Design of Watershed Based Water Quality Monitoring

The Case of Nitrate Pollution in the Aconcagua River, Chile

Dissertation

Zur Erlangung des akademischen Grades Doctor rerum naturalium
(Dr. rer. nat.)

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von Diplom Chemiker Lars Ribbe (M.Eng.)
geboren am 28.06.1968 in Bremen

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Gutachter:

1. Prof. Dr. Wolfgang Albert Flügel (Friedrich-Schiller-Universität Jena)
----
2. Prof. Dr. Hartmut Gaese (Fachhochschule Köln)

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Preface

The research which led to the present dissertation has been realized between 2004 and 2007 under the umbrella of the university cooperation between the Catholic University of Valparaíso, Chile and Cologne University of Applied Sciences, Germany. Both universities provided valuable support in terms of funding and personnel to render the research possible. In addition, the support of the German Ministry of Education and Science (BMBF) is appreciated as they provided support to the project for mobility and consumables. In particular, I would like to thank Prof. Dr. Hartmut Gaese for his incessant personal and institutional support and Prof. Dr. Eduardo Salgado for the invaluable help on the Chilean side throughout the study.

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In addition, there are other institutions and persons that generously supported the field work, above all the Chilean Water Service (DGA). DGA-Santiago provided the bulk of the required data on hydrology, water quality and GIS. The regional DGA in Quillota supported the sampling in the Pocochay sub-watershed. Personally, I would like to thank Mesenia Atenas, Monica Pardo, Cristian Nuñez and Francisco Riestra (Department of Water Conservation and Protection) and Ana Maria Gangas, María Angélica Alegría and Victoria Pozo (Department of Studies) for their kind support and advice.

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List of Acronyms

AIDIS	Adaptive Integrated Data Information System
AMC	Antecedent Moisture Condition
CIREN	Centro de Información sobre Recursos Naturales (Center for Information on Natural Resources, Chile)
CN	Curve Number
CONAF	Comisión Nacional Forestal (National Forest Commission)
CONAMA	Comisión Nacional del Medio Ambiente (National Commission for the Environment, Chile)
CSP	Critical Sampling Point
DEM	Digital Elevation Model
DGA	Dirección General de Aguas (National Water Service)
DGHM	Department of Geoinformatics, Hydrology and Modelling (FSU Jena)
DHI	Danish Hydraulic Institute
DIRECTEMAR	Dirección General del Territorio Marítimo y Marina Mercante (General Directorate for the Marine Territory and Trade)
DWW	Domestic Waste Water
EMC	Event Mean Concentration
ENSO	El Niño Southern Oscillation
EPA	Environmental Protection Agency, USA
FAO	Food and Agriculture Organization
FSU	Friedrich-Schiller-University (Jena)
GDP	Gross Domestic Product
GIS	Geographic Information System
GIWR	Gross Irrigation Water Requirement
HEC-HMS	Hydrologic Engineering Center - Hydrologic Modelling System
INE	Instituto Nacional de Estadísticas
IWR	Irrigation Water Requirement
IWRM	Integrated Water Resources Management
MINSAL	Ministerio de Salud (Ministry of Health, Chile)
MOP	Ministerio de Obras Públicas (Ministry of Public Works, Chile)
N	Nitrogen
NAWQUA	National Water Quality Assessment Program
NIWR	Net Irrigation Water Requirement
PDF	Probability Density Function
SAG	Servicio Agrícola y Ganadero (Agricultural and Cattle Farming Service)
SCS	Soil Conservation Service (USA)
SISS	Superintendencia de Servicios Sanitarios (Nacional Sanitation Control Agency)
SSP	Servicios de Salud Pública (Public Health Service)
SWAT	Soil and Water Assessment Tool
TMDL	Total Maximum Daily Loads
UN/ECE	United Nations Economic Commission for Europe
USACE	United States Army Corp of Engineers
USGS	United States Geological Survey
WASMOD	Water and Substance Simulation Model
WASP	Water Quality Analysis Simulation Program
WFD	Water Framework Directive of the European Union
WHO	World Health Organization

Abstract

The sustainable management of water resources is of high relevance with regard to overall socioeconomic development and environmental protection. Water quality monitoring plays a key role in this context as it provides the necessary information on the status of water resources and on the impact of human alterations of the hydrological cycle and hence forms an important basis for decision making. Current legislative approaches to water management like the European Water Framework Directive place a high importance to water quality monitoring. Monitoring systems have to provide relevant data in an efficient manner and are at the same time under budget constraints. This makes a case for optimization strategies for water quality monitoring networks, where the location of sampling stations and monitoring frequencies play a central role.

Scientific methods to optimize water quality monitoring systems have been extensively described in literature. However, they are hardly ever applied since most of them depend on a-priory knowledge of the spatial and temporal variability of water quality parameters – information which is seldom available. The objective of this dissertation is to develop a method which allows estimating long term variability of water quality parameters. The parameter *nitrate* is chosen as an example parameter and the Aconcagua watershed in Chile is selected as a case study.

The variability of nitrate concentrations over space and time is modelled on the basis of available hydrological, land use and point source data for the time period 1986 – 2006. For estimating nitrate exports to surface water the export coefficient method was used. The results are validated with measured nitrate concentrations of the same period.

Results show that the model represents nitrate concentrations well for the upper and lower part of the watershed while low agreement between modelled and observed values was found for the lower part of the watershed, probably due to an insufficient representation of the hydrology of that zone but it could also be related to shortcomings of the current sampling methods at that particular monitoring station.

Criteria for the location of monitoring stations and for the selection of monitoring frequencies were developed and applied together with the modelling results to develop recommendations for an optimized monitoring system. The main conclusions were on one hand that the current monitoring frequency of four samples per year is much too low recommending biweekly sampling instead; on the other hand one station could be omitted from the network as correlation between two stations was detected.

The described method can serve as a general approach to support optimizing monitoring design if a minimum of data is available in order to estimate variance of a water quality parameter. This refers to daily information on discharges and to reliable estimates of point and diffuse pollution loadings to surface water. Thus, the method can be transferred to other watersheds and to other parameters.

Zusammenfassung (Summary in German)

1. Einführung

Um angemessene Entscheidungen bezüglich Nutzung und Schutz von Wasserressourcen zu treffen, sind abgesicherte und aussagekräftige Informationen über deren quantitativen und qualitativen Zustand notwendig. Diese werden über unterschiedliche Arten von Monitoringsystemen bereitgestellt. Die effektive Planung von Wasserqualitätsmonitoring in Flusseinzugsgebieten erfordert eine Datengrundlage zur räumlichen und zeitlichen Verteilung von Wasserqualitätsparametern, die oftmals insbesondere in Ländern der südlichen Hemisphäre nicht gegeben ist. Ziel dieser Arbeit ist die Entwicklung einer Methode, die diese Datengrundlage schaffen und somit dazu beitragen soll, den Bedarf nach kostengünstigem Wasserqualitätsmonitoring zu decken. Am Beispiel des im semi-ariden Zentral-Chile gelegenen Río Aconcagua-Einzugsgebietes wird diese Methode für den Inhaltsstoff Nitrat angewandt. Anhand von Landnutzungsdaten, Abflussdaten, Wassernutzungen sowie punktuellen und diffusen Einleitungen wird die Nitratkonzentration über einen Zeitraum von 1986 bis 2006 modelliert. Verbunden mit einer Analyse des Einzugsgebietes ermöglicht dieses Verfahren, Empfehlungen für die räumliche und zeitliche Verteilung der Messungen auszusprechen und stellt damit eine Methode bereit, wissenschaftlich fundierte Informationen zur Wasserqualität kosteneffizient zu generieren.

2. Hintergrund

Wasserqualitätsmonitoring hat zum Ziel, den Zustand und die Entwicklung von Gewässergüteparametern zu erfassen, um somit grundlegende Informationen für Managemententscheidungen bereit zu stellen; es stellt damit einen essentiellen Teil des Wassermanagements dar (TIMMERMANN et al. 2000) und liefert darüber hinaus Daten für integrierte Informationssysteme und weiterreichende Modellierungen. Das Monitoring ist dabei in der Regel langfristig ausgerichtet und folgt einer klar strukturierten Planung, die sich aus den Notwendigkeiten der Datennutzung ergibt. Diese ist wiederum durch den gesetzlichen Rahmen bestimmt, wie etwa in der EU durch die Wasserrahmenrichtlinie oder in Chile durch das nationale Wassergesetz (*Código de Aguas*, MOP 2002). Ein Monitoringsystem bezieht sich immer auf hydrologische Einheiten wie Flusseinzugsgebiete oder Grundwasserkörper und kann in folgende Teilbereiche untergliedert werden:

- Messnetzwerk: Messfrequenz, Stationen; gemessene Parameter,
- Datenerhebung: Messmethoden, Feld- und Labormethoden,
- Datenauswertung: Datenanalyse (statistisch, modelltechnisch), Berichtswesen.

Monitoringsysteme unterliegen meistens starken finanziellen Beschränkungen und somit der Notwendigkeit einer effizienten Planung aller Komponenten. Besonders die

Messfrequenz und die Auswahl der Messorte bieten hierbei Möglichkeiten der Optimierung und damit des Informationsgewinns bzw. der Kostensenkung.

Eine optimierte ***Messfrequenz*** bzw. Gesamtzahl der Messungen steht in direktem Bezug zu der erwarteten räumlichen und zeitlichen Variabilität der gemessenen Parameter in dem betrachteten System, die wiederum das Ergebnis von Wechselwirkungen natürlicher und anthropogener Faktoren ist. Das Ziel der Optimierung ist dabei, mit den Messwerten einen hohen Informationsgehalt bei geringen Kosten zu erreichen. Die Aussagen, die ein Monitoringsystem dabei liefern soll, beziehen sich in den meisten Fällen auf zuverlässige Abschätzungen eines ***Mittelwertes*** bzw. auf die Ermittlung eines vorherrschenden zeitlichen ***Trends***. Der Mittelwert lässt sich dann hinreichend abschätzen, wenn bezogen auf die Varianz der zu Grunde liegenden Grundgesamtheit genügend Messungen vorgenommen werden. Um Aussagen mit der gleichen statistischen Sicherheit machen zu können, sind bei einem Gewässer mit hoher Varianz eines Parameters mehr Messungen erforderlich als bei geringer Varianz. Für die Ermittlung der Stichprobengröße für die Trendanalyse können unterschiedliche Verfahren angewendet werden. Statistisch gesehen liegt ein Trend dann vor, wenn sich die Grundgesamtheit eines Zeitabschnittes signifikant von der eines anderen Zeitabschnitts unterscheidet (LETTENMEIER 1976, HIRSCH et al. 1982).

Bei der Optimierung der ***Messorte*** spielt die räumliche Variabilität von Wasserqualitätsparametern in Flussgebieten eine entscheidende Rolle. Lassen sich etwa hohe Korrelationen der Zeitreihen von Parametern zwischen zwei Punkten im Netzwerk feststellen, ist die Einrichtung von nur einer Messstation ausreichend. Daneben muss bei der Ortung von Messstationen die räumliche Verteilung von lokalen Maxima der Wasserqualität, die etwa durch punktuelle oder diffuse Einleiter entstehen, berücksichtigt werden (NING AND CHANG 2005).

Methoden zur Ermittlung einer angemessenen Messfrequenz bzw. von Korrelationen in hydrologischen Netzen sind umfangreich in der wissenschaftlichen Literatur beschrieben. Bei allen Methoden ist eine ***a-priori Kenntnis*** bzw. Annahme der Variabilität (Varianz) der betrachteten Wasserqualitätsparameter eine notwendige Eingangsgröße (GILBERT 1987, WARD et al. 1990). Oftmals werden die Methoden auf Fälle angewandt, in denen lange historische Zeitreihen mit relativ hoher Messfrequenz vorliegen, so dass sich die Variabilität der betrachteten Population aus historischen Wasserqualitätsdaten abschätzen lässt (WARD et al. 1990). In einem Großteil der Flussgebiete weltweit liegen diese Datenreihen zur Wasserqualität jedoch nicht vor. Für diesen Fall werden in der Literatur keinerlei Verfahren zur Abschätzung der Variabilität von Wasserqualitätsparametern beschrieben. Hieraus definiert sich der Forschungsbedarf dieser Arbeit.

3. Problembeschreibung, Arbeitsziele und Methode

Soll die Planung von Monitoringsystemen auch in Flussgebieten mit schlechten historischen Wasserqualitäts-Datenbeständen wissenschaftlich fundiert durchgeführt werden, müssen Methoden entwickelt werden, welche die räumliche und zeitliche Variabilität von Wasserqualitätsparametern auf der Basis anderer Determinanten, die leichter verfügbar sind, ableiten. Bestehende Modelle zur Abschätzung der Wasserqualität bei schlechter Datenlage beziehen sich in der Regel auf die Modellierung von Jahres- oder Monatswerten von Konzentrationen oder Stoffausträgen (JOHNES 1996, BEHRENDT 1999, EVANS 2002). Für die Ermittlung der Varianzen von Stoffkonzentrationen in Fließgewässern sind jedoch Abschätzungen von Tageswerten nötig, weil sonst die Gefahr besteht, dass kurzzeitigere Fluktuationen herausgemittelt werden.

In der vorliegenden Arbeit wird der **Hypothese** nachgegangen, dass sich die Variabilität der Nitratkonzentration auf der Basis von verfügbaren Tageswerten des Wasserabflusses sowie der Stoffeinträge in die Gewässer mit Hilfe einer GIS- und modellbasierten Systemanalyse des Einzugsgebietes hinreichend genau wiedergeben lässt, und so wissenschaftliche fundierte Aussagen zur Wahl von Messorten und -frequenz getroffen werden können. Diese Hypothese wird am Beispiel des Einzugsgebiets des Aconcagua für den Fall des Nitrates überprüft.

Daraus ergeben sich folgende **Arbeitsziele**:

- Formulierung eines Modells, das die Variabilität von Nitratkonzentrationen in Fließgewässern über lange Zeiträume auf der Basis von Land- und Wassernutzungsdaten beschreiben kann,
- Anwendung des Modells auf eine Fallstudie, hier: Aconcagua-Einzugsgebiet in Chile,
- beispielhafte Anwendung der Modellergebnisse für das Design des Wasserqualitätsmonitorings im Aconcagua-Einzugsgebiet,
- Untersuchung der Übertragbarkeit der Methode auf andere Einzugsgebiete.

Hieraus wurde folgende **Methodik** abgeleitet:

1. **Modelldefinition** zur Ableitung von Nitratkonzentrationszeitreihen auf der Basis der verfügbaren Umweltsystemdaten *Abfluss*, *punktuelle* und *diffuse Nitrateinträge;*
2. **Systemanalyse** des Einzugsgebietes Aconcagua im Hinblick auf Stoffeinträge und Abflüsse. Hierzu ist die systematische Erfassung bzw. Modellierung der räumlichen und zeitlichen Variabilität von Landnutzung, Abfluss, Punktquellen und diffusen Einträgen (vornehmlich aus der Landwirtschaft) erforderlich;
3. Empirische Studie zur **Bestimmung der Stickstoff-Exportdynamik** der Bewässerungslandwirtschaft in einem Teileinzugsgebiet des Aconcagua ("Pocochay"). Bestimmung von Stickstoffexportkoeffizienten, mit dem Ziel der Übertragung auf die restlichen Teileinzugsgebiete des Aconcagua;
4. **Modellierung** des räumlichen und zeitlichen Verhaltens der Nitratkonzentrationen im Einzugsgebiet des "Rio Aconcagua" für den Zeitraum 1986-2006; Validierung der Modellergebnisse durch vorliegende Messwerte;
5. Exemplarische **Anwendung** der Modellergebnisse auf die Auswahl von Messorten und -frequenzen im Aconcagua.

In der Fallstudie wird der Stoff "Nitrat" als Beispiel betrachtet. Nitrat wurde vor allem aufgrund der hohen Relevanz für Ökosystem und Mensch aber auch wegen der vielfältigen Quellen und Prozesse, die eng mit der Landnutzung und mit anderen menschlichen Aktivitäten verbunden sind, gewählt. Das Untersuchungsgebiet ist das Einzugsgebiet des Rio Aconcagua in Chile, in dem alle wesentlichen Wassernutzungen vertreten sind (Bewässerung, häusliche und industrielle Wassernutzung).

4. Ergebnisse

4.1 Modellentwicklung zur Abbildung der Nitratkonzentration

Die Nitratkonzentration lässt sich durch die Abflussdynamik, Stickstoffeinträge und -transformationsprozesse im Fluss selbst beschreiben. Diese Faktoren müssen über den modellierten Zeitraum in angemessener zeitlicher und räumlicher Auflösung quantifiziert werden.

Als Basiseinheit der Betrachtung dienen Flussabschnitte sowie die dazu in Bezug stehenden Untereinzugsgebiete und Wassernutzer. Dies ist schematisch in der folgenden Graphik dargestellt:

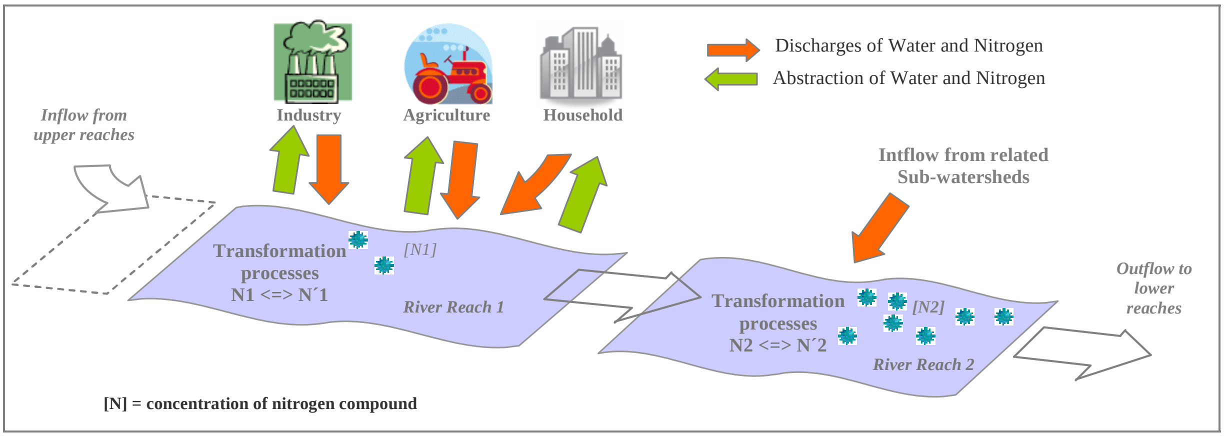


Abb. 1 Skizze der Prozesse der Stoff- und Wasserein- und -austräge in den Flussabschnitten

Als Ansatz für die Modellierung der **Stickstoffeinträge** wurde das Exportkoeffizientenmodell (JOHNES 1996, FERNANDEZ et al. 2003) herangezogen, das erlaubt, Aussagen über die Stickstoffeinträge in Flusssysteme bei schlechter Datenlage zu machen. Es geht davon aus, dass eine bestimmte Landnutzung eine bestimmte Menge Stickstoff exportiert, ohne die zu Grunde liegenden Prozesse im Detail abzubilden. Andere Einzugsgebietsmodelle, wie etwa SWAT (ARNOLD et al. 1993), AGNPS (BINGNER et al. 2001), WASMOD (REICHE 1994), benötigen für die Modellierung der Stickstoffdynamik detaillierte und flächendeckende Daten zu Bodeneigenschaften, Landnutzung und Klima. Diese Daten sind in der Fallstudie wie auch in zahlreichen anderen Fällen nicht verfügbar.

Das **Exportkoeffizientenmodell** und vergleichbare Ansätze (HAITH and SHOEMAKER 1987, BEHRENDT 1999, EVANS 2002) wurden bisher lediglich zur Ermittlung von Monats- oder Jahreswerten angewendet. In der vorliegenden Arbeit wurden die Exportkoeffizienten, die je nach Art des Eintrages unterschiedliche zeitliche Auflösungen haben, mit täglichen Abflusswerten kombiniert, um so die Variabilität der Nitratkonzentrationen besser zu beschreiben.

