metabolism (aerobic or anaerobic) over time (Alewell & Novak, 2001). Upland soils, which are dominated by assimilatory reduction processes, can generally be expected to have distinctively different isotopes signatures than associated wetlands and water bodies. The latter has been shown for sulphur (Morgan, 1995; Alewell & Gehre, 1999; Alewell & Novak, 2001) but not yet for nitrogen or carbon isotope dynamics.

We determined transects in stable isotopes from upland soils (oxic environment and erosion source) to lowlands (pre-dominantly anoxic environments and sink of erosion material, Figure 5-5). A second site, the Seebodenalp (near Küsnacht am Rigi, Switzerland; for site description see Rogiers et al., 2005) was investigated for method validation. Soil profiles were taken with a core sampler at five sampling points per site and transported to the laboratory where they were stored in a refrigerator at approximately 4 °C until further processing. Samples were 2 mm sieved, dried at 40 °C for 3 days and ground using a WC-swing grinder. Inorganic carbon was removed by acid fumigation following the method of Harris et al. (2001). Stable carbon and nitrogen isotope analyses were accomplished on a mass spectrometer (Thermo Finnigan Delta plus XP) coupled with an elemental analyzer (Flash EA 1112 Series).

![Figure 5-5. Fingerprint hypothesis of soil degradation: if soil erosion from upland A is influencing wetland B significantly, stable isotope signature of B should differ from undisturbed wetland C.](image)

Stable carbon isotopes in the upper mineral soil (0 – 15 cm) were significantly different between upland soils in the catchment and undisturbed wetlands (wetland C; Figure 5-6a). At the Urseren Valley, the wetland influenced by erosion processes (wetland B) had a mean δ¹³C signature of -27.51 ± 0.47 ‰, which was
between the upland ($\delta^{13}C = -26.62 \pm 0.60 \%o$) and the undisturbed wetland C ($\delta^{13}C = -28.29 \pm 0.59 \%o$). However, the difference between upland and wetland $\delta^{13}C$ signature was only minor. At some of the sites in the Urseren Valley, erosion features were visibly detectable (e.g. eroded areas at the upland and/or sediment layers at the wetland). At other sites, no such geomorphic difference was detectable. The difference between $\delta^{13}C$ of the upland ($-27.67 \pm 0.40 \%o$) and the undisturbed wetland C ($-28.33 \pm 0.23 \%o$) at Seebodenalp was even smaller but still significant. The latter site showed no visible soil erosion (e.g. sediment layers in the wetland B or visible detectable eroded areas at the upland site), but cattle trails and steep slopes on the upland site make leaching of soil and organic material into the wetland B very likely. $\delta^{13}C$ signature of the wetland B ($-28.15 \pm 0.25 \%o$) was again between the upland site and the undisturbed wetland C. Thus, at both sites, $\delta^{13}C$ seems to be a possible tracer for soil erosion processes, but the difference between $\delta^{13}C$ signature of upland and wetland soils was rather small.

**Figure 5-6.** Stable isotopes of carbon and nitrogen for the upland soils A (erosion source), wetlands B (erosion sink) and undisturbed wetlands C. Boxplots indicate medians, 10-, 25-, 75- and 90-percentiles. • = outliers.

Stable isotopes of nitrogen were also significantly different between upland site and undisturbed wetland C at the site Seebodenalp (Figure 5-6d). Confirming the results of the $\delta^{13}C$ values, $\delta^{15}N$ of the wetland B ($+0.59 \pm 0.46 \%o$) was very similar to $\delta^{15}N$
values to the upland soil (+0.75 ± 0.75 ‰), while δ^{15}N of the undisturbed wetland C was significantly different (-1.08 ± 0.35 ‰). Thus, influence by nitrogen leaching and erosion from the upland soil to wetland B is very likely at this site. δ^{15}N profiles at the Urseren Valley did not show the expected results. Median δ^{15}N values of all three sites were very similar. Farmyard manure (δ^{15}N = +5.80 ± 1.24 ‰) is used very intensively in the Urseren Valley at most of the pastures and meadows including our sampling sites. The influence of the organic N from the manure generally increases δ^{15}N signature of the soils and obviously obscured any differences between upland and wetland sites in the Urseren Valley.

In summary, stable isotopes of carbon and nitrogen seem to be a suitable tool to track qualitatively early stage soil erosion and may thus be a promising method for future planning processes. However, stable isotopes are not suitable for quantitative description of erosion rates.

5.6. New concepts for soil erosion modelling in mountain areas

Distributed physically and empirically based models have been applied to soil erosion quantification in several nations in Europe (De Jong et al., 1999; Millward & Mersey, 1999; Van der Knijff et al., 2000; Jetten et al., 2003; Van Rompaey et al., 2003; Van-Camp et al., 2004). Distributed models reflect the spatial variability of processes and outputs in the catchment. They explicitly calculate soil erosion rates within a given landscape and thus provide a more realistic model output than lumped models (Van Rompaey et al., 2001). A sound conceptual soil erosion model is the PESERA. However, it has not been validated for mountain regions yet and comparisons to other models show for Mediterranean regions that PESERA underestimates the erosion rate significantly (De Vente et al., 2008). Generally, major discrepancies between calculated soil erosion and measured erosion were found in mountain watersheds because models were mainly designed for agricultural environment (Van Rompaey et al., 2003). The extreme topography and climate in mountain regions often cause spatially explicit soil erosion models to fail. Thus, existing models generally have to be modified for applications in mountainous terrain.

We believe that the process of erosion should generally be separated in two sub-processes: detachment and transport. While detachment is mainly dependent on soil texture, soil structure, soil cover, vegetation cover and kinetic energy of contacting water (rain drop and surface flow), transport is dependent on surface water flow, topography and soil cover. Separating the two sub-processes allows for a more accurate description and sensitivity analysis of crucial input parameters.

To our understanding, one major problem within the algorithms of existing erosion models is the calculation of transport processes, especially of the water flow routing in mountainous terrain with steep slopes. Within the PESERA model (Van Rompaey et al., 2003) the environmental properties are defined for each grid cell and erosion rates are estimated separately for each grid cell. Mass transfer towards other grid
cells is not calculated. Thus, with this model it is not possible to route mass transport on a hill slope. The physically based WEPP model (Nearing et al., 1989) calculates erosion rates from hill slope profiles but does not consider the three-dimensional spatial extension of the real earth surface. Thus, it is only partly possible to capture influences of the micro-topology on soil erosion (e.g., return flow, which often triggers soil erosion). The soil erosion model LISEM (De Roo & Jetten, 1999) describes the site of interest by a regular gridded digital elevation model and water flow routing is calculated with the D8 algorithm. The D8 algorithm searches for the neighbouring cell with the lowest altitude, to which the water is then routed. Water flow routing with D8 works fine for plane hill slopes, but is generally a weak description for the hydrology of undulating hill slopes because this algorithm routes the water preferentially in directions of multiples of 45 ° (Figure 5-7a). The latter is improved within the model Erosion3D (Schmidt et al., 1999) by using an algorithm which weights the outflow to its neighbouring cells according to the altitude difference. However, directions of water flow routing are still not regulated by multi directional topography but by the possible directions of the underlying algorithm. Thus, new concepts for water flow routing are needed to improve existing approaches.

In a first step we propose two new approaches: (1) spatial discretisation is commonly done by taking regular grids. We propose to use triangulated irregular grids because they have the advantage that small-scaled regions (e.g., transitions from hill slope to bottom of a valley) can be discretised by a finer grid resolution than large-scaled regions (e.g., bottom of a valley). Shape and size of the irregular triangular grids have to be optimized according to the given heterogeneity of the digital elevation model. (2) Algorithms like D8 and multiple-direction flows based on slopes are often used but are physically imprecise because of the limited number of possible water flow directions (Tarboton, 1997; Figure 5-7 a). The results of D8 algorithm are moderate for regular and weak for irregular grids. Thus, using irregular grids – which is favourable for efficient space description – asks for an accurate water flow routing algorithm. We developed a new algorithm for regular and irregular grids which routes the water depending on any topography physically correct within the given grid resolution (Bänninger, 2007; Figure 5-7 b).