Während punktuelle Einträge, hier vor allem häusliches Abwasser, relativ leicht quantitativ abzuschätzen sind, ist dies bei Stickstoffeinträgen aus landwirtschaftlichen Nutzungen problematisch, weil es zahlreiche Faktoren gibt, die den Export von Stickstoff aus der Fläche beeinflussen (Düngemenge, Boden, Bewässerungswassermenge, Niederschlag, etc.). Von daher können Exportkoeffizienten, die für eine bestimmte Landnutzungsform für bestimmte Regionen ermittelt wurden (u.a. BEAULAC und RECKHOW 1982, CAVERO et al. 2003) nur unter Vorbehalt auf andere Regionen übertragen werden. Aus diesem Grunde wurde für die vorliegende Arbeit eine dreijährige Studie zur

Bestimmung des N-Exports durch die Bewässerungslandwirtschaft in einem Bewässerungssektor des Aconcagua durchgeführt (siehe unten Punkt 4.3).

Um die jährliche und langfristige Dynamik zu erfassen, müssen die Exportkoeffizienten für jeden Monat des Jahres als Fraktion der jährlich eingesetzten Düngermenge bekannt sein (C_{eb} in Gleichung 1). Daneben wird dem Austrag durch Regenereignisse Rechnung getragen, indem ein niederschlagsabhängiger Term für den Stickstoffaustrag aus den Bewässerungsgebieten bestimmt wird ($P \cdot C_{ep}$ in Gleichung 1) Somit lässt sich der **Nitrataustrag** für ein betrachtetes Bewässerungsgebiet ermitteln nach:

$$ENO_{3I} = \sum A_i F_i (C_{eb} + PC_{ep}) \qquad \textbf{(1)}$$

ENO_{3I} = Export von Nitrat je Bewässerungsgebiet I [Kg]
Ai = Fläche der Landnutzung i [ha]
Fi = Düngeranwendung bezogen auf Landnutzung i [Kg ha^{-1}]
P = Niederschlag [mm]
C_{eb} = Exportkoeffizient bezogen auf den Bewässerungsbasisabfluss
C_{ep} = Exportkoeffizient bezogen auf Austrag pro mm Niederschlag [mm^{-1}]

Die Verteilung der Landnutzung (A_i) und der Düngereinsatz (F_i) unterliegen dabei zeitlichen Änderungen, die bekannt sein müssen und auf der Basis von Landnutzungs-. und Düngerstatistiken bestimmt werden können.

Wesentliche **punktuelle Einträge** sind häusliche und industrielle Abwässer. Liegen keine empirischen Werte vor, so werden die Stickstoffeinträge aus häuslichen Abwässern über die Bevölkerungszahlen quantifiziert. Ammonium- und Nitratausträge werden dabei separat betrachtet (Gleichungen 2 und 3).

$$ENH_4wwtp = \sum_i P_i N_{inh} (1 - C_r)(1 - C_{nit}) \qquad \textbf{(2)}$$

$$ENO_3wwtp = \sum_i P_i N_{inh} (1 - C_r) C_{nit} \qquad \textbf{(3)}$$

ENH_4wwtp = Täglicher Ammoniumaustrag (je einleitende Gemeinde)
ENO_3wwtp = Täglicher Nitrataustrag (je einleitende Gemeinde)
Pi = Angebundene Bevölkerungszahl
N_{inh} = Stickstoffproduktion je Einwohner (10g day^{-1})
C_y = Koeffizient der gesamten N-Reduktion (abhängig von Technologie der Abwasserbehandlung)
Cnit = Koeffizient der Nitrifikation (abhängig von Technologie der Abwasserbehandlung)

Zur Beschreibung des **Abflusses** je Untereinzugsgebiet wird auf gemessene Werte zurückgegriffen bzw. die etablierte Curve-Number-Methode (SCS 1972) verwendet.

Die **Wasserentnahme** für Städte und Gemeinden ist an die Bevölkerungsentwicklung gekoppelt und wird für jede Gemeinde separat berechnet. Die Entnahmemenge pro Kopf ist für jede Gemeinde unterschiedlich, wird jedoch als zeitlich konstant betrachtet.

Entnahmen für die **Bewässerung** werden anhand von monatlichem Pflanzenwasserbedarf sowie der Feld- und Zuleitungseffizienz modelliert. Für jedes Bewässerungsgebiet ergibt sich eine Zeitreihe mit Monatswerten des Wasserbedarfs, entsprechend der Verteilung und zeitlichen Entwicklung der Landnutzung. Die Dynamik der Landnutzung wurde anhand von Agrarzensen und Satellitenbildinterpretation ermittelt.

Um das gesamte **System "Flusseinzugsgebiet"** abzubilden, müssen die Wasser- und Stoffflüsse der Flussabschnitte als Netzwerkmodell insgesamt betrachtet werden. Je Flussabschnitt muss die Verweildauer bestimmt werden, um den Transport von Wasser und Nitrat sowie die Umwandlungsprozesse Nitrifikation und Denitrifikation zu bestimmen.

Die **Konzentration**, der Quotient von Substanz und Wassermenge zu einem gegebenen Zeitpunkt in einem Flussabschnitt, lässt sich somit für jeden Zeitpunkt abschätzen, wenn realistische Eingangswerte für die Stoff- und Wasserflüsse verwendet werden. Somit lassen sich Zeitreihen für die Nitratkonzentration bestimmen, die als Grundlage für das Monitoringdesign herangezogen werden können.

Für die Umsetzung des Modellansatzes wurde das Modellsystem ***Mike Basin*** (DHI 2005) gewählt, welches das Flusssystem als Netzwerk darstellt und erlaubt, dieses mit Flächenprozessen (Abfluss, Nitrateinträge aus der Landwirtschaft) zu verknüpfen. Gründe für die Auswahl waren die Möglichkeit der variablen Verknüpfung von unterschiedlichen Zeitskalen (je nach Parameter Tages-, Monats-, bzw. Jahreswerte), die problemlose Kombinationsmöglichkeit von Flächen- mit Gerinneprozessen sowie die direkte GIS-Anbindung, was die Datenein- und -ausgabe erleichtert.

4.2 Systemanalyse der relevanten Faktoren im Aconcagua-Einzugsgebiet

Um die Eingangsparameter für das oben beschriebene Modell zu bestimmen, wurde eine umfassende Systemanalyse des Flusseinzugsgebietes durchgeführt, um die zeitliche und räumliche Dynamik von Landnutzung, Hydrologie, Wassernutzung und Stoffeinträgen zu quantifizieren.

Das **Aconcagua-Einzugsgebiet** (7550 km²) liegt in Zentralchile zwischen 32°20´ und 33°15´ südlicher Breite (s. Abb. 2). Es ist durch ein mediterranes Klima und ein steiles Relief gekennzeichnet und erfüllt wichtige Funktionen vor allem in Bezug auf die exportorientierte Agrarproduktion (etwa 60 000 ha bewässerte Fläche) und die Trinkwasserversorgung von insgesamt etwa einer Million Menschen innerhalb des Einzugsgebietes und im Großraum Valparaiso.

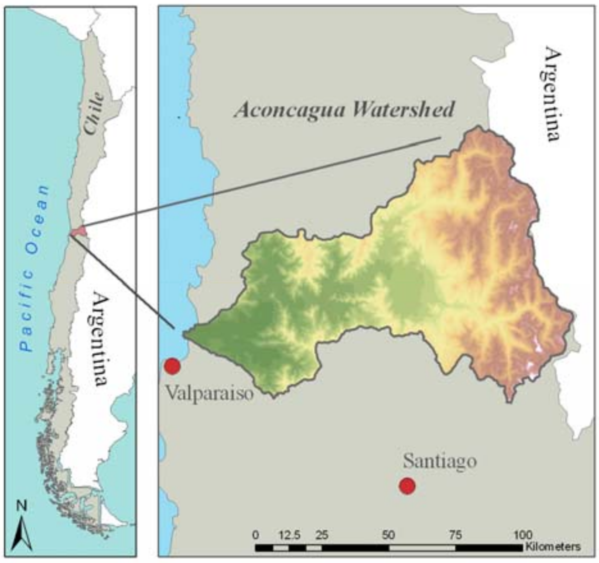
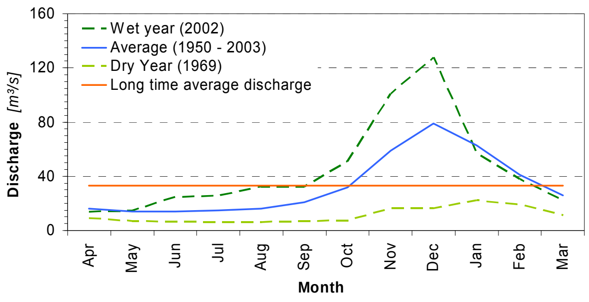


Abb. 2 Lage des Aconcagua-Einzugsgebietes

Etwa 80 Prozent des jährlichen **Abflusses** stammen aus den Anden im oberen Teil des Einzugsgebietes.

Von den wichtigsten Stationen liegen tägliche Abflussmesswerte vor. Als Beispiel zeigt die folgende Abbildung das Abflussverhalten an der Station Chacabuquito und verdeutlicht die hohe saisonale und langjährige Variabilität dieses Systemparameters.



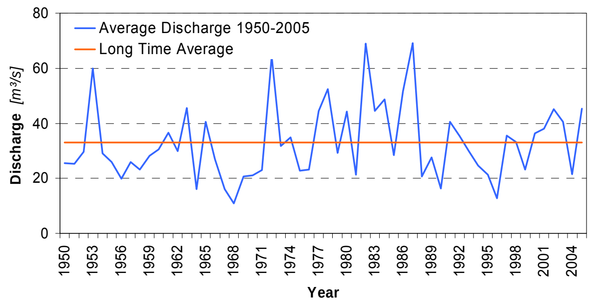


Abb. 3 Chacabuquito: Jährliche Abflusskurve

Abb. 4 Langjährige Abflussvariabilität (Orange: Langjähriges Mittel)

Die **Landnutzung** hat sich in den letzten Jahrzehnten geändert, mit einer Tendenz von jährlichen Kulturen hin zum Obstbau, wobei die Bewässerungsmethoden (überwiegend Furchenbewässerung) sich nicht grundlegend geändert haben; lediglich im unteren Bewässerungssektor wurden seit den 1980er Jahren zunehmend Aspersions-bewässerungsmethoden eingesetzt.

In den 80er Jahren wurde die Fläche des Weinanbaus im oberen Einzugsgebiet stark ausgeweitet, in den 90ern die Fläche des Avocadoanbaus im unteren Einzugsgebiet, so dass diese beiden Kulturen heute den Bewässerungslandbau dominieren. Die Landnutzungsänderungen wurden durch die Agrarstatistiken (INE 1976, INE 1997) und durch Interpretationen einer Landsat ETM7 Szene (2003) erfasst. Die zeitliche Dynamik des Bedarfs für **Bewässerungswasser** sowie die **Düngeranwendungen** wurden basierend auf der Landnutzungsänderung modelliert. Bei den Düngeranwendungen wurde dabei auf Erhebungen in dem Einzugsgebiet sowie auf langfristige Statistiken des Landwirtschafsministeriums und der FAO zurückgegriffen, die mit den Änderungen der Anbaukulturen pro Distrikt (*municipalidad*) kombiniert wurden. Abb 6 zeigt die eingesetzte Düngermenge aggregiert für das gesamte Einzugsgebiet. Die Entnahmen des Bewässerungswassers und entsprechend die Rückflüsse des Entwässerungswassers sind neben dem Bewässerungswasserbedarf abhängig von der Wasserverfügbarkeit im jeweiligen Flussabschnitt, die durch das integrierte Modell (s.u.) bestimmt wird.

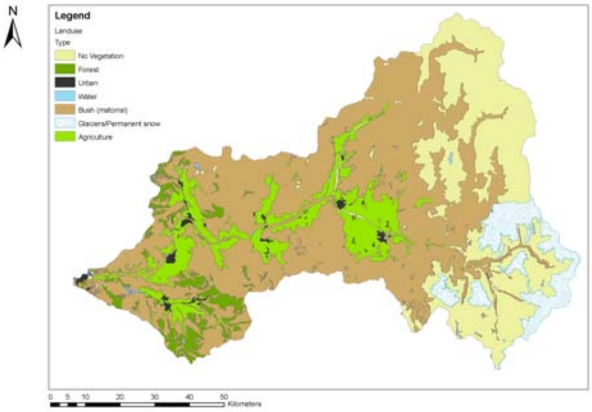


Abb. 5 Landnutzung im Einzugsgebiet

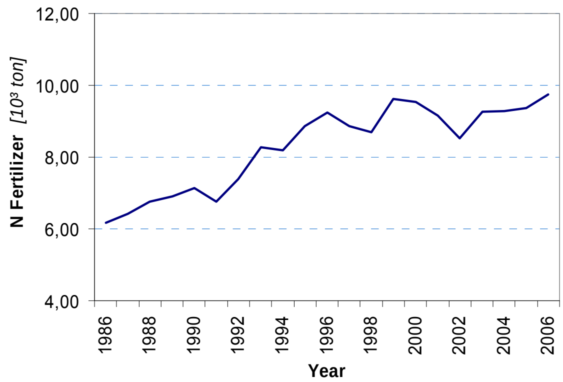


Abb. 6 Zeitliche Entwicklung der gesamten Stickstoffdüngeranwendungen im Einzugsgebiet (1986-2006)

Die **Abwassereinleitungen** setzten sich bis 2003 durch lediglich vorgeklärte Abwässer zusammen, 2003-2004 wurden drei neue Kläranlagen in Betrieb genommen. Damit werden derzeit etwa 95 % der Abwässer im Einzugsgebiet geklärt. Die Zeitreihen für die Stickstoffeinleitungen (Abb. 7) durch Abwässer sowie für die **Trinkwasserentnahme** wurden anhand von Bevölkerungsdaten für jede Gemeinde errechnet (Abb. 8). Seit 2004 liegen Messwerte der Stickstoffeinleitungen vor (ESVAL 2007).

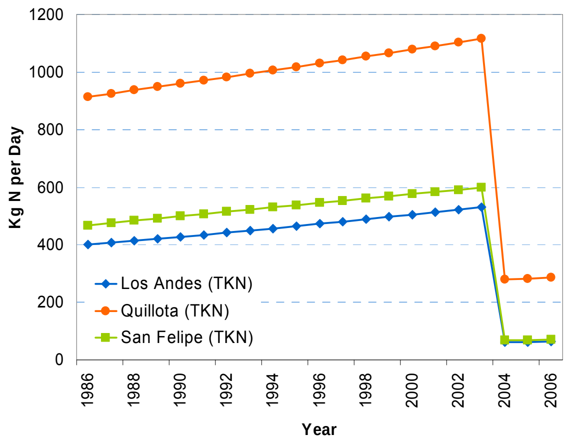


Abb. 7 Modellierter Eintrag von NH4-Stickstoff aus Abwasser (1986 – 2006)

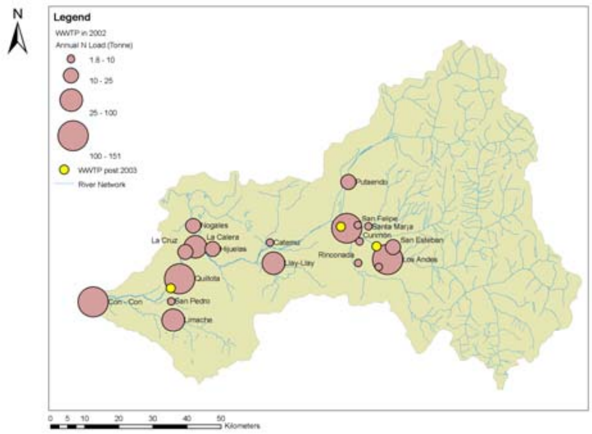


Abb. 8 Lage und Quantifizierung von punktuellen Stickstoffeinleitern

4.3 Bestimmung von Exportkoeffizienten für Stickstoff, Detailstudie im Pocochay Untereinzugsgebiet

Da für die Erfassung der diffusen Einträge aus der Bewässerungslandwirtschaft nicht hinreichend Daten verfügbar waren, wurde hierfür eine gesonderte Studie in einem Teileinzugsgebiet, dem Pocochay, durchgeführt (Abb. 9). Dieses Gebiet wurde gewählt, weil es repräsentative Eigenschaften in Bezug auf Agrarkultur, Bewässerungstechnologie und Böden im Einzugsgebiet des Aconcagua aufweist.

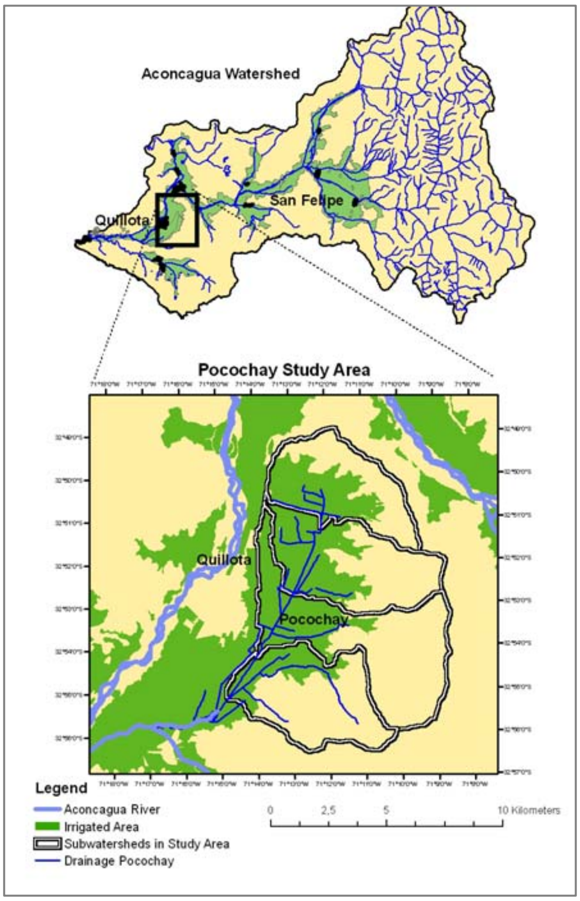


Abb. 9 Lage des Pocochay Untereinzugsgebietes

Im Bewässerungsgebiet des Pocochay (3500 ha Bewässerungsfläche) wurden detaillierte Messungen von Landnutzung, Düngeranwendung, Wasserqualität und Abfluss durchgeführt, um damit die Exportkoeffizienten von bewässerten Flächen im Einzugsgebiet zu bestimmen. Für die Landnutzung und Düngeranwendung wurden Daten auf 356 Betrieben in der Bewässerungssaison 2004/2005 erhoben.

Stickstoffkonzentration und Abfluss wurden alle 1-2 Wochen über einen Zeitraum von drei Jahren gemessen.

Während der Regenzeit (Mai bis August) wurde der Stickstoffaustrag während drei Niederschlagsereignissen mit hoher zeitlicher Auflösung alle zwei Stunden bemessen. Damit konnten Exportkoeffizienten für die monatlichen Nitratausträge als Funktion der jährlich eingesetzten Düngermenge und Exportkoeffizienten für niederschlags-abhängige Nitratausträge ermittelt werden (s. folgende Tabelle, vgl. hierzu Gleichung *1*).

Tab 1: Monatlicher durchschnittlicher Nitrataustrag aus dem Bewässerungsgebiet des Pocochay und Exportkoeffizienten (Basisabfluss)

		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
Absoluter Austrag	*[KgN ha^{-1}]*	4.30	3.70	3.64	3.44	2.69	1.48	1.60	2.89	4.95	2.89	3.33	4.90	39.3
Exportkoeffizient des jährlichen N-Düngereinsatzes	$C_{eb,}$ %	2.57	2.22	2.18	2.06	1.61	0.89	0.96	1.73	2.96	1.73	2.00	2.93	23.8

Bemerkung: Durchschnittliche N-Düngeranwendung im Pocochay Einzugsgebiet: 167 Kg/ha

Der **niederschlagsabhängige Austrag** (Mittelwert aus drei Niederschlagsereignissen an der Station "La Palma") wurde ermittelt als 17 g NO_3-N ha^{-1} pro mm Niederschlag. Bezogen auf die eingesetzte Düngermenge im Einzugsgebiet entspricht dies 0,011 % per mm Niederschlag. Dies bedeutet, dass bei 400 mm Niederschlag pro Jahr etwa 4 % des eingesetzten N-Düngers als Funktion des Niederschlags und 23,8 % als Basisabfluss exportiert wurden.