Current modeling approaches of water flow routing can be improved significantly with the described modeling approach. To describe sediment loads and its transport mechanism in space it remains to develop new concepts in the same way we did it for water flow routing. This includes the detachment and transport processes of soil particles. Regarding planning processes ecosystem research and planning is still in need for a suitable model to describe and predict soil erosion processes quantitatively in Alpine systems.
5.7. Conclusions

Because mountain areas are mostly remote regions and difficult to access, the classical survey of soil erosion is connected to high efforts in labour, time and costs. Remote sensing can overcome these difficulties and aerial photographs have been shown to be a suitable tool to measure soil erosion over time. We were able to track down landslides ≥ 10 m² and heavy cattle trail erosion with aerial photography. Landslides ≥ 25 m² can be mapped accurately. However, smaller landslides which are often the start of steadily or event based growing degradation can not be identified. Furthermore, sheet erosion can not be detected. Thus, for careful planning processes new techniques in remote sensing are required for future mapping of soil degradation in mountainous regions.

Stable isotopes of carbon and nitrogen seem to be suitable as an early warning system for soil erosion in mountain areas on a plot scale, if transects from upland (erosion source) to wetland soils (erosion sink) are investigated. The method is a retrospective qualitative estimate of erosion. Erosion can be detected based on a single site visit, where spatially distributed information for individual points in the landscape can be assembled. The advantage of the method is its sensitivity, because carbon and nitrogen isotopic fingerprints reflect the displacement of organic matter. Thus, the technique might track down erosion processes before they are visibly seen. The technique might become a promising future tool for planning processes in mountain areas prone to erosion if transects from upland oxic to wetland anoxic soils are available for investigation. However, the difference in δ^{13}C signature between erosion sources and sinks was relatively small, so careful planning of sampling design and sufficient replications (n ≥ 5) have to be taken into account. Stable nitrogen isotopes are not applicable at sites with manure application because δ^{15}N signals of soils will be equalized by organic fertilizer addition.

To quantify soil erosion in mountainous regions improvement of existing modelling is needed. We presented an algorithm which calculates water flow routing and
transport in multiple directions on irregular grids. The latter ensures dependency of the water routing and transport processes on topography and not on the possible flow directions of the underlying algorithm which is often the case in existing modelling approaches. Similar improvements have to be done in the future for all other processes involved in erosion charge generation (e.g., detachment and transport of soil particles). There is no doubt that modelling is the ultimate tool for comprehensive planning processes in mountain regions. However, future work on model development is clearly needed which might include improvement and validation of existing models as well as developing entirely new modelling approaches as we discussed in this study.

5.8. Acknowledgement

This study was partly founded by the Swiss National Found (200021-105579) and by the Swiss Federal Office for the Environment.
Final remarks & Outlook

Soil erosion is a serious problem in mountain ecosystems. In order to have a better understanding of soil degradation processes and the extent new approaches are needed for detection and quantification of soil erosion. In this study we investigated the suitability of stable and radiogenic isotopes for tracing soil erosion at steep mountain slopes. One focus of the study was a methodological approach adapting methods for their use in mountainous regions. The second focus was a test of suitability of stable and radiogenic isotopes as tracers for soil erosion.

6.1. Methodological approach

Cs-137 gamma spectrometry is commonly used for soil erosion measurements but mostly in lowlands. In order to adapt the method to mountainous environments an in-situ NaI detector was tested for its suitability for Cs-137 measurements at steep alpine slopes. Our comparison of Cs-137 measurements from the laboratory and in-situ measurements at the same site in the Urseren Valley shows that despite the big heterogeneity in Cs-137 distribution both methods achieve similar mean Cs-137 activities. This means that in-situ measurements are suitable for erosion application in high alpine environments. Thus, Cs-137 measurements can provide reference data to back up stable isotope data.

Further, a method for δ18O measurements of soil using TC/EA was developed. The ideal pyrolysis temperature at which standard materials and soils are pyrolysed completely was estimated. At this temperature (1325 °C), subsequently, standard materials, soil components and a series of soil samples from the Urseren Valley were measured. A gradient towards increasing δ18O in isotopic signatures from phyllosilicates of bedrock samples to upland and wetland soils to vegetation was found indicating that soil δ18O signature is the result of mixing of components with varying δ18O signatures.