Bei der Anwendung der Exportkoeffizientenmethode wird angenommen, dass die Düngeranwendung der entscheidende Faktor für den Nitrataustrag ist. Zur Übertragung auf das gesamte Einzugsgebiet des Aconcagua wurde der Düngereinsatz pro Bewässerungssektor ermittelt, indem die Düngeranwendungen pro Kulturpflanze mit der kultivierten Fläche multipliziert wurden. Die Austräge aufgrund der Regenereignisse wurden durch die niederschlagsbezogenen Exportkoeffizienten mit den Zeitreihen der Niederschläge multipliziert. Dabei wurde der Nitrataustrag auf den Tag des Niederschlagsereignisses und auf drei Tage danach verteilt (entsprechend der Messwerte im Pocochay).

Die Übertragung der Exportkoeffizienten auf die anderen Bewässerungssektoren des Aconcagua-Einzugsgebietes wird dadurch gerechtfertigt, dass die Böden, Bewässerungsverfahren und –kulturen eine hohe Homologie aufweisen.

4.4 Modellierung der Nitratkonzentration im Aconcagua

Wie unter Punkt 3 beschrieben, wurde die Modellierung mit dem Modellsystem Mike Basin (DHI 2005) durchgeführt. Hierzu wurde nach Ableitung des hydrologischen Netzes, basierend auf einem eigens erstellten digitalen Höhenmodell, das Einzugsgebiet in Untereinzugsgebiete aufgeteilt, die sich anhand von wichtigen Wassernutzern, -einträgen oder -messstellen orientierten.

In das Modell wurden die Daten aus der vorab beschriebenen Aconcagua-Systemanalyse, ergänzt durch Ergebnisse der Pocochay-Studie, eingebracht. Wesentlich ist hierbei die Modellierung der Abflussdynamik, die mit täglichen Werten simuliert wird. Sie ergibt sich aus dem natürlichen Abfluss sowie der zahlreichen Wasserentnahmen und –rückflüsse.

In Abb. 10 sind die modellierten Nitratkonzentrationen für die Station "San Felipe" dargestellt. Abb. 11 greift die Tageswerte heraus, für die Messungen vorliegen und stellt sie neben diesen dar.

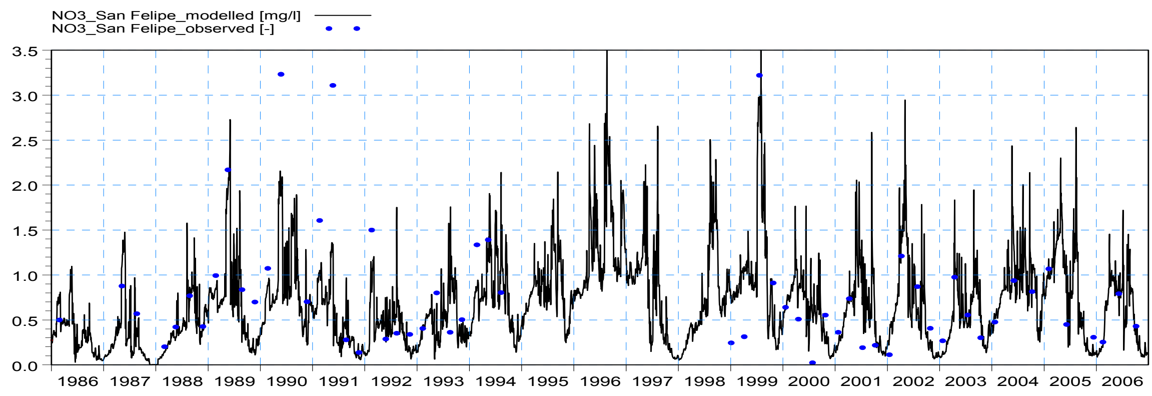
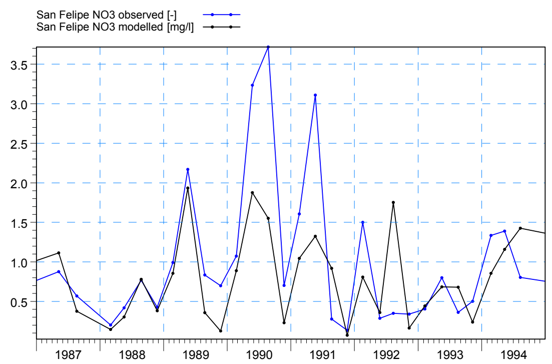


Abb. 10 Modellierte Nitratkonzentration Station "San Felipe"



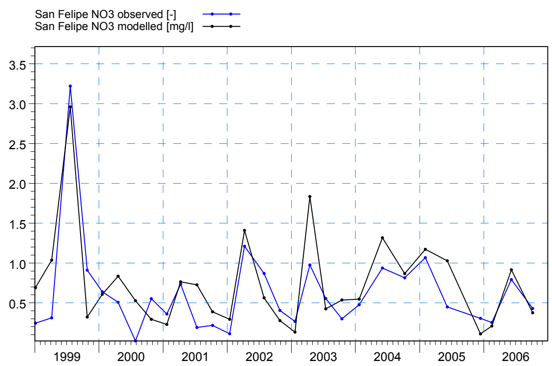


Abb. 11 Gegenüberstellung von gemessenen und modellierten Nitratwerten (San Felipe)

Die durchschnittliche Konzentration des Nitrates wird hier gut repräsentiert, ebenso das zeitliche Verhalten des Nitrates. Auch an der Station Romeral im mittleren Einzugsgebiet wird die Nitratkonzentration recht gut abgebildet, im unteren Einzugsgebiet (Puente Colmo) hingegen schlecht (s. Vergleich für drei Stationen in Tab. 2) was unter anderem durch einen negativen Nash-Sutcliffe Effizienzindikator zum Ausdruck kommt.

Tab. 2: Vergleiche von modellierten und gemessenen Nitratwerten für drei Standorte

Ort	Durchschnitt (beobachtet)	Durchschnitt (Modell)	Bestimmtheits-maß	Nash-Sutcliffe Indikator
	mg l^{-1}	mg l^{-1}	R^2	*E*
San Felipe	0.82	0.76	0.50	0.49
Romeral	1.70	1.72	0.44	0.12
Puente Colmo	1.54	3.0	0.03	-0.29

Während das Modell also die Nitratkonzentration im oberen Teil des Einzugsgebietes gut beschreibt, gilt dies für das untere Einzugsgebiet nicht. Erklärungen hierfür sind mögliche Stickstoffausträge (Einbindung in organische Substanz und abschließender Austrag über Sedimente, hohe Denitrifikation im unteren, stark verästelten und langsam fließenden Flussabschnitt) und eine schlechte Abbildung der Abflussdynamik durch das Modell. Hierbei liegen mögliche Fehlerquellen vor allem in den modellierten Abflüssen der seitlichen Einzugsgebiete des mittleren und unteren Aconcagua, die lediglich mit Hilfe der *Curve Number* Methode abgeschätzt werden konnten, da keine Daten für die Kalibrierung vorlagen. Da Tageswerte der Nitratkonzentrationen modelliert werden, spielt die Dynamik von Oberflächen-, Interflow- und Basisabfluss jedoch eine entscheidende Rolle. Daneben liegt in diesem Teil des Einzugsgebiet der Abfluss des Aconcagua während der Bewässerungssaison sehr niedrig und somit spielt die Entnahmemenge und der Rückfluss von Bewässerungswasser eine entscheidende Rolle bei der Simulation von Nitratwerten, da Niedrigwasser kombiniert mit Nitratausträgen aus den Bewässerungssektoren zu hohen simulierten Werten führt. Bei der Modellierung der Rückflüsse wurden jedoch lediglich einfache Kennzahlen der chilenischen Wasserbehörde übernommen, was Fehler in der Simulation verursachen kann, die zu der schlechten Validierung führen.

4.5 Monitoringdesign

Die Systemanalyse und Modellierung ermöglichen klare Aussagen über die zukünftige Planung von Monitoringsystemen. Als wichtigstes Ergebnis sind die generierten Zeitreihen der Nitratkonzentration an verschiedenen Punkten des Einzugsgebietes anzusehen. Sie können nunmehr zur Auswahl geeigneter Stationen und Messfrequenzen herangezogen werden.

Für die Wahl von **Monitoringstationen** wurden zusätzlich die derzeitigen Wassernutzungen berücksichtigt. Da im unteren Einzugsgebiet (Puente Colmo) sowohl Wasser für die Trinkwasserbereitstellung entnommen wird als auch die höchsten modellierten und gemessenen Nitratwerte verzeichnet werden, wird dieser Station die höchste Priorität zugeordnet. Die nächst höhere Priorität erhält die Station Romeral, da hier große Mengen Trinkwasser entnommen werden und gleichzeitig Werte von bis zu 5 mg l^{-1} NO_3-N modelliert wurden. Diese liegen zwar noch unter dem Grenzwert für Trinkwasser, sollten jedoch beobachtet werden.

Zwischen den Zeitreihen der Stationen Romeral und San Felipe wurde eine hohe Korrelation der gemittelten Monatswerte festgestellt (Pearson Korrelationskoeffizient 0,77); somit würde ein intensives Monitoring an beiden Stationen zu redundanten Informationen führen. Daher können Messungen an der Station San Felipe eingestellt bzw. eingeschränkt werden. Zudem finden unterhalb dieser Station, außer für die Bewässerungslandwirtschaft keine Entnahmen statt. Abb. 12 stellt die Prioritäten bei der Lokalisierung der Monitoringstationen dar.

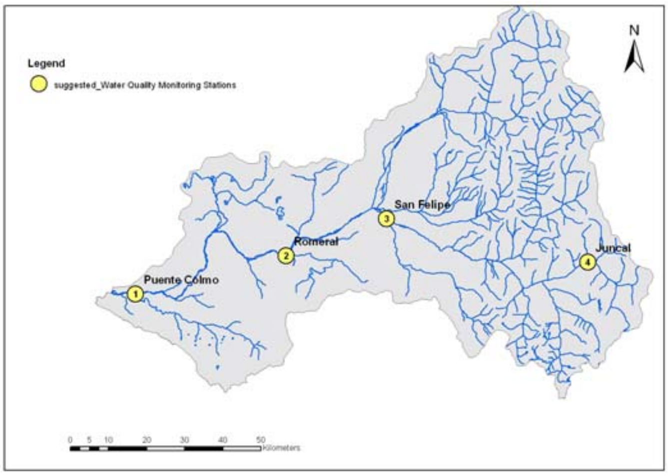
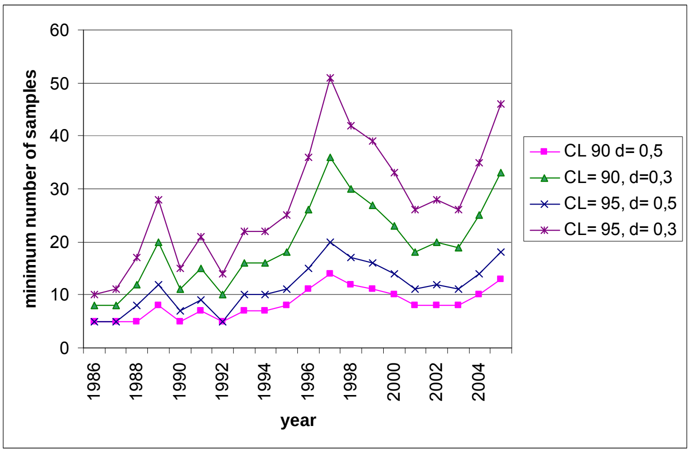


Abb. 12 Vorschlag zur Priorisierung von Monitoringstationen

Messfrequenzen

Aus den sich ergebenen Varianzen der modellierten Nitratzeitreihen kann nunmehr für jedes Jahr die Anzahl der erforderlichen Messungen ermittelt werden, um den Mittelwert mit hinreichend statistischer Sicherheit abschätzen zu können. Dies wurde für die Station Romeral für verschiedene statistische Designkriterien getan (Abb. 13). Jahre mit hoher Variabilität der Nitratkonzentration erfordern grundsätzlich eine höhere Messfrequenz.



Wählt man eine hohe statistische Sicherheit (Konfidenzniveau von 95% und einen maximal erlaubten Fehler von 0,3 mg l^{-1} NO3-N), so wären in den modellierten Jahren (1986-2006) zwischen 10 (1986/1987) und 51 (1997/98) Messungen erforderlich gewesen, um die mittlere Nitratkonzentration verlässlich abschätzen zu können.

CL= Konfidenzniveau; d = maximal erlaubter Fehler

Abb. 13 Minimale Messfrequenzen pro Jahr bei verschiedenen statistischen Kriterien

Welche statische Sicherheit und Messgenauigkeit als ausreichend erachtet wird, ist nicht eindeutig zu benennen. Wählt man mindestens 26 Proben pro Jahr (zweiwöchentlich), hätte man zumindest eine Genauigkeit von +/- 0.5 mgl^{-1} bei einem Konfidenzniveau von 95 % in allen betrachteten Jahren erreicht. Will man gewährleisten, dass auch in Jahren mit hoher Varianz der Nitratkonzentration verlässlich der Mittelwert erfasst wird, so lautet die Empfehlung eine wöchentliche Probennahme einzuführen.

Die **wesentlichen Ergebnisse** der Arbeit lassen sich wie folgt zusammenfassen:

1. Beschreibung eines Verfahrens zur Abschätzung des Nitrataustrages und der Nitratkonzentration als Basis für die Quantifizierung der Variabilität von Nitratkonzentrationen;
2. Bestimmung von Exportkoeffizienten für den Nitrataustrag für ein typisches Bewässerungsgebebiet im Aconcagua;
3. Quantifizierung von zeitlicher (1986-2006) und räumlicher Variabilität des Nitrates in dem Einzugsgebiet des Aconcagua;
4. Entwicklung einer Entscheidungsmatrix zur Priorisierung von Monitoringstationen; Anwendung auf den Fall Aconcagua;
5. Ableitung von Empfehlungen für die Wahl optimaler Messfrequenzen im Aconcagua auf der Basis zeitlicher Variabilitäten der Nitratkonzentration.

5. Diskussion und Schlussfolgerungen

Die vorliegende Arbeit weist nach, dass eine Rekonstruktion von Zeitreihen der Nitratkonzentration im Aconcagua-Einzugsgebiet unter Berücksichtigung der zeitlichen Dynamik von Land- und Wassernutzung sowie der Anwendung des Exportkoeffizientenmodells möglich ist. Solch ein Verfahren ist besonders für Entwicklungs- und Schwellenländer sinnvoll, in denen das Monitoring schlecht entwickelt ist und eine geeignete Planung aufgrund einer fehlenden Datenbasis vor großen Problemen steht.

Für verschiedene Flussabschnitte des Aconcagua lässt sich die Nitratkonzentration über den Zeitraum 1986-2006 bei täglicher Auflösung bestimmen. Diese Ergebnisse können genutzt werden, um daraus Vorschläge für ein optimiertes Monitoring abzuleiten. So können eine angemessene Messfrequenz bestimmt und, zusammen mit weiterreichenden räumlichen Analysen, Aussagen über die Wahl der Messstationen gemacht werden.

Die Auswahl der hier verwendeten Modellierungsmethode ist vor allem durch die geringe Datenverfügbarkeit bestimmt und durch die Notwendigkeit, Zeitreihen 20 Jahre in die Vergangenheit zu betrachten, weil nur so die langfristigen Variabilitäten der Stickstoffkonzentration erfasst werden können. In einem Land wie Chile, ohne eine ausgeprägte Tradition des Umweltmonitorings, liegen nur sehr begrenzte Datenbestände vor. Somit müssen durch den gewählten Modellansatz zahlreiche Vereinfachungen in Bezug auf die komplexen Prozesse der Hydrologie und Stoffdynamik gemacht werden.

Das für den Stickstoffaustrag aus der Fläche verwendete Exportkoeffizientenmodell nimmt das gleiche Verhalten für alle Bewässerungsperimeter an. Unterschiede in Bezug auf Böden oder Kulturtechnik werden nicht berücksichtigt. Es ist offensichtlich, dass durch diesen *Black Box* Ansatz große Fehler in die Modellierung eingehen könnten. Das gleiche gilt für die Abschätzung der Abflüsse auf Basis der *Curve Number*-Methode und die Abschätzung der Stickstoffeinträge durch häusliches Abwasser auf Basis der Bevölkerungsdaten. Wenn auch die Validierung der Modellergebnisse recht zufriedenstellend ist, muss berücksichtigt werden, dass die Menge der Daten, die für die Validierung zur Verfügung stand, sehr gering ist (vier Messungen pro Jahr an nur drei Stationen).

Die Ergebnisse der Validierung der Abflüsse und der Nitratkonzentration lassen jedoch den Schluss zu, dass die Variabilität zumindest im oberen und mittleren Teil des Einzugsgebietes gut abgebildet wird und damit die abgeleiteten Empfehlungen in Bezug auf das Monitoring gerechtfertigt sind. Die Ergebnisse zeigen vor allem, dass bei konstantem Budget die Messfrequenz deutlich erhöht und im Gegenzug eine Monitoringstation weniger betrieben werden sollte.

Auch wenn diese Aussagen zunächst auf die Fallstudie "Aconcagua" beschränkt sind, ist eine **Übertragung** der Methode auf andere Einzugsgebiete möglich. Wesentliche Voraussetzungen für die Anwendbarkeit der Methode sind:

- das Vorhandensein bzw. die zuverlässige Modellierung von täglichen Abflusswerten und
- eine realistische Abschätzung der wesentlichen Stickstoffeinträge, vor allem aus der Bewässerungslandwirtschaft.

Daten zur Landnutzungsdynamik und zu punktuellen Einleitungen sollten verfügbar sein, können jedoch auch durch Satellitenbildinterpretation bzw. Agrar- und Bevölkerungsstatistiken abgeschätzt werden.

Die weiteren Flusseinzugsgebiete von Zentral- und Nordchile sind durch ähnliche Rahmenbedingungen in Bezug auf Hydrologie, Böden, Kulturen und Bewässerungssysteme wie im Aconcagua gekennzeichnet, so dass dort mit den gleichen Exportkoeffizienten realistische Abschätzungen des Nitrataustrags gemacht werden können. In anderen Gebieten ist dies ein Faktor, der erneut empirisch ermittelt werden muss.

Das entwickelte Modell lässt sich gut in das nationale Wasserqualitätsmonitoringsystem von Chile einbinden. Nicht nur zur Ermittlung von angemessenen Messfrequenzen und -standorten, sondern auch zur begleitenden Analyse der Messergebnisse. Mit dem Modell lassen sich auch für Zeitpunkte und Standorte, die nicht direkt bemessen werden, Aussagen über die Nitratkonzentration machen. Darüber hinaus kann das Modell auch dazu genutzt werden, die Auswirkungen von Landnutzungsänderungen oder einer weiterreichenden Behandlung von Abwässern auf die Wasserqualität in Form von Szenarien abzuschätzen.

Die wesentliche Erkenntnis dieser Arbeit ist, dass es auch in Einzugsgebieten mit relativer Datenarmut möglich ist, Aussagen über die zeitliche und räumliche Variabilität von Wasserqualitätsparametern zu treffen, wenn die Determinanten *Abfluss* sowie *punktuelle und diffuse Stickstoffeinträge* in einer Systembetrachtung und Modellierung entsprechend verknüpft werden. Dies schafft eine Grundlage für die effiziente Planung von Monitoringsystemen und kann damit dazu beitragen, den Informationsgewinn der aus diesen Systemen generiert wird, erheblich zu erhöhen bzw. Kosten für das Monitoring einzusparen, indem redundante oder unsignifikante Messungen ausgeschlossen werden. Darüber hinaus ist die Methode schnell umsetzbar, ohne vorab lange Zeitreihen der Wasserqualität zu erheben, was zu einer zusätzlichen Effizienzsteigerung bei der Planung von Monitoringsystemen führen kann.

1. Introduction

Any decision making process in the water sector demands sound knowledge on the state or the processes of the system which ought to be managed, be it a river, a wastewater collector or a watershed. This knowledge is typically provided through surveys or monitoring programs, the latter being long term measurements of variables of the natural or human environment. Many water quality monitoring programs do not provide the necessary information as they measure the wrong variables at inadequate locations with an insufficient frequency.

Monitoring programmes need to be designed under budget constraints. Thus, a selection of most relevant monitoring sites, variables and frequencies, omitting a waste of resources, is important. However, if detailed data on the water resources system is missing, it is difficult to design an appropriate monitoring program. Especially in lower income countries the problem of insufficient data availability is common while the need to economize is even more prevalent.

In the case of Chile, the National Water Service (*Dirección General de Agua*s, DGA) measures water quality four times a year in all major rivers since the mid 1980s. It is questionable if any reliable information is acquired with these sparse measurements and to which extent conclusions can be drawn regarding an optimized water quality program i.e. an improved selection of monitoring points and sampling frequencies of the variables in any given watershed.

It is the overall aim of this research to contribute to the improvement of monitoring design with the help of watershed system analysis and modelling. In particular a method is being developed which allows estimating the variance of a water quality parameter over long time spans. The "a priori" knowledge of the temporal and spatial variability of water quality parameters is a prerequisite for optimisation of monitoring design. Especially in semi-arid environments, the natural variability can be very pronounced within a single year but also inter-annually and is furthermore impacted by human influences of the system.

It is the hypothesis of this study that an adequate analysis of information on the natural and human environment of the watershed will permit to model water quality variability over long periods and thus provide the basis for an optimized monitoring system design. For this purpose, a conceptual model for the modelling of spatio-temporal behaviour is developed for the example of nitrate and applied to the Aconcagua Watershed in Chile. Nitrate was chosen as it is a contaminant of major ecological and human health concern and furthermore is related to the domestic, industrial as well as to the agricultural sector.

After a short description of the state of the art of water quality monitoring design, deficits and research demands are analysed leading to the research question, hypothesis, objectives and methods of the study (**chapter 2**).

A modelling approach is developed to estimate nitrate inflow to sub-watersheds stemming from point and non-point sources after reviewing and discussing the environmental behaviour of nitrogen and nitrate in watersheds (**chapter 3**).

The present study takes the Aconcagua watershed in Chile as a case study and consequently, this watershed is described providing all relevant information which is subsequently being used for the modelling of nitrate. The relevant determinants of water quality are analysed and quantified. Here, remote sensing data and information from various institutions related to the water sector is interpreted together with the available water quality and hydrological data from the Chilean water authorities (**chapter 4**).

In a next step, a sub-watershed of the Aconcagua, the Pocochay near Quillota, is analysed in more detail in order to acquire data with higher spatial and temporal resolution, especially to quantify the impact of irrigated agriculture on surface water quality and to derive the N-export coefficients (**chapter 5**).

Subsequently, the watershed model is populated with data derived from the analysis provided in chapters 4 and 5 according to the modelling approach developed in chapter 3. The modelling environment "Mike Basin", was chosen for this task. The result is a simulation of daily nitrate concentrations for the main stem of the Aconcagua River for the period 1986 – 2006. Predicted values are validated with available observed nitrate concentrations from the same period. This step allows simulating the water quality of the Aconcagua main river in order to estimate its spatio-temporal variability (**chapter 6**).

The obtained results are analysed regarding their suitability for water quality monitoring design. With the simulated behaviour of the river water quality, conclusions are drawn on an optimized monitoring network for the Aconcagua resulting in some recommendations for placement and measurement frequencies of sampling stations (**chapter 7**).

Finally, the overall results of the study are discussed and the method’s transferability to other areas and parameters is considered (**chapter 8**).

2. Background

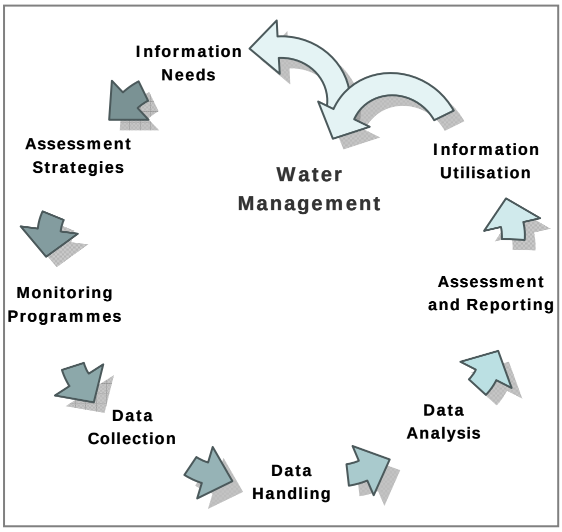
In this chapter, the context of this study – water quality monitoring design – is presented; in particular the importance of monitoring for water management is described (chapter 2.1). Next, the state of the art of water quality monitoring design is summarized and shortcomings are elaborated (chapter 2.2). Based on the review it is concluded that there are many scientifically sound methods to aid monitoring design available in literature. Most of these approaches rely on an *a priori* knowledge or estimate of the variability of the underlying water quality population. This knowledge -or estimator- is often not available due to lack of historic water quality measurements and consequently the state-of-the-art methods of monitoring design are hardly ever applied in current water management practice. This shortcoming leads to the definition of the research problem which forms the basis for the hypothesis (chapter 2.3). Chapters 2.4 and 2.5 describe the objectives and methodology of this research.

2.1. Significance of Monitoring

Water quality monitoring can be defined as the systematic, long term observation of water quality parameters. The task of monitoring is to provide the necessary information on the system behaviour of constituents over time and space as much as these are of concern for water-related decision making. Another common justification for monitoring is to contribute to a deeper understanding of natural or anthropogenic processes (epistemological value of monitoring).

The ultimate driver for monitoring activities is that the gained information will be used to manage water resources adequately, which creates direct social or economic benefits. In China, for example, economic losses due to water pollution were estimated at 286 billion Yuan (36 billion US$) for the year 2004, which amounts to 1.7 % of national GDP in that year (CHINESE GOVERNMENT 2006). Adequate monitoring would contribute to decide where and which types of hazard exist and which countermeasures are most urgent.

2.1.1. Relation between Monitoring and the Decision Making Process



Source: modified based on UN/ECE 2000

Fig. 1 Monitoring cycle

Water quality monitoring forms an important element of water management as it provides necessary information for sound decision making. **Fig. 1** illustrates the monitoring cycle and the role of data collection, processing and interpretation for water management. Water quality monitoring is part of the wider information management, where diverse data types at different scales need to be managed and interpreted in a systematic and holistic manner. Here, water quantity data as well as other environmental and socio-economic information need to be managed and assessed comprehensively. FLÜGEL (2007) elaborates the requirements for an adaptive integrated data information system (AIDIS) as a basis to implement IWRM at the river basin scale. The *AIDIS* system was applied to collaborative research on the European Tiza river basin and is currently being developed further at the Department of Geoinformatics Hydrology and Modelling at the Friedrich-Schiller-University Jena. Monitoring results need to be integrated in such kind of information system in order to serve for comprehensive modelling and decision making processes.

WARD et al. (1986) state that many water quality monitoring programs can be classified as *data rich but information poor*, referring to the fact that often large data sets of water quality monitoring are available but they were gathered without clearly defined objectives derived from actual water management issues. This leads to a large amount of "useless" data. Today, there are many approaches to streamline monitoring design in order to measure only data which actually provide the relevant information necessary for decision making. However, in many less developed countries, due to budget constraints and other capacity bottlenecks, one could even state that they are actually not only information but also *data poor*.

Nowadays, the approach to water management is based on the hydrological unit "Watershed". Therefore, monitoring concepts have to be reconsidered in order to correspond to this new paradigm.

In the **European Union**, for example, the Water Framework Directive (WFD) (EU 2000) clearly demands all water management activities to be based on the watershed approach. Regarding monitoring it is required that all river basin institutions define a monitoring plan in order to support river basin characterization and to allow identifying the impacts of measures which will be established in accordance with the main objective of the Directive to achieve good status of all water by 2015. In particular, monitoring under the WFD should be designed to support:

- The classification of status;
- Supplementing and validating the Annex II risk assessment procedure;
- The efficient and effective design of future monitoring programmes;
- The assessment of long-term changes in natural conditions;
- The assessment of long-term changes resulting from widespread anthropogenic activity;
- Estimating pollutants loads transferred across international boundaries or discharging into seas;
- Assessing changes in status of those bodies identified as being at risk;
- Application of measures for improvement or prevention of deterioration;
- Ascertaining causes of water bodies failing to achieve environmental objectives where the reason for failure has not been identified;
- Ascertaining the magnitude and impacts of accidental pollution;
- Use in the intercalibration exercise;
- Assessing compliance with the standards and objectives of Protected Areas; and,
- Quantifying reference conditions (where they exist) for surface water bodies.

(EU 2003:8, abridged)

Here, the multiple objectives of monitoring become obvious. The objectives to classify status, reference conditions, temporal trends, impacts, effectiveness of measures and to check for compliance all need to be related to different design criteria. In addition, the objective to improve future monitoring design refers to the iterative nature of water quality monitoring design.

In the **USA**, the *Clean Water Act* determines the current water quality regulations. Here, the watershed approach is implemented to a large extend (FORAN et AL. 2000). The GOVERNMENT ACCOUNTABILITY OFFICE (2002) documented the inadequacy of current environmental monitoring practices. The subsequent process of redesign of the monitoring efforts led to a new strategy. In 2006, the National Water Quality Assessment Program (NAWQUA) started with a revised status and trends network with the ultimate aims to:

- Developing regional criteria and reference values in streams for the protection of aquatic and human health;
- Determining the trends in stream impairment (required in EPA 303(d) reports);
- Developing of TMDLs (Total Maximum Daily Loads);
- Identifying useful ecological indicators of nutrient enrichment and pesticide contamination;
- Prioritizing streams and geographic regions for land-management activities;
- Evaluating the effectiveness of environmental protection and management programs over time; and
  Using limited monitoring resources to gain maximum information about water-quality conditions and trends.

(USGS 2006)

DETENBECK et al. (2005) suggest a procedure to design watershed based surveys as response to the demands of the Clean Water Act in the USA. The method they described relies on the widespread availability GIS databases on elevation, land use and soil characteristics.

As a third example, a look at **Chile** gives further insights into the framework of monitoring design. In Chile, the broad objectives for monitoring are set by the water policy and are specified by the DGA (Chilean Water Service). The DGA's Department for Water Resources Conservation and Protection defined the following objectives for a future water quality monitoring network. Monitoring activities should be designed to permit to:

- Characterize water quality at national, regional and watershed level and determine spatial and temporal trends;
- Determine reference (natural) water quality;
- Identify point and non-point pollution sources;
- Verify compliance of water quality standards regarding public health (“Normas Primarias”) and the environment (“Norma Secundaria”); identify zones of non compliance (“Zona Saturada”) and zones in danger of not meeting compliance (“Zona de Latencia”);
- Follow/track the plan for decontamination and prevention;
- Determine the impact of specific projects and the efficiency of means of mitigation, contingency, restoration and prevention;
- Detect and control environmental emergencies, provide necessary data for management of emergencies;
- Provide data for reports on the compliance of international agreements;
- Effectively control compliance (“Fiscalización”);

- Provide data for environmental education and information of the public.
  (DGA 1999b)

These are the qualitative objectives of the monitoring program. In many cases it is extremely difficult to base the design of a monitoring network on general statements like these and they should be transformed to quantitative statements of information demand. Generally, the above mentioned objectives can be translated to information on the "state" (e.g. mean) or "trend" of one or more water quality variables in a given system. To some extent, suggestions on the quantification of information needs are made in the following paragraphs, but it is necessary that this process is conducted by those institutions and decision makers actually using the information generated by the monitoring system, as the ultimate selection of design criteria always involves subjective judgement on the importance of the generated information regarding the demands of society and on the related costs.

2.1.2. Definitions and Types of Monitoring

Monitoring is a type of data acquisition. In simple terms, it is the activity, which allows obtaining information on the state of a system or process. Related to water quality it is usually distinguished from assessment and survey (compare Box 1).

Box 1 *Definitions*

Monitoring:

Monitoring is the process of repetitive observing, for defined purposes, of one or more elements of the environment according to pre-arranged schedules in space and time and using comparable methodologies for environmental sensing and data collection. It provides information concerning the present state and past trends in environmental behaviour.

Assessment:

Evaluation of the hydrological, morphological, physico-chemical, chemical, biological and/or micro-biological state in relation to reference and/or background conditions, human effects, and/or the actual or intended uses, which may adversely affect human health or the environment.

Survey:

A finite duration, intensive programme to measure, evaluate and report the state of one or more components of the environment for a specific purpose.

Definitions after UN/ECE (2000)

Whereas *monitoring* is a general term, which can be applied to almost any type of systematic, long term data collection, *water quality monitoring* can be classified according to the system from which data is being collected (compare Fig. 2). In a broad sense "natural" (ambient) and "technical" (artificial) systems can be distinguished. The first is related to saline or freshwater ecosystems and the latter to drinking water, wastewater or industrial water networks. Ambient water quality monitoring can be subdivided according to the water body that is subject to monitoring, as the design and operation of the respective monitoring systems differs significantly. This study deals with stream monitoring as a part of surface freshwater monitoring. Stream water monitoring is usually classified by the high temporal variability of the underlying data, whereas lakes, coastal and groundwater systems usually have more stable conditions, since their higher volumes make them more inert to rapid environmental fluctuations.

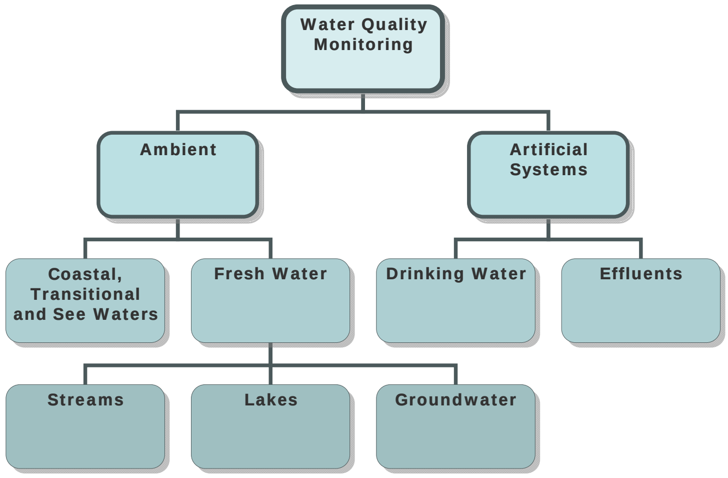


Fig. 2 Classification of monitoring approaches according to water body

(Own concept)

Monitoring systems can further be classified according to their purpose. Tab. 1 relates the different objectives of monitoring programs with the characteristics related to sampling design.

Tab. 1 Overview of major types of monitoring according to their purpose

Type	Objective	Characteristics
Reconnaissance	screen system under study, detect areas of concern	shorter periods, less systematic
Impact	detect and quantify the impact of activities/measures	before/after, upstream/downstream, and/or paired watershed approach
Alert	send signal if trigger value is reached	high frequency/continuous, online
Trend	detect long term trends	long term, fixed station
Compliance	check if standard or limit values are met	legislation driven
Load/effluent	quantify pollutant load of flowing water	discharge related

Source: own concept

Furthermore, water quality monitoring can be classified according to the approach of the monitoring regarding the type of parameters and media of concern:

- Physico-chemical analysis of water, suspended matter, and sediments;
- Eco-toxicological monitoring;
- Biological monitoring.

Biological and eco-toxicological monitoring is typically performed at low frequencies, usually every few years to several times per year.

2.1.3. Conclusions

Monitoring is a pivotal part of the decision making process in water resources management. In order to provide the necessary information for an effective water management, monitoring needs to be designed to cater the information requirements. Different types of monitoring can be differentiated according to the medium of concern (lake, river, groundwater etc.) and according to the purpose (trend, compliance, impact, etc.).

The legal framework and the budgetary constraints are important elements of the network design process. In the case of Chile, which serves as a case study in this work, the most relevant design criteria are determined by the recently introduced water quality law (Norma Secundaria) implemented by the Chilean Water Service (DGA).

2.2. Review of Monitoring Network Design

2.2.1. Introduction

As described above, water quality monitoring is an essential and significant part of water management as it provides the necessary information for the decision making process. A thorough planning of monitoring systems is indispensable in order to provide the required information and to realize it in a cost-effective way, omitting the production of redundant information or of data with low information content. Box 2 reviews basic rules for designing monitoring programs.

Box 2

Ten Rules for a Successful Monitoring Programme (UN/ECE 2000):

1. The information needs must be defined first and the programme must be adapted to them afterwards and not vice versa (as was often the case with multi-purpose monitoring in the past). Adequate financial support must then be obtained.
2. The type and nature of the water body must be fully understood (most frequently through preliminary surveys), particularly the spatial and temporal variability within the whole water body.
3. The appropriate media (water, particulate matter, biota) must be chosen.
4. The parameters, type of samples, sampling frequency and station location must be chosen carefully with respect to the information needs.
5. The field equipment and laboratory facilities must be selected in relation to the information needs and not vice versa.
6. A complete and operational data treatment scheme must be established.
7. The monitoring of the quality of the aquatic environment must be coupled with the appropriate hydrological monitoring.
8. The quality of data must be regularly checked through internal and external control.
9. The data should be given to decision makers not merely as a list of parameters and their values, but interpreted and assessed by experts with relevant recommendations for management action.
10. The programme must be evaluated periodically, especially if the general situation or any particular influence on the environment is changed, either naturally or by measures taken in the catchment area.

The **monitoring network** can be defined as the sum of sampling stations within a system such as river basin or a particular water body, where selected parameters are determined according to a specific sampling schedule. It forms part of a larger system of data management, consisting of the following elements (compare WARD et al. 1990, chapter 2):

- Sample Collection
    - sampling procedures
    - field measurements
- Laboratory Analysis
    - standard laboratory methods
    - quality assurance and management
- Data Handling
    - data storage and processing, Meta-data
    - statistical data interpretation
    - tests for validity of data
- Reporting
    - reported values, statistics
    - graphs, figures, maps
    - reporting guidelines
- Information Utilization
    - check compliance with laws and standards
    - management decisions: measures, revision of legal framework
    - re-define objectives of monitoring, redesign monitoring network.

The water quality monitoring network design refers primarily to the first point "sample collection". The main questions to be answered are:

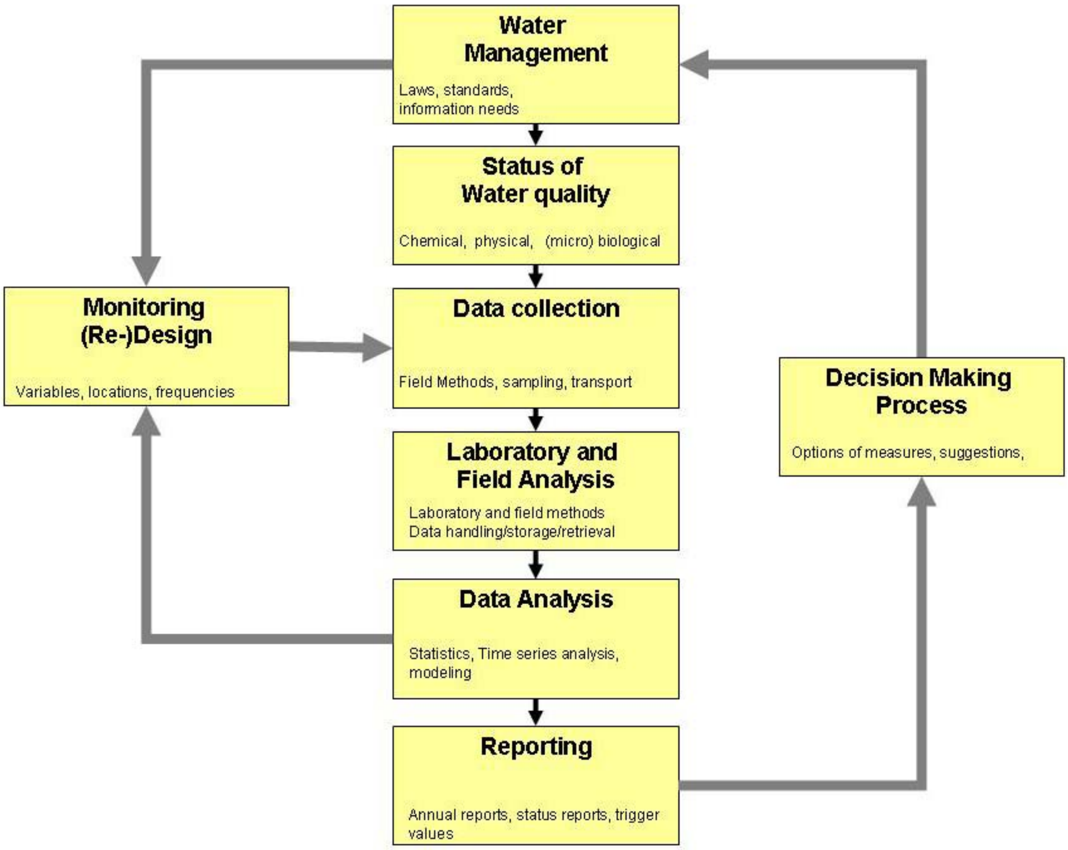
- Where to sample?
- When to take samples and how frequently?
- Which parameters to analyse?