6.2. Erosion measurements

We tested the suitability of stable isotopes of carbon, nitrogen and oxygen for tracing soil erosion in transects from upland to wetland soils as they often occur in
alpine environments. All studied elements meet the prerequisite of differing stable isotopic signatures for upland and wetland soils for soil erosion tracing in transects from uplands to wetlands. Hence, they can theoretically be used for soil erosion measurements. However, manure application had a strong influence on δ^{15}N signature of soils obscuring differences between soil types. As most sites in the Urseren Valley are manured, δ^{15}N could not be used for erosion detection there. As a result of soil erosion impact a mixed signature between typical upland and wetland soil signatures was found for wetlands beneath uplands with soil erosion damages, both for δ^{13}C as well as for δ^{18}O. However, as δ^{18}O measurements are only the first results of a new method no definite conclusion for its suitability for soil erosion measurements can be given. In order to back up our δ^{18}O data there is still need for further investigation. In the Urseren Valley Cs-137 measurements could confirm erosion activities estimated by δ^{13}C and δ^{18}O measurements. For carbon it was even possible to distinguish between short- and long-term soil erosion influences. To conclude, δ^{13}C, δ^{18}O (and δ^{15}N at unmanured sites) are promising tracers for soil erosion in the Urseren Valley.

6.3. Outlook

It could be shown that stable and radiogenic isotopes are suitable for soil erosion detection in the Urseren Valley. It remains to transfer these methods to other alpine environments.

Stable isotopes of carbon and nitrogen have shown to give information about the behaviour of organic matter during soil erosion while δ^{18}O reflects changes in bulk soil composition. If only minerals but no organic matter are redistributed during soil erosion, an effect should be visible in the δ^{18}O signature of the influenced wetland but δ^{13}C and δ^{15}N should not be affected. To have a complete overview over all soil components and in order to understand the dynamics of soil erosion better, it is crucial to also have a look at minerals redistributed over the landscape by soil erosion. By comparing the influence of input of eroded material on δ^{13}C, δ^{15}N, δ^{18}O and mineral composition in the wetland evidence might be given whether organic or mineral constituents are preferentially eroded.

The simultaneous analysis of gradients in minerals (phyllosilicates, quartz, feldspars) along the toposequences might be used as a backup to detect mineral influences on organically dominated wetlands. The composition of clay minerals in soils is dependent on bedrock, conditions during bedrock formation and degree of soil development. Clay minerals in soils from clay-free bedrocks are of pedogenic origin (acid magmatites -> illite, vermiculite; basic magmatites -> smectite) while soils of sedimentary bedrocks are dominated by the primary clay minerals of the bedrock. Topography is a factor contributing to translocation of mineral compounds as the direction of waterflow is not only vertical but also downslope. This flow results in a lateral transfer of minerals from higher parts of the slope, which gets depleted, to
lower parts where minerals are accumulated. Mobility of clay minerals in soils is often attributed to fine clays. Our aim within a current master thesis (B. Probst) is (i) to quantify the amount of minerals translocated by erosion as well as (ii) to determine the quality and type of minerals preferentially eroded.

Knowing the behaviour of organic matter and mineral components of the soil and simultaneous quantification of soil erosion with Cs-137 might enable a modelling of soil erosion processes over time. This would be a big step in the direction of developing an early warning system of soil erosion for alpine environments which, in future, could help avoid damages.


Beniston, M. 2006. Mountain weather and climate: A general overview and a focus on climatic change in the Alps. *Hydrobiologica*, **562**: 3-16.


OcCC/ProClim- 2007. Klimaänderungen und die Schweiz 2050 - Erwartete Auswirkungen auf Umwelt, Gesellschaft und Wirtschaft. OcCC/ProClim-.


Upland sites generally show a shift towards heavier $\delta^{15}N$ values with depth (except Spissen AAA and Laui A). Increasing $\delta^{15}N$ with depth is typical for mineralisation processes in the soil (e.g. Balesdent et al., 1993, Chen et al., 2002, Novak et al., 2003), because of preferential release of the lighter isotope during decomposition. Relatively heavy stable nitrogen isotope signals are reported for the transects Spissen AA, AAA, Bielen AA and Laui A, all of which are treated with farmyard manure. A significant influence of manure on stable nitrogen isotope compositions resulting in heavier signals than comparable unfertilized soils has been reported before (e.g. Riga et al., 1971; Bol et al., 2005).
Increasing δ¹⁵N values with depth are reported for all wetland sites (except Ob. Moos C which shows a great variability in δ¹⁵N signals). The wetlands Spissen B and Bielen B situated at the foot of the hillslope show a similarity in depth profiles to the upland transects (compare Spissen B with Spissen AAA and Bielen B with Bielen AA). The latter is most likely reflecting the long-term influence of eroded and/or leached material from the upland slopes.
δ¹³C/ δ¹⁵N/ δ³⁴S - Seebodenalp