In order to answer these questions, the monitoring network design, often also called "re-design" since in most cases some prior monitoring network is in place, needs to consider two major aspects:

- The information requirements defined through the legal and operational aspects of water resources management;
- The spatio-temporal variability of the parameters under consideration.

Fig. 3 visualizes the role of monitoring network design as related to the overall water quality management and monitoring cycle.

Monitoring design relates to all elements of the monitoring cycle. The choice of laboratory methods and the related analytical error has an impact on the number of samples which needs to be taken; the statistical method of data analysis impacts the sampling frequency, validity tests may influence the number of samples to be taken and the selection of parameters (ion balance), and reporting requirements may add further elements to the monitoring design.



Own concept based on various figures in WARD et al. (1990) and TIMMERMANN et al. (2000)

Fig. 3 The role of monitoring network design in the context of the water management and monitoring cycle

Science is primarily asked to support the monitoring design in two major fields: i) developing adequate methods to quantify information needs and to analyse data accordingly ii) to assess the underlying spatio-temporal variability of water quality parameters.

This scientific basis for water quality monitoring design has been elaborated in many textbooks and journal publications. The following provides an overview of the status of water quality network design as discussed in scientific literature. It names the most essential works without intending to repeat their content in detail, rather to look which methods are available regarding the scientifically based determination of sampling locations and frequencies.

SANDERS et al. (1983) in their book "Design of Networks for Monitoring Water Quality" provide the first comprehensive summary on the process of monitoring system design. They emphasise the importance of the clear definition of information requirements and the role of statistics for water quality monitoring design. In chapter 7, they summarize the network design procedures: Regarding the sampling location, they propose Sharp's method (SHARP 1971) while for the micro-location they provide several formulas to determine the mixing length. Regarding monitoring frequencies, they discuss general approaches of determining measurement frequencies on the basis of watershed size, or on assumptions on seasonal flow variation. They emphasize the importance of variability of constituents in order to select the optimal measuring frequency. The importance of analysing data for seasonality and trend before determining monitoring frequencies is highlighted as well. Quantitative, statistics based approaches are elaborated to determine sampling frequencies. They all depend on an estimator for the underlying data variability, which usually enters as the sample variance s^2 in to the formulas.

WARD et al. (1990) comprehensively describes the design of the whole monitoring system emphasising the "information context" defined by the water management system and intended information utilization. Concerning the selection of the sampling frequency (pp.115-116), they name the following criteria to be considered (abridged):

1. Information sought
2. Statistical method to employ
3. Statistical characteristics of the water quality population
4. Budget available
5. Distance to laboratory
6. Number of sampling sites
7. Ability of laboratory to process samples

While the first two points describe issues related to transforming qualitative information demands into quantitative objectives and selecting adequate data analysis techniques, and points 4-7 are practical restrictions to derive monitoring frequencies, point 3 refers to the natural characteristics of the water quality population under study. However, no further reference is made on how to determine these statistical characteristics.

HARMANCIOGLU et al. (1999) provide an equally comprehensive guide to water quality monitoring design. Next to the approaches and concepts for monitoring design mentioned in SANDERS (1983) and WARD et al. (1990), they introduce the "entropy method" based on the entropy theory described by SHANNON (1948) as a further tool for determining monitoring frequencies and locations. Important to note is that in this method the major input for the variable of concern is the probability density function, making an estimate of the statistical characteristic of the variable necessary. They applied this method for sampling site locations in a stretch of the Mississippi river, where 26 years of monthly data were available. CHAPMAN (1996; Annex 10.1) and UN/ECE (2000; chapter 5) provide another useful overview on the design of water quality sampling programs.

2.2.2. Monitoring Frequency

Monitoring systems typically need to be designed to be able to answer the following questions:

- What is the "true" mean of the variable x?
- What is the temporal trend of variable x?

For the monitoring design this means: how many samples are necessary in order to detect a trend, assess a mean or check if a defined portion of variables is below or above a set limit value.

2.2.2.1. Assessing the True Mean

Water quality variables can be expressed in form of a frequency distribution showing all measured values and their relative frequency. If the distribution of the variable is assumed to be normal, the underlying population can be described through a normal probability density function (pdf) with mean (μ), and variance (σ^2). Sample estimators of the population are the sample mean ($\bar{x}$), sample variance (s^2) or sample standard deviation (s).

If the objective of monitoring is to define the mean value of the water quality population, the temporal distribution of the required measurements depends on the objective of the monitoring system and of the variability of the constituents. A high variability requires more frequent measurements in order to obtain the statistical certainty to estimate the mean (WARD et al. 1986).

Once a unbiased estimate for variability of the different variables is available, a very critical point in monitoring design, the approach to optimise measuring frequency is to define a confidence limit for the variable and station to be determined and then calculate the minimum number of samples to guarantee that the samples measured will lie within this confidence interval.

$$\left[\bar{x} - t_{\alpha/2}s \le \mu \le \bar{x} + t_{\alpha/2}s\right] \tag{1}$$

x = sample mean
$t_{\alpha/2}$ = student t value
s = standard deviation
(compare SANDERS et al., 1983:68)

The interval is defined for a certain confidence level 100·(1 - α) where α is also referred to as the "power" of the statistical test and relates to a certain t-value (see above formula). If, for example, we assume a 95 % confidence level it can be written as

$$\left[\bar{x} - 1.96\frac{s}{\sqrt{n}}; \bar{x} + 1.96\frac{s}{\sqrt{n}}\right] \tag{2}$$

$\bar{x}$ = sample mean
s = standard deviation
n = number of samples

If a normal distribution of the water quality variables is assumed and there exists an estimate of the variance between them, the minimum number of measurements to certainly obtain the average, can be determined according to formula *3* (compare SANDERS et al. 1983:157).

$$n = s^2 \frac{t_{(\frac{\alpha}{2})}^{2}}{d^2} \tag{3}$$

Where:
n = minimum number of measurements
d = maximum permitted error ($\bar{x} - \mu$)
t = value t-Student for the selected significance level (α)
s² = variance

The underlying assumption is that the data is random, independent and identically distributed. The maximum permitted error (d) and the significance level (1-α) will be chosen according to the desired accuracy of the estimates of the mean as defined in the monitoring program objectives and the correspondent standards. The variance, on the other hand is an intrinsic characteristic of the system under scrutiny.

SANDERS and ADRIAN (1978), due to lack of water quality data, applied this formula to stream flow data, where it showed reliable results. TOKGOZ (1992, cited in HARMANCIOGLU, 1999) tested the method on a set of water quality measurements for the Sakarya basin in Turkey and found that it could not be applied to determine reliable estimates on minimum number of measurements since the available historic data of the Sakarya basin was not sufficiently dense.

2.2.2.2. Assessing tendencies

To decide if a temporal trend in any given data set is prevalent can be statistically determined by hypothesis testing. A Null hypothesis (H_0) can be formulated stating that there is no change between the data of period A and period B. Typically the hypothesis is based on the means: H_0: $\mu_A=\mu_B$. This hypothesis can be accepted or rejected. An alternative hypothesis can be formulated stating that there is a significant difference between the two datasets (H_1).

In the two cases a decision rule is required on when to reject or accept the hypothesis. There is a risk of rejecting H_0 while actually there is no trend (Type I error, false alarm) and there is a risk of detecting no trend while there actually is one (Type II error, "slipping through the net"). These two error types are determined by the confidence level (1-α) and the power (1-β) (LETTENMAIER, 1976).

The selection of the method to detect a trend depends on (HIRSCH et al., 1991):

- The type of trend hypothesis: testing for a step trend versus monotonic trend;
- The assumed distribution of the population (parametric versus non-parametric methods;
- The type of data (e.g. load versus concentration);
- The occurrence of censored data.

Techniques used for step trend analysis include parametric tests like the two sample t-test and non-parametric alternatives such as the Mann-Whitney test if the underlying population is assumed to be non-normally distributed (LETTENMAIER, 1976). Parametric procedures for the monotonic trend alternative are regression analysis of the water quality variable as a function of time: URI (1991) applies a parametric method of Box and JENKINS (1970) for trend detection which he successfully applied to the case of sediment loading of the Iowa River. A non-parametric approach is the Mann-Kendall test (Hirsch and Slack 1984, Hirsch et al. 1991) or Spearman's Rho test (LETTENMAIER, 1976). HIRSCH et al. (1982) describe testing trend detection for data sets with seasonality, skewness and serial correlation. In this case they propose the Kendall test as the best option to detect a trend. How to proceed with data showing non-detects is discussed in detail in HELSEL AND HIRSCH (2002), chapter 12.7. LETTENMAIER (1991) successfully applies the seasonal Kendall test to 403 stations of the US-NASQAN network, defining as criterion a relatively moderate significance level of 10 %. A more comprehensive summary on parametric and non-parametric methods applicable for trend detection is found in HARMANCIOGLU et al. (1999, pp. 252).

If parametric methods are intended to be applied the number of required samples necessary in order to detect a trend with a specified confidence level, power and minimum detectable difference can be formulated as (compare LETTENMAIER 1976; WARD et al. 1990).

$$n = \frac{12s^2\left(t_{\alpha,(n-2)} + t_{\beta(1),(n-2)}\right)^2}{\delta^2} \quad \textbf{(4)}$$

Where:

n = minimum number of measurements
δ = minimum detectable difference between the time periods
t = value t-Student for the selected significance level (α)
s^2 = variance

To conclude it can be stated that a large array of methods is available to aid selection of optimum sampling frequencies if the objective of the monitoring program is trend detection or determination of the true mean of the sampled population. All these methods depend on a prior knowledge or estimate of the sample variance.

2.2.3. Monitoring Locations

The sampling location, even more than determination of measuring frequencies, is typically decided upon by water managers according to intuition or due to practical concerns. The literature shows very few approaches to support this part of monitoring design. The most applied method is the one of SHARP (1971) who uses HORTONS (1945) stream order concept to divide the hydrological network in half, quarters, eighth etc., through weights he assigned according to the stream order. SANDERS et al. (1983) enlarge this concept in coupling stream order with known or expected pollution load or concentration, leading to priority stations which represent the largest part of the hydrological network and pollutant. DIXON et al. (1999) brought Sharps method a step further by applying simulated annealing techniques and cost functions to evaluate the relative priority of sampling locations. OZKUL et al. (2000) applied the Entropy method as a measure of information content to the combined optimization of frequencies and locations to a stretch of the Mississippi River. Their method allows reducing redundant information by adequate spacing of sampling sites. STROBL et al. (2006a and 2006b) propose a methodology to determine priority monitoring sites called CSP (Critical Sampling Points) for the case of phosphorous and applicable to small, upland, predominantly agricultural-forested watersheds. They define a series of crucial factors that are important for Phosphorous loadings:

- Slope
- Profile curvature
- Plan curvature
- Aspect and solar radiation
- Topographic Wetness Index
- Sediment transport index
- Stream Power Index

- Buffering Potential
- Flow Path length
- Soil Permeability
- Land Use

All but the last factor were considered as continuous values and incorporated into a fuzzy logic approach, values between 0 and 1 representing the relative pollution potential. Land use was classified according to major classes and export coefficients were derived from literature for each class. The model developed on the basis of theses variables is raster based. Providing a value for each of the 11 variables for each cell permits to estimate potential loadings. Later these loadings are aggregated for basins and sub-basins. The result is a prioritisation of sub-basins according to their potential pollution impact. From this a prioritization of monitoring locations is derived. However, this methodology of assigning sampling locations is based on the pollutant load (here total phosphorous) and not on the expected concentration in the receiving stream.

All the above mentioned approaches refer to the macro location of sampling stations within a river or a watershed system. SANDERS et al. (1983) point out that there are three levels of monitoring station locations: (i) macro-location (defining the river reach to be included in the monitoring network), (ii) micro-location (dependent on the mixing lengths of waters entering from pollutant outfalls or tributaries) and (iii) the representative location (points in the cross-section to represent the water quality of the whole stream).

For the selection of monitoring locations often the choices and thus room for optimization are limited due to practical restrictions. Background sites necessarily need to be taken upstream of human impacts while impact stations need to be taken downstream of disturbing activities.

National guidelines on monitoring provide general support on monitoring design to practitioners in the selection of monitoring sites. The following is a list of best practices compiled from various sources.

Criteria for site selection are:

- Relevance: hot spot, probability to exceed limit values
- Omit spatial correlation
- Accessible all weather (bridge, solid shore)
- Riparian use / ownership / cooperative landowner
- Power available
- Equipment protected from vandals
- Stable streambed, Sufficient stream gradient, not at meander
- “complete mixing”
- No road or other drainage influence directly upstream

(compare USDA, 1996; UNECE, 2000; ANZECC, 2000)

For regulatory monitoring, the probability that a certain limit value is exceeded can serve as a selection criterion. At sites, where the data population is expected to be below limit values at all or most times, no significant information can be gained from sampling and they can be excluded from monitoring. For this decision the mean and the variance of population should be known and decision criteria need to be established in order to determine if the station can be excluded.

Another important factor to decide to exclude sampling sites is **spatial correlation.** If water quality parameters of two sites show a high correlation, the additional information gained from including both stations is low.

If the monitoring requires detecting the **impact of a certain activity** or measure, various design strategies are possible:

- Before and after (site location downstream of the impact location, monitoring needs to start before impact occurred)
- Top and bottom (site location upstream of activity and downstream of activity)
- Paired watershed approach (compare two or more test watersheds with the one where the measure or activity is taking place)

In any of the above cases, the sampling sites downstream of the impact should be determined according to mixing length formula to guarantee representative sampling. SANDERS et al. (1983) provides a review of various mixing length formula.

Another aspect of monitoring site selection refers to the determination of control sites to establish reference conditions. Here GIS can support the selection of representative areas with similar environmental conditions (geology, climate, ecoregions and human impacts). Currently this issue is intensively discussed under the task to implement the EU Water Framework Directive and the related intercalibration excercise (compare WALLIN et al. 2003).

It can be concluded that for the selection of monitoring sites less stringent methods are available than for the determination of measurement frequencies. However, for many of the above mentioned methods, a profound prior knowledge of the temporal and spatial behaviour aids monitoring design, for example to assess spatial correlation or to estimate the probability that water quality parameters are above a set limit or a guidance value.

2.2.4. Variability of Water Quality Parameters

From the above it can be concluded that for the optimum design of monitoring frequencies an appropriate knowledge on the variability of the parameters under scrutiny is indispensable. First, it is necessary to estimate variance in order to make any informed guess on the monitoring frequency. Second, it is import to estimate if the data is normally distributed and independent or if seasonal trends are likely to occur in order to select an adequate method of analysis (e.g. non parametric or parametric methods for trend detection).

The variability of a water quality parameter is product of a multitude of aspects. There is a natural variability caused by the temporal and spatial distribution of environmental factors like climate, rock material, soils and vegetation. This natural variability is overlain by human interventions to the hydrological cycle like municipal, industrial and agricultural water uses and related pollution sources as well as land use changes. Even more variance is added to each data set through sampling, analytical, and reporting errors.

Inter-annual water quality parameters in semi-arid watersheds are extremely variable as the discharge -one of the major driving forces of water quality variance- is more variable than in temperate climates. MEYBECK et al. (2004) report that, for example, average annual nitrate concentrations in the Ebro (Spain), range between 0.5 mgl^{-1} and 3 mgl^{-1}

and N-fluxes in the Aude basin (France) vary between 0.5 $\cdot 10^6 Kg \cdot a^{-1}$ and 8 $\cdot 10^6$ $Kg \cdot a^{-1}$ in the time period 1975-2000.

Next to large inter-annual variability, rivers in subtropical and temperate climate zones also show a high intra-annual variability of water quality parameters mainly due to high seasonality of discharges. However, in the Elbe River, for example, nitrate concentrations show a marked seasonality in some years but not in others (compare LEHMANN & RODE, 2001).

Finally, it should be noted that in some cases also diurnal variability may be significant. These could be due to biological causes, especially photosynthesis or a result of human factors like industrial production patterns and related discharges, irrigation cycles etc. FOGLE et al. (2002) observed relatively strong diurnal variations for pH and temperature. However, those for nitrate and electrical conductivity variations were not significant.

2.2.5. Shortcomings of Monitoring Design Methods

From the discussion on monitoring design the conclusion can be drawn that quantitative, statistical approaches of monitoring network design are described in literature since the 1970s. A multitude of advanced methods to optimize the selection of sampling frequencies are elaborated, discussed, applied and approved in scientific literature. However, every method on monitoring design depends on a realistic estimate of the variance of the population of the water quality parameter under scrutiny. All of the above cited authors use existing water quality measurements as a basis to estimate variance and subsequently to derive an optimal sampling location or frequency. In most cases the methods are applied to cases where high frequent (weekly, monthly) measurements of water quality variables are available for long data records. In other cases, the methods are applied to time series other than water quality, like discharge data due to lack of consistent water quality data sets.

While many authors stress the need to have knowledge of sample variance prior to monitoring design, little is said about how to obtain it. WARD et al. (1990) assert that "to determine the sampling frequency and the duration of the operation of a network needs to have an *a priori* knowledge of temporal variability" (WARD et al., 1990:188). CHAPMAN (1996) states regarding monitoring design: "The main difficulty lies in having already available an acceptable estimate of the variance of the population about to be sampled!" (CHAPMAN, 1996, appendix 10.1:2). In the same sense STROBL (2007) in a more recent review article on monitoring network design points out that "More statistically advanced approaches [...] have been developed, but often rely on extensive time series data for determining the optimal sampling frequency. Unfortunately, with the general exception of mean daily discharge, water quality databases of adequate size, length, as well as reliability are commonly the limiting factor in applying these techniques".

COCHRAN (1977) suggests the following four options to estimate *a priori* variance: "(i) using existing information from the same system or a similar system, (ii) using an informed judgement (expert knowledge), (iii) a two-step sample where the results of the first step are employed to estimate monitoring design factors for implementing the second step, and (iv) use of a "pilot study" to estimate design factors" (Cochran, 1977:76).

While the first alternative is often not possible in "data poor" regions the second is difficult to be grasped in scientific terms. The third and the fourth option both depend on the long term variability of water quality variables and the duration of the first step sampling or pilot study. Nevertheless, as discussed above, the long term variability of water quality parameters highlights the difficulty of estimating variance based on a sampling program of a few months or even a year, especially for areas with high climatic variability as most semi-arid regions and for areas with a high temporal dynamic of human impacts which makes inter-annual variance of a water quality parameter particularly high.

SANDERS et al. (1983) suggest the rough estimator $s^2=(Range/4)^2$ where s^2 is an estimator of the variance and Range is the expected range of the sampled population.

We can summarize that monitoring design does not face the shortcoming of unavailable methods to derive optimized frequencies or locations but rather the inability to provide an informed *a priori* estimate of the variability of the water quality parameters. This, at a first glance, does not seem to represent a scientific but rather a practical problem as it highlights the need to establish long term water quality measurements.

However, asking the question if there are means to estimate long term variability of water quality parameters based on other environmental variables, for which long term data records are available, then a scientific approach can be formulated to describe water quality variance as a dependent variable of these determinants.

Thus, the need arises to find other ways to estimate the variance of water quality populations in order to design water quality monitoring networks more adequately.

2.3. Research Problem

The previous discussion made clear that:

- Statistical approaches to optimize water quality monitoring design are well developed and described in scientific literature;
- These approaches all depend on prior knowledge or estimates of water quality variability (expressed as variance);
- Reliable estimates of water quality variance are often not available due to lack of sufficiently dense and long term water quality measurements;
- Described methods to estimate water quality variance, if no historic measurements are available, are very crude or depend on expert judgement.

Thus, the question arises whether it is possible to model water quality variability based on other environmental parameters for which data is available. Then, the **problem** can be formulated as "how to estimate water quality variance based on other environmental factors for a sufficiently long period as to account for long term environmental variability".

Based on this problem the following **hypothesis** is formulated for this study:
"The long term variability of water quality constituents in a stream can be hindcasted based on temporal data sets of the determinants `water discharge´, `point sources of pollution´ and `diffuse sources of pollution´ using a watershed based modelling approach."

This hypothesis is to be tested and validated in a sample watershed. For this purpose, a river of a semi-arid environment (Aconcagua River in Chile) and the constituent "nitrate" are chosen as a case study. The available data on past nitrate measurements will be taken to validate the model.

Furthermore, it has to be validated that useful monitoring design recommendations can be elaborated on the basis of the above mentioned estimate of variance and the related watershed analysis. This should be demonstrated through using the analysis results for a monitoring design for the case of nitrate leading to appropriate location and measurement frequencies in the Aconcagua basin.

The **Aconcagua Watershed**, located in central Chile, was chosen as a case study. It is a medium size watershed (7550 km²) in a semi-arid environment with relatively strong human impacts regarding water use and contamination stemming from settlements, irrigation and to a minor extent from industry and mining. Available water quality data is limited to four measurements per year, in some years even less or nil. This low data availability does not permit to obtain any direct conclusion regarding the temporal variability of constituents. On the other hand, data on water discharges, water use, land use and point sources is available, permitting to test the hypothesis of deriving water quality time series on the basis of these determinants.

Nitrate was chosen as an example parameter since it is related to several human activities like land use, urban and industrial developments. Furthermore, it is a constituent of concern regarding eutrophication of rivers and the receiving coastal waters as well as it is related to human health impacts. It is a variable included in the legislation for the control of surface waters of the Aconcagua basin (Norma Secundaria) and thus mandatory to be considered in future monitoring activities.

2.4. Objectives

In line with the previously stated research problem, the main objective of this study is to determine the spatial and temporal distribution of nitrates in the Aconcagua River as a function of other environmental parameters and to derive estimates of the variance of nitrate as a basis for a statistically based design of the water quality monitoring network.

This main objective leads to a series of further specific objectives:

1. Develop a conceptual model which describes the nitrate concentrations over space and time in watershed with overall poor data availability;
2. Analyse the natural and anthropogenic factors that determine the water flow in the Aconcagua River as the main variable influencing nitrate transport and dilution;
3. Describe and quantify the factors relevant for point and diffuse nitrate contamination over space and time in the Aconcagua watershed;
4. Model the behaviour of nitrate concentrations in the Aconcagua river in space and time and validate the data with existing nitrate measurements;
5. Develop and apply design criteria for monitoring nitrate according to the spatio-temporal variability of nitrate in the Aconcagua River;
6. Analyse aspects of transferability of the proposed method to other constituents to other watersheds.

2.5. Methodology

Based on the above mentioned objectives, the following methodological approach visualized in Fig. 4 was developed:

1. Development of a model approach, which is able to simulate nitrate concentration in the river network for daily time steps for watersheds with limited data availability regarding point and diffuse pollutions sources (Chapter 3).

2. The Aconcagua watershed is analysed taking into account those factors with a major influence on the hydrology and hydrochemistry of the receiving water. The spatio-temporal analysis considers available data on precipitation, runoff, land use and irrigation practices, groundwater storage, municipal and industrial point sources. These data are prepared in formats as necessary for the subsequent nitrate modelling (Chapter 4).

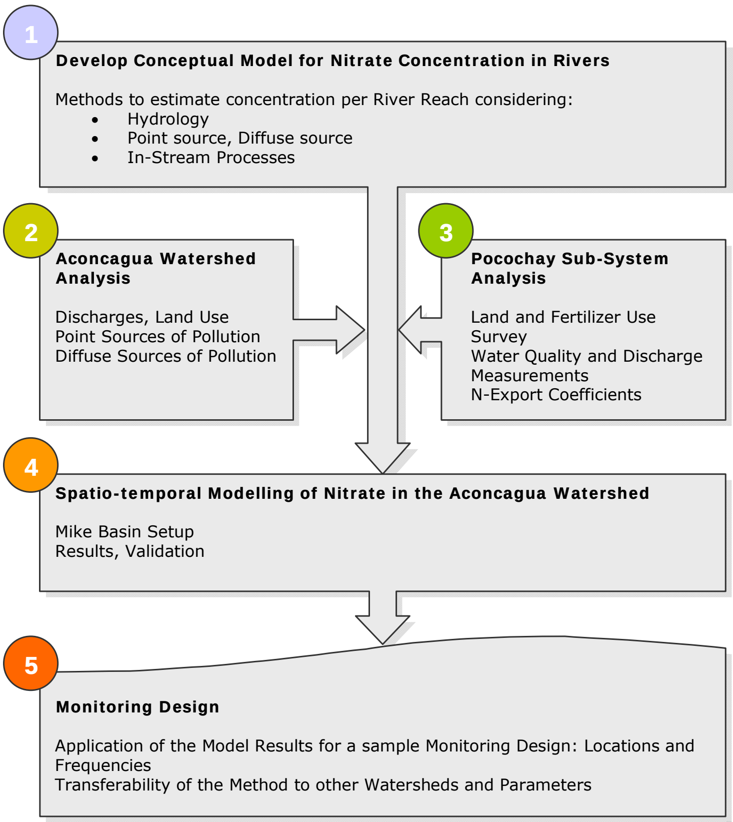


Fig. 4 Overview of methodological approach

3. Since data on the diffuse pollution stemming from irrigated agriculture — a crucial factor with impact on water quality — are neither available for the Aconcagua nor for similar watersheds in Central Chile, a special study was designed in one sub-watershed, resembling the typical characteristics of other agricultural areas in the Aconcagua watershed. Here, in the Pocochay sub-watershed, water quality and discharges were measured over a period of three years. The land use and agricultural practices as well as the driving force for diffuse pollution were analysed, based on a specially designed land and fertilizer use survey. The main results of this study are estimates on export coefficients of nitrate stemming from irrigated agriculture (Chapter 5).

4. Based on the information acquired in steps 1 to 3, the behaviour of nitrate in the Aconcagua River is modelled in space and time. For this purpose a GIS-based network

model (Mike Basin) is employed which allows to model the transport of water and constituents within the system. The water quantity is modelled based on measured inputs from gauged upper watersheds, estimates of discharges from ungauged basins and the withdrawal as well as return flows from all major water users (irrigated agriculture, municipalities and industries). The water quality is determined by the combination of river flows with spatially distributed N-loads from irrigation return flows, municipal and industrial wastewater discharges as well as kinetic factors of in-stream transformation and decay processes. The result is an estimate of the variability of nitrate concentrations over space and time on a daily basis for the period 1986-2006. This estimate is validated based on the existing measurements of nitrate within this period. If the measured values are represented well through the modelling results, it can be assumed that variability can adequately be expressed by the approach (Chapter 6).

5. Subsequently, statistical and other criteria for monitoring design are established and applied to the results of the nitrate modelling. Regarding the location of monitoring sites, these refer to the probability of a certain point in the river to reach critical concentrations of nitrate. Minimum sampling frequencies per year are calculated based on the modelled variability of nitrate concentrations and different levels of statistical confidence and maximum allowable errors (Chapter 7).

6. Finally, the results are interpreted according to their transferability of the methodology to serve as a basis for monitoring design a) in the concrete case of the Aconcagua, b) for other watersheds and c) related to other constituents (Chapter 8)

3. Nitrate Processes and Modelling

With the aim to derive a concept to model variability of nitrate concentration in surface water this section first discusses the environmental behaviour of nitrate with relevance to impacts on surface water. After considering different approaches to modelling nitrate concentration at the watershed level, an appropriate method is developed which allows providing long term data on nitrate variability. The latter is related to objective 1 of this study.

3.1. Environmental Behaviour of Nitrate

Since nitrate is the component taken as an example for monitoring design in this study, it is necessary to review the behaviour of this component related to the aquatic environment with a special view on semi-arid environments and on irrigated agriculture which is the main nitrate emitting activity in the Aconcagua watershed. Subsequently, the major sources and processes of nitrate which are relevant for the modelling exercise are discussed.

3.1.1. Significance of Nitrate Pollution in Surface Waters

Due to heavy impacts of humans to the global nitrogen cycle, levels of nitrogen, especially nitrate as the most stable and soluble form of nitrogen, in surface and groundwater have increased significantly over the past decades (HOWARTH et al., 1996). Today, anthropogenic nitrogen fixation is in the same order as natural nitrogen fixation through biological N fixations and lightning (VITOUSEK 1997; MEA 2005). Fertilizer use at a global scale tripled between 1970 and 2005 and is likely to increase further, especially in developing countries (IFA 2006). This overall trend follows a similar pattern in all regions of the world also followed by Latin America and Chile (MARTINELLI et al. 2006; DONOSO et al. 1999).

Nitrate in surface water, together with the presence of phosphates, contributes to eutrophication. One impact of eutrophication is algal blooms. This increases biomass production leads to anaerobic or low oxygen conditions on one hand and to the release of toxic or bad smelling or toxic substances on the other hand (EC and WHO 2002).

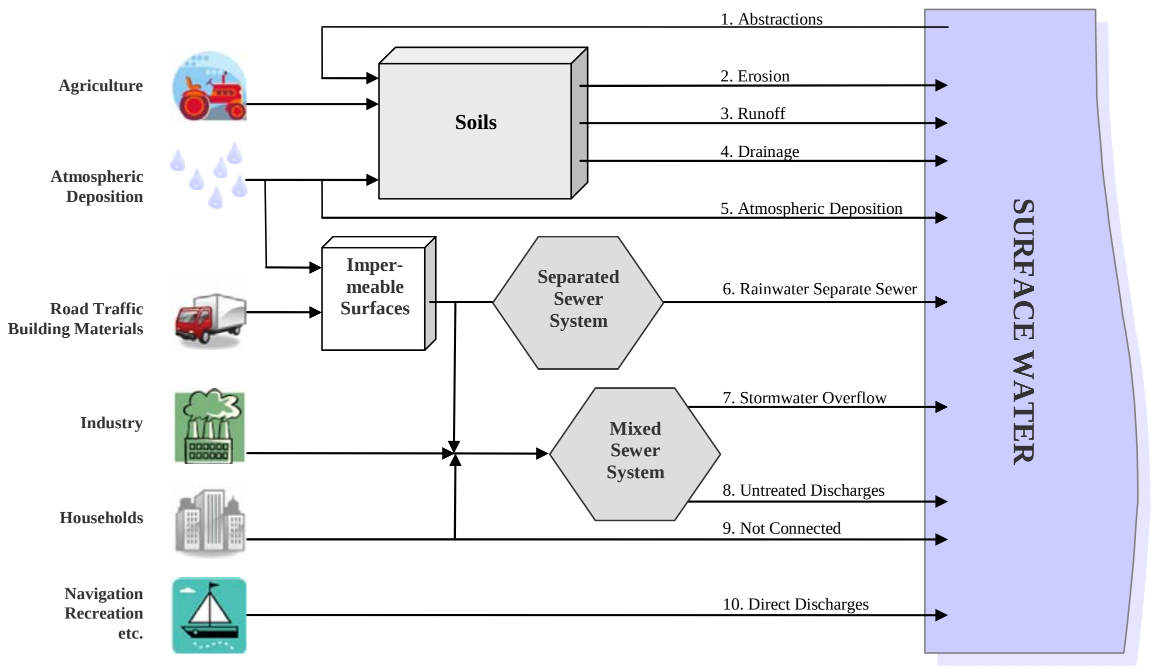
In other studies, nitrate pollution, even at levels that are considered safe for human consumption, showed having effects on amphibian aquatic life (ROUSE et al. 1999). In New Zealand, nitrate-N trigger values (protection level of 95% of species) for freshwater is 7.2 mg l^{-1} based on acute toxicity levels of nitrate to 45 aquatic species (NIWA 2002).

Furthermore, nitrate in drinking water is related to the blue baby syndrome, caused by methemoglobin formation, which can lead to death if high concentrations are prevalent (COMLY 1945; GELBERG et al. 1999). Drinking water with high nitrate concentrations has been linked to stomach cancer and negative impacts reproductive health in humans, and to lower productivity in livestock (CUELLO et al. 1976, FRASER et al. 1980). There are also indications of a positive correlation between nitrate in drinking water and colorectal cancer and non-Hodgkin lymphoma (GULIS et al. 2002). Nevertheless, CHILVERS et al. (1984) found that less than 30 % of the total daily nitrate uptake of humans stems from drinking water, which puts the relative importance of nitrate contamination of drinking water in a different perspective.

Further problems directly related to nitrate leaching are the associated economic losses. Fertilizer transported to ground or surface water is a valuable resource which is not converted to crop yield. Thus, nitrate leaching generally contributes to low N-use efficiency. RAUN AND JOHNSON (1999) estimate for worldwide grain production that in 1996 nitrogen use efficiency was a mere 33 %; the unaccounted 67% represent an economic loss of 15.9 billion US $. In irrigated agriculture low N-use efficiency is typically closely related to low water use efficiency.

3.1.2. Nitrogen Pathways to Surface Waters

Nitrogen (N) enters the aquatic environment as inorganic nitrate, nitrite and ammonia and in many forms of organic nitrogen transported by water. Thus the ways it enters surface waters are closely related to the general hydrological cycle. Next to point sources, nitrogen species reach surface waters from land surfaces transported with rain or irrigation water. Major point sources are treated or untreated domestic or industrial waste water as well as runoff collected from impermeable surfaces (compare Fig. 5).



Based on IKSR cited in UNECE (2000), Fig. 10; altered.

Fig. 5 General pathways of pollutants into surface water

A major source for diffuse nitrogen pollution to surface water is agriculture, especially if intensive agriculture with high fertilizer applications is prevalent. According to SPALDING AND EXNER (1993), agricultural leaching is the most important cause for groundwater contamination with nitrate. The transport of nitrogen from soil to surface and groundwater is controlled by the factors land use, soil type, drainage, climate, fertilizer application rate and timing and by management practices.

While ammonium is rather firmly attached to clay and organic matter in the soil, nitrate is highly soluble and mobile and thus the dominant form of nitrogen found in surface water and groundwater.

The process of mineralization by soil bacteria permits the conversion of organic nitrogen to ammonium and later to nitrate and is a key process that determines the levels of mineral nitrogen available for plant uptake and the availability of nitrate for loss by leaching.

High loadings of soils with artificial fertilizers increase the potential for leaching. The main pathway of nitrogen export to streams is by subsurface flow with high concentrations following fertilizer application in winter and during storm events. The winter peaks in temperate climates are associated with a period of soil mineralization of nitrogen compounds while there is a lack of plant uptake. The presence of macro pores or cracks can act as short circuits, accelerating the losses of nitrate. (GISH AND SHIRMOHAMMADI, 1991)

Organic nitrogen in association with topsoil can reach streams via surface runoff, which can occur following a rainfall event. The effect is especially pronounced when strong rainfall events occur right after application of mineral fertilizers, manures and slurries.

Nitrogen **inputs** to agricultural soils are first of all fertilizers (organic and mineral fertilizers). Other input pathways are biological N-fixation as well as dry and wet deposition. The latter can stem from natural (lightning) as well as from anthropogenic activity (e.g. NO_x emissions).

The major **transformation** processes within the soil include the mineralization of organically bound nitrogen, nitrification, denitrification, and NH_3 volatilization.

Nitrogen **outputs** from the agricultural system can occur in form of harvest (after nitrogen uptake by plants), leaching to deeper soil layers and groundwater or surface runoff. If there is more nitrogen in the soil than the plant needs, it is available in access and can potentially be leached. From land surfaces nitrogen is transported to surface water via groundwater flow, interflow, surface runoff or (tile) drainage runoff.

Fig. 6 summarizes nitrogen inputs, outputs and processes relevant to agricultural lands. Next to harvest, volatilization of ammonium and denitrification, runoff and leaching are important pathways exporting nitrogen, especially in the form of nitrate which is highly soluble and as an anion not very tightly bound to soil clay and organic material.

ROLSTON (1978; cited in RITTER AND MANGER, 1985) reported that denitrification occurs only in the anaerobic fraction of the upper soil. In deeper layers (>60 cm), the organic carbon content – indispensable for denitrification to occur – is very low. Nitrogen present in soil zone below rooting depth is considered to be available for leaching since plants can not access nitrate from this depth any more. In the strict sense this is not completely true, since capillary rise can cause an upward vertical movement of nitrogen (MAGETTE (2001) in RITTER AND SHIRMOHAMMADI, 2001:316).

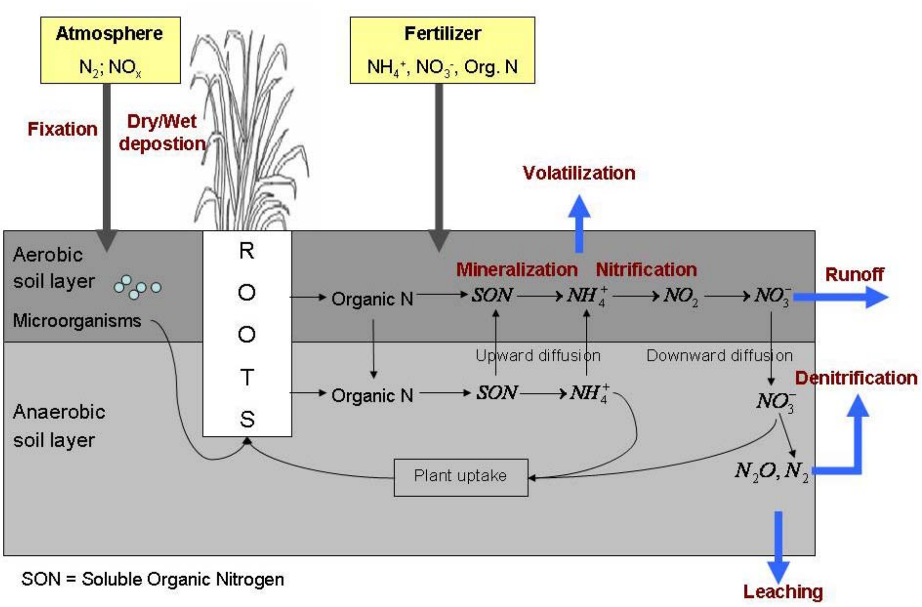


Fig. 6 Nitrogen processes in the soil

3.1.3. Factors influencing Nitrogen Export from Irrigated Areas

Since irrigated agriculture is the only significant land use in the study area, the following discussion focuses on the impact of irrigated agriculture on surface water quality.

3.1.3.1. Water management

SMIKA et al. (1977) quantified the relation between amount of percolating water and nitrate leaching. He conducted a three year study applying different amounts of irrigation water and studied three different irrigation plots on sandy soil with different water but similar fertilizer applications and found that the annual percolation of drainage water was 16, 29 and 73 mm while nitrate leaching was 19, 30.4, and 59.7Kg ha^{-1}, respectively indicating a strong relationship between the two factors.