Stable carbon isotope depth profiles are very similar for upland and for wetland sites, both in range of values as well as in gradients. Thus, there is no evidence for an effect of soil degradation on soil δ¹³C values at Seebodenalp.

Upland soils show an overall increase in δ¹⁵N with depth. For the two wetland sites different δ¹⁵N depth profiles were determined. Stable nitrogen isotope composition of the wetland site unaffected by erosion (C) gets heavier with depth, which is similar to the upland transect, but values are generally lighter. The lighter isotopic values in wetland sites are mainly due to badly or not decomposed organic matter. In contrast, the two top horizons of transect B (erosion sink area) are shifted towards heavier values, thus obscuring a clear depth profile. The latter is interpreted as a mixed signal of upland and wetland material indicating the influence of erosion on the upland site to the wetland beneath.
Alewell & Novak (2001) have shown that stable isotopes of sulphur in organic material in wetlands is significantly lighter than in uplands because of the discrimination of $^{34}$S during dissimilatory sulphate reduction. Positive $\delta^{34}$S values are recorded both, for the upland soil (A) and for the reference wetland (C). Generally wetland soils are expected to have $\delta^{34}$S values significantly lighter than uplands (Alewell & Novak, 2001). However, the anomalous values for the reference wetland may be due to samples taken too close to a drainage system. Alewell & Novak (2001) describe analogue to our observations $\delta^{34}$S depth profiles similar to those of uplands for drained wetlands. The wetland influenced by erosion (B) has more negative $\delta^{34}$S values for the upper two organic horizons than the upland. No influence of the drainage is observed here. The increasing $\delta^{34}$S with depth of the upland and the lower mineral soil horizons of the wetland sites might be explained by fractionation during mineralisation.
Da alle Personen, an die sich dieser Dank richtet deutsch verstehen, verfasse ich diesen Text auf deutsch. [Please find a short English version below.]

Danke…

… Christine Alewell, dass ich diese spannende und phantasievolle Projektidee bearbeiten durfte. Es war wie mit einem Überraschungsei – Spannung, Spass und Isotope!

… Rolf Siegwolf (PSI) für die Übernahme des Korreferats und die Diskussion der Sauerstoff-Daten. Für letzteres möchte ich natürlich auch Matthias Saurer (PSI) danken!


… Bärbel für die Hilfe bei all meinen Isotopenmessungen. Was auch bei meinen Messungen am Gerät kaputt gegangen ist, sie konnte es immer reparieren.

… Claude, Heinz, Heidi für Eure Unterstützung bei labor-, mess- und allen anderen technischen Problemen.

… Katrin & Nadine für die gute Zusammenarbeit und dafür, dass ich fast nie alleine im verlassenen Urserental sitzen musste.

… Thomas dafür, dass er es so lang mit mir im selben Büro ausgehalten hat, und für die harte Konkurrenz bei der Ski Challenge.

… der ganzen UGW-Gruppe für vier Jahre lang unterhaltsame und produktive Pausen…

English version:
I would like to thank everybody who actively or passively contributed to the development of this PhD-thesis.
**Monika Schaub-Brodbeck**

born on 16 January 1979 in Basel, Switzerland

**Education**

<table>
<thead>
<tr>
<th>Year</th>
<th>Education</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986 – 1990</td>
<td>Primarschule, Basel, Switzerland</td>
</tr>
<tr>
<td>1990 – 1998</td>
<td>Gymnasium, Basel, Switzerland</td>
</tr>
<tr>
<td>1998 – 2004</td>
<td>Diploma student in Earth Sciences, University of Basel, Switzerland</td>
</tr>
<tr>
<td>2004 – 2008</td>
<td>PhD student in Geosciences, University of Basel, Switzerland</td>
</tr>
</tbody>
</table>