LETEY et al. (1977) found that the volume of drainage water had the most significant correlation with nitrogen exported from agricultural soils. Several studies confirmed the findings of above cited works that the amount of drainage water is a crucial factor determining nitrate leaching in irrigated agriculture (RITTER et al., 1991; BJORNEBERG et al., 1996). CAVERO et al. (2003) studied two intensively irrigated drainage areas in the Ebro valley and quantified that each mm of drainage leaches 0.25 and 0.27 Kg ha^{-1} nitrate-N, respectively. The amount of drainage water depends on the irrigation technology. Drip irrigation significantly lowers the amount of surface and subsurface drainage (ASSOULINE 2002). Thus, irrigation methods in principle can have an impact on nitrogen export of irrigated agricultural lands as with more efficient irrigation methods less water is expected to leave the irrigation perimeter. However, the above cited study of CAVERO et al. (2003) as well as a study by BJORNEBERG et al. (2007) do not prove that more efficient irrigation automatically leads to less nitrogen export. BJORNEBERG et al. (2007) suggests that the reason why nitrogen export in sprinkler and surface irrigated areas was not significantly different lies within the inefficient water allocation system in the schemes he compared.

3.1.3.2. Fertilizer Application

Next to drainage, fertilizer application is the most decisive factor which influences nitrate export from irrigated areas. Tab. 2 summarizes values for nitrate export which are reported in literature for irrigated areas in semi-arid environments.

Up to a certain quantity, increased amounts of fertilizer do not necessarily lead to an increase in runoff or leaching since plants take up the nutrient before they are leached vertically or horizontally. SYVERTSEN AND SMITH (1996) applied different amounts of N (NH_4, NO_3) via fertigation to 5-6 year old Citrus (grapefruit) trees in Florida during two years with 7.9 m³ lysimeters filled with native Candler sand. Recommended nitrogen application is 180 Kg/ha. Results clearly show that significant leaching of nitrogen only occurs if recommended fertilizer rates are surpassed (see Tab. 3). Tab. 4 reports on a similar relationship for the case of irrigated corn in southern Minnesota.

The following major **types of nitrogen fertilizer** can be distinguished and need to be taken into consideration according to their composition and environmental behaviour:

1. Nitrate Fertilizers: the mayor form of nitrogen taken up by plants; it is immediately susceptible to leaching. Typical forms of nitrate fertilizer are KNO_3, NH_4NO_3, $NaNO_3$ (WICHMANN, 2005)
2. Urea: is water soluble. It is hydrolyzed with the coenzyme Urease to CO2 and NH_4 which is subsequently oxidised to NO_3. Hydrolysis occurs fast with 90 % of the hydrolysis taking part in the first two days at 26 °C (BUNDY et al. 1992).
3. Ammonium Fertilizers: Ammonium nitrate, -phosphate, -sulphate. NH4 is more firmly bound to the soil and not available for leaching until converted to nitrate, oxidation to nitrate usually takes place within several days.

4. Organic Nitrogen Fertilizers: animal manure and guano, plant organic material. It is first mineralized to ammonium and subsequently to nitrate compounds, both forms can be taken up by plants.

Tab. 2 Typical nitrate export rates from irrigated agriculture

Region of Study	NO_3 in Drainage Waters [Kg ha^{-1} a^{-1}]	Fraction of Applied Fertilizer-N in Drainage NO3	Time Period	Main Crops Irrigation Method	Source
Northern Spain, Monegros II Watershed A	24.4	0.1	04/1997 - 03/1998	corn and alfalfa sprinkler	CAVERO et al. (2003)
	12.4	0.07	04/1998 - 03/1999		
Northern Spain, Monegros II Watershed B	50	0.22	10/1997 – 09/1998		
Northern Spain, Bardenas I	35 - 59	0.16 - 0.3		surface	BASSO (1994)
Northern Spain, Ebro basin, La violada	68	0.23		surface	ISIDORO et al. (2006)
Northern Spain, Bardenas	98 - 195	0.44 – 0.56		surface	CAUSAPÉ et al. (2004)
West-Central Nebraska	52	0.27	1993-1998	corn lysimeter study	KLOCKE et al. (1999)

Tab. 3 Applied versus leached nitrogen in lysimeter trials for grapefruit

Variety of rootstock	N applied [Kg/ha]	N leached [Kg/ha]
VL	31.9	8.5
	105.6	5.5
	234.8	19.7
SO	33.9	8.2
	98.1	9.8
	213.8	61.0
No tree	105.6	71.3

The values reported here are annual averages of NH_4 + NO_3 based on measurements in 1992 -1993; they were converted to Kg ha^{-1} considering 321 trees ha^{-1} for the plot in Florida. Two varieties for rootstocks: VL Colkamer lemon (Citrus volkameriana) rootstock, SO sour orange (Citrus aurantium) rootstock; nine lysimeters were installed per variety, one for "no tree".
Source: SYVERTSEN AND SMITH (1996)

Tab. 4 Relation of fertilizer application on nitrogen export in irrigated corn

N applied *[Kg/ha]*	N in Drainage *[Kg/ha]*
20	19
112	25
224	59
448	120

The reported values of leached N refer to means of the year 1975, after repeating the same dose of fertilizer for three years in a row. Exported nitrogen determined through tile drainage water.
Source: GAST et al. (1978) cited in Bjorneberg 1999

Another factor impacting nitrogen export from irrigated areas is **soil characteristics**. Drainage of nitrogen compounds is higher in sandy soils than in soils with higher clay content. SOGBEDJI et al. (2000), for example, in a three years study of drainage water under maize found consistently higher values of nitrogen leaching in loamy sand than in clayey loam.

3.1.4. Nitrogen impacts from Point Sources

Major point sources are municipal and industrial water users. Per capita production of nitrogen is around 8-12 g N d^{-1} (HELMER, 1997, tab 3.3). Nitrogen concentrations in wastewater depend upon the per capita water consumption. A typical wastewater N concentration in urban wastewater is around 50 mg l^{-1} (equivalent to a per capita wastewater production of around 200 ld^{-1}). In urban wastewater, nitrogen occurs to around 75 % in the form of ammonium, the rest occurs as organic nitrogen, half of which in biodegradable forms (BOARI et al., 1997). Different wastewater treatment technologies remove nitrogen to different degrees. Aerated lagoons usually have a limited effect on nitrogen removal. Around 20 % of the total nitrogen load is removed through primary treatment, another 20 % through biological treatment. Advanced aeration technologies like the aerated ditch or activated sludge process convert large part of the ammonium to nitrate (nitrification) while another fraction of the nitrogen is removed through sedimentation, converting it to the solid waste fraction. Denitrification is added as a further process and nitrate levels can be reduced by up to 99 % (TSCHOBANOGLUS, 1996).

3.1.5. Nitrogen Processes in Surface Waters

Organic nitrogen released to streams or present in dead biomass is mineralized to ammonium (ammonification), which is subsequently oxidised to nitrate (nitrification, compare equation 5). The same conversion applies to ammonium released from waste water treatment plants to water.

Nitrate may be reduced to gaseous nitrogen if anaerobic or anoxic conditions prevail through the process of denitrification. Another factor reducing the content of dissolved nitrate in water is by incorporation into biomass. However, the incorporated nitrogen may be released later in the river when the organic matter decays and mineralization and nitrification apply again.

Nitrification in Streams

Nitrification is realised in two steps by Nitrosomas (ammonium to nitrite) and Nitrobacter (nitrite to nitrate) bacteria. The overall stochiometry is depicted in equation 5. The first step occurs slower, explaining the fact that usually nitrite concentrations are close to zero in natural waters (CHAPRA 1997:421).

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \tag{5}$$

The rate of nitrification depends on temperature, pH and oxygen content. At optimum conditions: pH 7-8, oxygen content above 2 mg l^{-1} and around 20 °C a typical rate of nitrification is 0.1 – 0.2 day^{-1} (NOVOTNY 2003:286).

Denitrification in Streams

Denitrification is a microbiological reaction that reduces nitrate. The overall equation for denitrification is shown in equation 6.

$$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O\ . \tag{6}$$

It depends on the same environmental factors as nitrification. In streams, denitrification preferentially takes place in the anaerobic zones like reaches with low oxygen content (often as a result of high BOD, or lower local stream flow velocity), in deeper layers close to the bottom sediments or within the sediments. In any case the presence of organic carbon species is necessary since denitrification is realized by heterotrophic bacteria. Denitrification proceeds through some combination of the following steps:

Nitrate > nitrite > nitric oxide > nitrous oxide > dinitrogen gas.

Due to the dependence of denitrification on zones of low oxygen, river morphology can largely impact the actual N-removal in streams. So far little comparisons are available on actual rates of in-stream denitrification in different river reaches. It can be assumed that oxygen rich, fast flowing, straight streams have lower denitrification rates than slow running, oxygen poor, meandering streams. BÖHLKE et al. (2004) determined in-stream denitrification rates through tracer studies (^{15}N) and found a denitrification of 120 ± 20 µmol m^{-2} h^{-1} in a 1.2 km stretch of a nitrate-rich stream in an agricultural watershed in September 2001. This corresponds to a zero and first order denitrification rate constant of 0.63 µmol m^{-2} h^{-1} and 0.009 h^{-1} (0.216 d^{-1}), respectively. However, it is difficult to upscale this datum in space and time. SEITZINGER et al. (2002) studied 16 watersheds in north-eastern USA and found that 37 % - 76 % of known nitrogen inputs are being removed by the river network. They established a clear relationship between removal rate and watershed size (500 km² - 70 000 km²). As nitrification and denitrification - even more - are complex microbiological processes which depend on a multitude of factors and are difficult to be determined empirically, they remain a variable with high uncertainty in any nitrogen modelling activity at watershed scale.

3.2. Modelling Nitrate in Watersheds

In order to model the behaviour of nitrogen in general or nitrate in particular many approaches are described in literature. First of all, these models differ in complexity, data requirements of the models, temporal and spatial scales of data input and output.

Relatively simple approaches for watershed based modelling of total nitrogen loads are set up on the basis of export coefficients. Here each land use type is correlated with a value for typical leaching (in most cases derived from literature), often weighted by precipitation rates. Based on an appropriate land use map the annual nitrogen exports can be computed using a GIS. The basic concept of the export coefficient approach to determine nutrient export from land areas is presented in BURT and JOHNES (1996)

JOHNES (1996) and MATTIKALI and RICHARDS (1996) achieved good results using this approach for estimating annual loads and average concentrations of total nitrogen and phosphorous. However, as a consequence of the methodology applied, results are restricted to annual values.

FERNANDEZ et al. (2002) extended the model described by JOHNES (1996) with a term representing the attenuation of nutrient export due to time of travel in the drainage area and coupled the export coefficient model with DRAINMOD model for daily runoff estimates. The results were monthly estimates of nitrate N exports for a model watershed of 29 km². FERNANDEZ et al. (2002) achieved very high correlations between predicted and observed data (correlation coefficients between 0.9 and 0.99).

HAITH AND SHOEMAKER (1987) developed an approach with the idea to model substance and water dynamics in watersheds with limited data availability. The General Watershed Loading Function (GWLF) generates monthly estimates of nutrient and sediment loadings (HAITH et al. 1992). In the GWLF model nutrient inputs were derived through event mean concentrations (EMC). EMC, like the export coefficients are empirically determined coefficients and are reported in literature for typical land uses. EVANS et al. (2002) created a GIS (ArcView) based interface for the GWLF model (AVGWLF) and applied it to 32 watersheds in Pennsylvania state. For the monthly nitrogen loads Nash-Sutcliffe coefficients were 0.7 at average for modelled nitrate data compared with observed data.

DUNN et al. (2003) describe a model which combines nutrient export from different land uses with a hydrological sub-model and stream transport (Nitrogen Risk Assessment Model for Scotland, NIRAMS). The main objectives of the model are to predict N concentrations for ungauged catchments and to fill gaps in monitoring data. They achieved to simulate the time series for Total nitrogen for eight watersheds in Scotland (sizes between 149 km² and 526 km²).

MONERIS is a model applied to many rivers, especially in Europe but also elsewhere, to determine annual fertilizer loads of rivers (BEHRENDT 2007). A similar approach is followed by the SPARROWS model (SMITH et al. 1997). These models are also adequate for areas with lower data availability, however, their limitation is that they are not dynamic models and provide only annual estimates.

At the field scale GLEAMS (LEONARD et al. 1987) and DAISY (HANSEN et al. 1991) are two examples for models used to predict the hydrologic and water quality response to agricultural management practices at the field level. More complex watershed models with water quality components include SWAT (ARNOLD et al., 1993; NEITSCH et al. 2005), AnnAGNPS (BINGNER et al. 2001), ANSWERS-2000 (BOURAOUI and DILLAHA 1998), Mike SHE (REFSGAARD and STORM, 1995) and WASMOD (REICHE 1991). However, these largely physically based models are rather complex and as a consequence have a detailed data requirement. Especially for large watersheds in countries where data availability is rather poor, they are not adequate modelling tools.

In-stream water quality processes can be described by models like Qual2K (CHAPRA et al. 2005), WASP (AMBROSE et al. 1993, BONGARTZ et al. 2007) and Mike 11 (DHI 2007).

Mike Basin (DHI, 2005) is a network based model which allows connecting the river reaches with catchment properties based on GIS layers. Next to water quantity dynamics it can model various in-stream water quality parameters including nitrogen species ammonium and nitrate. It has been applied various times successfully to model hydrology and nutrient transport in large basins under data scarce conditions (e.g. IRESON et al. 2006).

3.3. Conceptual Model to Develop Long Term Nitrate Concentrations

As discussed in chapter 2 nitrate variability needs to be known in order to apply advanced, scientifically sound methods of water quality monitoring design. According to represent the variability of nitrate concentrations adequately a method or model needs to simulate nitrate concentrations

i) on a high frequent basis, as significant changes in nitrate concentrations may occur in the order of a few days or even hours,

ii) over long time periods as major differences of nitrate concentration are expected to occur from year to year, especially in semi-arid environments which are exposed to high climatic variability,

iii) at different points of the river under study in order to account for the spatial variability of nitrate concentration.

An additional challenge is to realize these simulations even in "data poor" environments where neither large, long term coverages of previous water quality monitoring efforts nor detailed spatial and temporal data sets on other environmental parameters are available.

Nitrate concentrations at any point in a river network are determined by constituent and water influxes or abstractions as well as transformation processes within the river. The river network can be represented by chain of river reaches. For each reach nitrogen in- and outputs as well as water in- and outputs next to in-stream transformation processes or water losses need to be described and quantified. Fig. 7 depicts this system as a sketch.

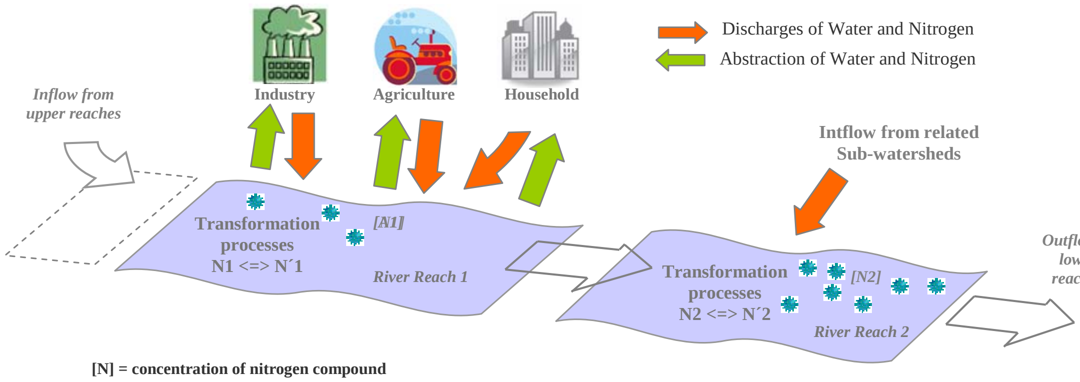


Fig. 7 Conceptual model of Nitrogen and water flow depicting two river reaches

The concentrations are calculated as the quotient of total mass of substance and water volume (or mass). The *variability* of a parameter can be calculated on the basis of the generated time series of nitrate concentrations either for the whole model period, for hydrological years or for months.

3.3.1. Nitrogen Inputs to River Reaches

For the purpose of this study, the following sources of nitrogen are distinguished and modelled separately:

- agricultural drainage from irrigated lands,
- storm water runoff from urban areas,
- point source inputs from municipal areas (wastewater), and
- Industrial nitrogen point discharges.

The following sections describe the details of the processes underlying these nitrogen inputs to the surface water reaches.

3.3.1.1. Irrigation Drainage

Each irrigation section releases nitrogen to the associated river reach via runoff and via leaching to drainage waters. Fig. 8 provides this relationship in form of a sketch.

The detailed description of nitrogen uptake by plants, determination of residual N, pathways in the unsaturated zone, quantification of runoff, transport via shallow groundwater and drainage ditches would require an enormous amount of data (and a complex modelling approach) which is not available for many cases as for the case of the Aconcagua river basin. Thus, a simplified, lumped approach of export coefficients is applied here. The approach considers a lumped response for a given irrigated area depending on the total N-fertilizer input. Of this total Fertilizer input, a certain fraction is being exported each month. The export coefficients for each month are being determined through empirical studies on irrigation perimeters which are representative for the whole watershed. This way, different N-exports are determined for each month. Within each month of the irrigation season the N-export is considered to be constant. This assumption is being supported by empirical studies (compare chapter 6). While short term fluctuations of nitrate export do occur during the irrigation season at field level due to irrigation scheduling, fertilization timing and other management practices, at the level of a whole drainage section these individual peaks mutually compensate each other which leads to a levelling effect of nitrate exports to the receiving river system. For this reason the time steps considered for nitrate export from irrigation drainage is in months.

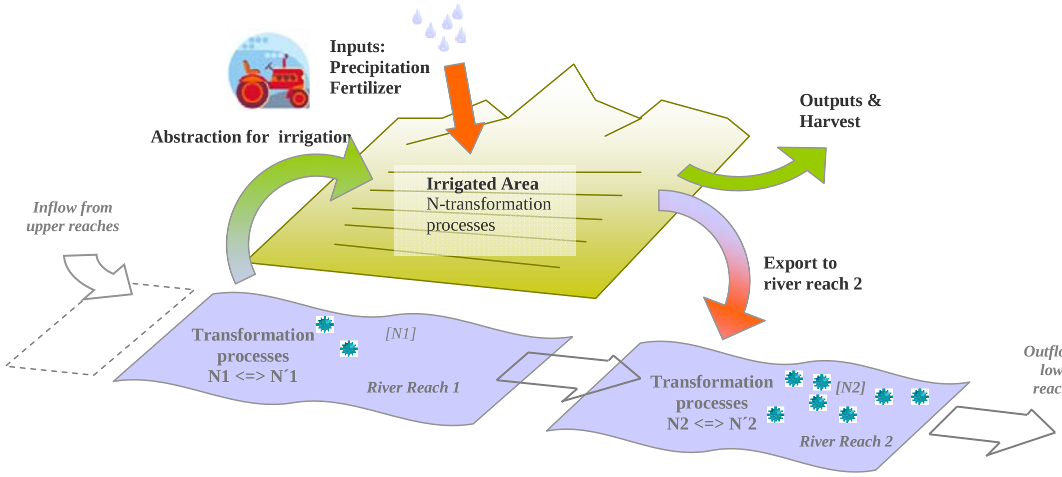


Fig. 8 Sketch visualizing relation of irrigated areas with river reaches

The long term dynamics and spatial distribution of nitrate export are being considered in the model. For this purpose the land use dynamics over the whole modelling period, crop specific fertilizer applications and long term dynamics of fertilizer applications need to be quantified.

During rainfall events, however, a temporal higher N-load is entering the surface water system. This effect is considered by a second export coefficient which determines the amount of nitrogen which is being exported from each area unit (ha) at average per mm of rainfall.

Thus, the nitrate export can be expressed by the sum of two terms, one relating to the permanent export from irrigated areas and the other to the nitrate, which is being exported as a response to rainfall (equation 7).

$$ENO3_I = \sum A_i F_i (C_{eb} + PC_{ep}) \qquad (7)$$

$ENO3_I$ = Export of Nitrate [Kg]
Ai = Area of land use i [ha]
Fi = Fertilizer application related to land use i [Kg ha^{-1}]
P = Precipitation [mm]
C_{eb} = Export coefficient for base flow. Empirical factor determined for each month [-]
C_{ep} = Export coefficient related to precipitation [mm^{-1}]

It should be noted that this approach is a broad simplification of the detailed processes which occur within an irrigated area regarding N-transformation and export, but it is adequate with respect to areas with limited available data and in respect to the objective of this study to estimate the variability of nitrate concentrations. The nitrate export determined through the export coefficients relates to drainage outlets of irrigation areas to surface water. Thus, it incorporates all nitrate losses stemming from runoff and subsurface drainage flow. It does not cover nitrate flows which percolate to aquifers and subsequently discharge to surface water outside of the irrigation drainage area. Including this nitrate pathway would improve the overall modelling approach but requires rather detailed knowledge of the prevailing aquifer system dynamics.

3.3.1.2. Urban Stormwater

Nitrogen accumulates on urban surfaces and is transported to surface water during rainfall events. Nitrogen export coefficients from urban areas are available from several studies in literature (e.g. LIN et al. 2004). They can be used to quantify nitrate export related through a storm event (equation 8). Nitrogen in storm water runoff is not limited to nitrate. For this study a share of 70 % nitrate content and 30 % ammonium and organic nitrogen was assumed, based on literature values (Taylor et al. 2005).

$$EN_U = \sum_i A_u C_{eu} P \tag{8}$$

EN_U= Export of Nitrogen from urban areas through stormwater runoff [Kg]
A_u = Urban area [Km²]
C_{eu} = Export coefficient of urban area per mm precipitation [Kg km^{-2} mm^{-1}]
P = Precipitation [mm]

If combined systems exist, stormwater is collected together with wastewater. In this case the subsequent treatment technologies and related N-removal need to be considered as well.

3.3.1.3. Municipal and Industrial Waste Water

Municipal wastewater abstractions and the return flow of wastewater to surface waters can be estimated according to the number of inhabitants and the return flow fraction. Abstraction and return flow can be related to different river reaches. Fig. 9 provides a sketch on this part of the system.

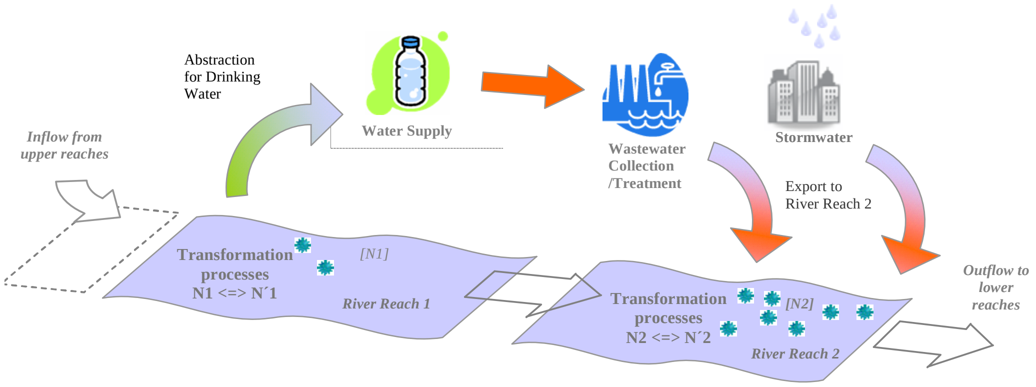


Fig. 9 Municipal water uses and its impact on surface water

Nitrogen loads are considered separately for ammonium and for nitrate, they depend on the number of inhabitants and the treatment processes at place. The process is expressed by two coefficients. One coefficient (C_r) expresses the overall N-removal through steps of preliminary, primary or advanced treatment. The other describes the conversion of ammonium to nitrate (C_{nit}). Nitrification occurs to a significant extent in more advanced treatment technologies like activated sludge or trickling filters. Equations 9 and 10 describe the calculation of nitrogen inputs. If denitrification is present in any treatment plant under consideration it should be considered separately. For this study it was not relevant. The amount of organic nitrogen released to surface water was also neglected as most of the effluent nitrogen after primary or secondary treatment usually occurs as ammonium or nitrate (Tschobanoglus 1996).

$$ENH_4wwtp = \sum_i P_i N_{inh}(1-C_r)(1-C_{nit}) \qquad \textbf{(9)}$$

$$ENO_3wwtp = \sum_i P_i N_{inh}(1-C_r)C_{nit} \qquad \textbf{(10)}$$

ENH_4wwtp = Daily Ammonium export from wastewater treatment plants
ENO_3wwtp = Daily Nitrate export from wastewater treatment plants
Pi = Population connected to WWTP (inhabitants)
N_{inh} = Nitrogen load per inhabitant (default value 10g day^{-1})
C_y = Coefficient of N-removal (depending on treatment technology)
C_{nit} = Coefficient of Nitrification (depending on treatment technology)

In this study the ammonium or nitrate exports to receiving surface waters was considered to be constant over the year.

3.3.2. Watershed Hydrology

The quantity of water discharged by sub-watersheds to tributaries and to the main river is of utmost importance for modelling substances concentration. In order to model the quantity present in a river reach natural runoff as well as human alteration through abstractions and discharges need to be quantified for the whole study period.

3.3.2.1. Catchment Runoff

Wherever measured river discharges are available as daily observed data, they are entered directly as input to a river reach. In the ungauged basins runoff is estimated by the rainfall runoff model in HEC-HMS applying the Curve number method (USACE 2000). Currently more advanced techniques are being developed to estimate the runoff from ungauged basins (SIVAPALAN et al. 2003; FLÜGEL 2007). They will contribute to improve predictions of the kind developed in this study.

3.3.2.2. Irrigation Water Abstractions and Recharges

Irrigation abstractions are considered per irrigation sector and are modelled according to crop water demand as well as field and conveyance efficiencies.

The net irrigation water requirement per section can be calculated as:

$$NIWR = \sum_i CWR_i A_i \qquad \textbf{(11)}$$

NIWR = Net Irrigation Requirement ($m^3\ a^{-1}$)
CWRi = Crop Water Requirement of Crop i (m)
Ai = Area of Crop i (m^2)

The gross irrigation requirements take field and conveyance efficiencies into account and provide the amount of water which needs to be abstracted in order to supply a given irrigation sector (equation 12).

$$GIWR = \frac{NIWR}{Ef \cdot Ec} \qquad \textbf{(12)}$$

GIWR = Gross Irrigation Water Requirement
Ef = Field Efficiency
Ec = Conveyance Efficiency

Crop water requirements can be calculated according to well established methods defined by FAO (Allen et al. 1998) on the basis of evapotranspiration which is either calculated according to Penman-Monteith formula or according to field measurements (Class A Pan evaporation, meteorological data). Field and conveyance efficiencies need to be estimated (for example Mann 1986), if not available from local irrigation services.

Irrigation return flow rates have two components: a surface and a base flow. For the Aconcagua Watershed DGA (2004_b) determined these coefficients for all irrigation sectors within the Aconcagua River: surface water drainage coefficient as fraction of applied irrigation water and a base flow coefficient related to the amount of the annual irrigation requirements. Surface and base return flow depend on soil permeability, tillage, aquifer characteristics, and drainage system characteristics and on the practice of irrigation applications. In order to model return flow according to the underlying physical processes detailed data are needed. For this study an approach in which the coefficients determined by DGA (2004_b) could be applied was used to model the irrigation return flow:

$$IRF = AIW \cdot Ec \cdot Cs \cdot C_{Sub} \qquad \textbf{(13)}$$

IRF = Irrigation return flow
AIW = Abstracted Irrigation Water
Ec = Conveyance Efficiency
Cs = Coefficient of surface drainage
Csub = Coefficient of subsurface drainage

The abstracted irrigation water (AIW) depends on the gross irrigation requirements (GIWR) and the water available at source. The latter is a result of the water balance of the reach where abstractions take place.

3.3.2.3. Domestic Water Abstractions and Recharges

Water abstraction for domestic purposes can be modelled if per capita water demand and water distribution efficiencies are known. Population time series can be developed for each settlement according to population statistics.

$$A_{dom} = Pop \cdot WD_{cap} \cdot D_{ef}^{-1} \tag{14}$$

A_{dom} = Abstraction for domestic water
Pop = Population
WD_{cap} = Water demand per capita
D_{eff} = Water conveyance and distribution efficiency

Return flow depends on wastewater collection and treatment system at place. The local water company in the Valparaíso region (ESVAL) calculates with a value 80 % of the domestic water demand.

3.3.2.4. Flow Routing Within the River System

The runoff, abstractions, discharges and recharges provide the water balance for each river reach. The transport of water and substances is further determined by the flow velocity and the resulting delay of transport to the next river reach. This is considered with a routing concept. In this study simple linear routing is applied. The routing coefficient can be determined by the Manning formula, if no measured flow velocity data are available.

3.3.2.5. In-stream Nitrogen Processes

During the presence of nitrogen compounds in a river stretch nitrification and denitrification occur.

In-stream nitrification and denitrification are considered as first order rate transformations with temperature dependent kinetics as depicted in the following formula:

$$\frac{dNH4}{dt} = k_{nit} \cdot [NH4] \tag{15}$$

$$\frac{dNO3}{dt} = k_{denit} \cdot [NO3] \tag{16}$$

k_{nit} = Nitrification rate coefficient at 20°C (day^{-1})
k_{denit} = Denitrification rate coefficient at 20°C (day^{-1})

k_{nit} and k_{denit} are temperature dependent which is modelled (in Mike Basin) as

$$R(T) = R20 * RateCorr^{(T-20)} \tag{17}$$

R(T) = rate coefficient
R20 = rate coefficient at 20 °C (knit, kdenit)
Rate Corr = correction coefficient describing temperature dependence of the reaction rate

The default value for RateCorr is 1.07, which means that a temperature increase by 10°C leads to a doubled rate coefficient. Typical rate coefficient for K_{nit} (20 °C) is 0.09 - 0.2 and for k_{denit} (20 °C) 0.09 (CHAPRA 1997; LINDENSCHMIDT 2005).

4. Aconcagua Watershed Analysis

In this chapter, the Aconcagua watershed is being analysed regarding those factors which are important in order to be able to model the spatial-temporal behaviour of nitrate concentrations and to support subsequent monitoring design. The aim is to establish time series for the nitrogen compounds and water flows as described in the previous chapter related to river reaches, water users, and sub-watersheds. Another aim is to provide data on the spatial distribution of elements with relevance to the monitoring design process. The results of this chapter refer to *objectives number 2 and 3* of this study.

4.1. Introduction to the Study Area

Whereas in the Northern parts of Chile agricultural development is comparatively low due to restrictions in water availability and in the southern part due to adverse climatic conditions (short growing season due to low temperatures), the central part of Chile, where irrigated agriculture is intensive, contributes to the major agricultural production of the country.

The Aconcagua watershed represents a typical watershed in central Chile. Like other watersheds in this area it could be classified as a “heavily modified watershed” since a large part of the watershed area is altered by water infrastructure and land uses resulting in hydro-morphological and hydro-chemical characteristics far from the natural conditions. Due to the fact that water availability is the limiting factor in crop production, almost each litre of available water is used at least once during the summer months. Large quantities of water are transferred in channels – the longest of them (Waddington) being over 100 km long – from the main river to those places where water is needed for agricultural production, typically to the alluvial plains or valleys with fertile soils along the main river or along tributaries. Even in the winter months when rainfalls typically occur, water is being collected by small reservoirs or by irrigation channels and stored or transported to locations outside the sub-watershed with the effect that the natural hydrological regime is completely altered.

A simple model applied to the watershed can demonstrate to what extent the disturbance occurs. Fig. 10 shows the modelled discharge in the Aconcagua, not considering human intervention. The values displayed are the result of flow accumulation based on a 500 m gridzise DEM (Digital Elevation Model) applied after overlaying the precipitation grid with one of discharge coefficients taken from CICA (1982). If we compare these (rough) estimates with the measured discharge at two locations in the Aconcagua (San Felipe and Las Vegas, see Tab. 5), we see that the actual discharge in the main river at `San Felipe´ is much lower than expected due to water abstractions from the river. At the tributary `Las Vegas´, the measured discharge is much higher due to irrigation return flows. In fact, at natural conditions the tributaries of the Aconcagua in the middle and lower section would dry out during summer months (Sept.-April), whereas the long term observed discharge is even higher during the irrigation season than in the rainy season (May-August). In addition, the established irrigation infrastructure in a tributary may collect rainwater to some extent and divert it to other irrigation areas or to the drainage system without entering the surface water stream of the tributary. For these reasons, a precipitation-runoff model can not be calibrated to model discharge and attempts by the author to relate precipitation to stream discharge in the tributaries of the Aconcagua failed completely.

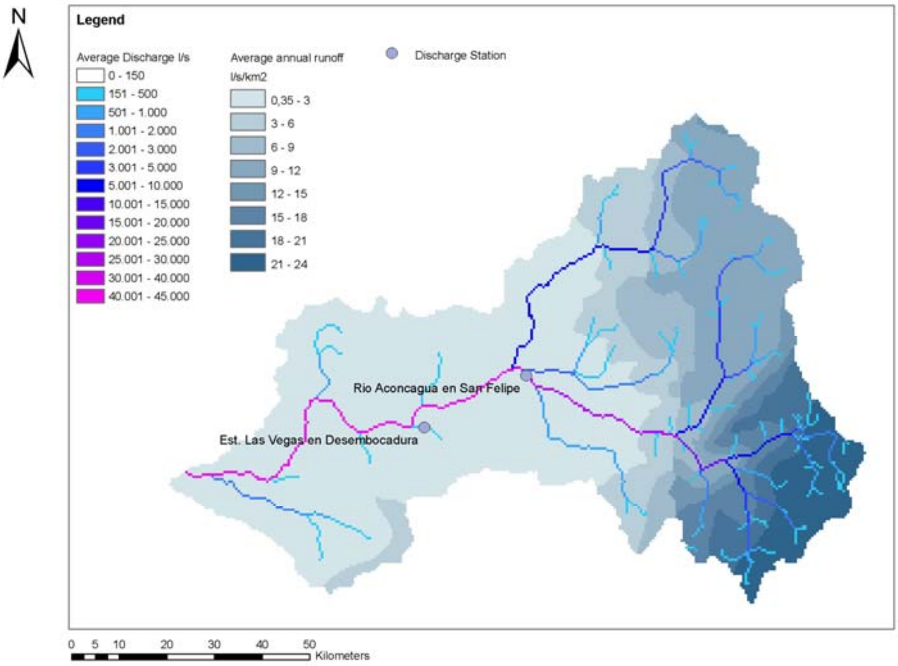


Fig. 10 Estimated average discharge of the Aconcagua River without human impacts

Runoff estimate based on specific yield as provided by CICA (1982), discharge based on flow accumulation calculated on basis of a DEM (500m grid size)

Tab. 5 Comparison of estimated and measured discharge at two stations

Station Name	**Estimated Average Discharge** (No human impact) *[m^3s^{-1}]*	**Measured Discharge** (DGA station) *[$m^3 s^{-1}$]*
San Felipe	32.1	22.4
Las Vegas, mouth	0.3	2.9

San Felipe average measured discharge based on 6340 daily measurements between 1981 and 2001; Las Vegas: average measured discharge based on 6024 measurements between 1981 and 2001.

4.2. Watershed Description

4.2.1. Location and General Description of the Watershed

The Aconcagua Watershed is located in the central part of Chile, around 100 km north of the capital city Santiago. Its headwater is in the Andes Cordillera and it flows into the Pacific Ocean near the city of Concón. It extends from 70°00′ - 71°35′ W and from 32°20′ – 33°10′ S (see Fig. 11). The Watershed area is 7550 km².

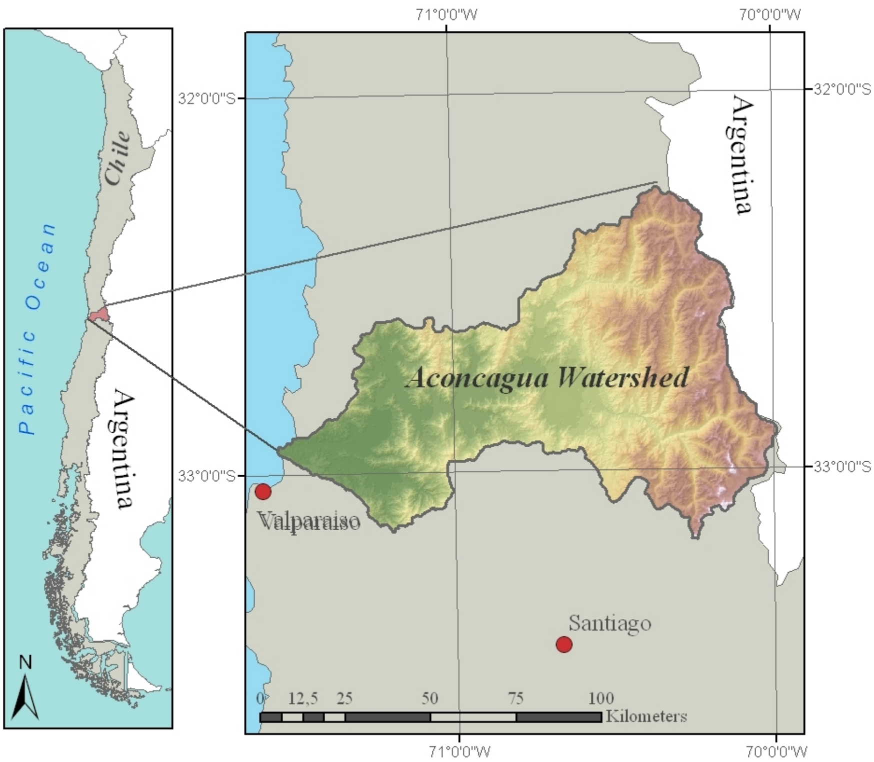


Fig. 11 Location of the Aconcagua Watershed

The entire Watershed is located in the Valparaiso Region (or Fifth Region) of Chile. Within its area, there are four provinces and 18 municipalities (compare Fig. 12 for political boundaries) pertaining to four provinces with a total population of 485,108 of which 85 % are classified as urban (INE, 2002). Most of the population is living in the alluvial plains close to the Aconcagua River. The four major cities are Quillota, San Felipe, Los Andes and La Calera. Average population growth within the municipalities of the watershed was 1.61 % p.a. between 1982 and 1992 and 1.65 % p.a. between 1992 and 2002 (INE, 1982; INE, 1992; INE, 2002).

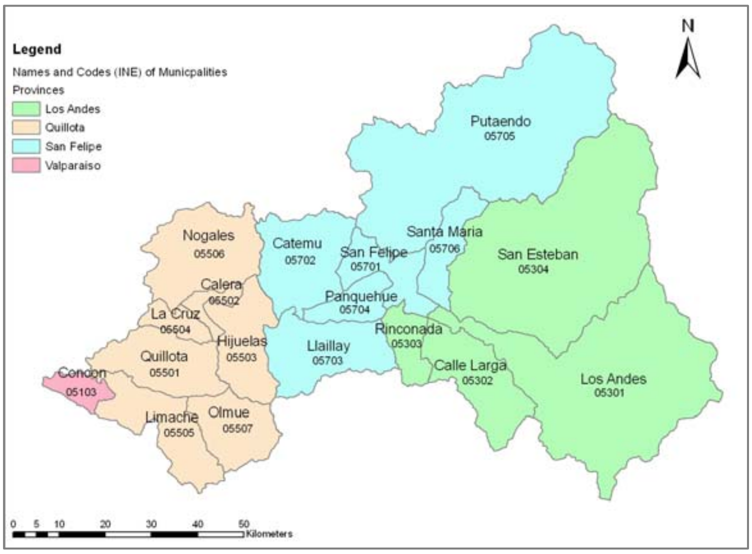


Fig. 12 Location of the 18 municipalities in four provinces located in the Aconcagua watershed

The water resources of the watershed are mainly used for irrigation purposes and in addition for industrial uses and the supply of the population within the boundaries of the basin as well as the greater Valparaiso Region (total population 561.000; INE, 2002) located outside the basin.

This makes the Aconcagua watershed by far the most important water source in the Valparaiso Region. Fig. 13 provides data on the population distribution within the watershed and Fig. 14 depicts the traffic infrastructure.

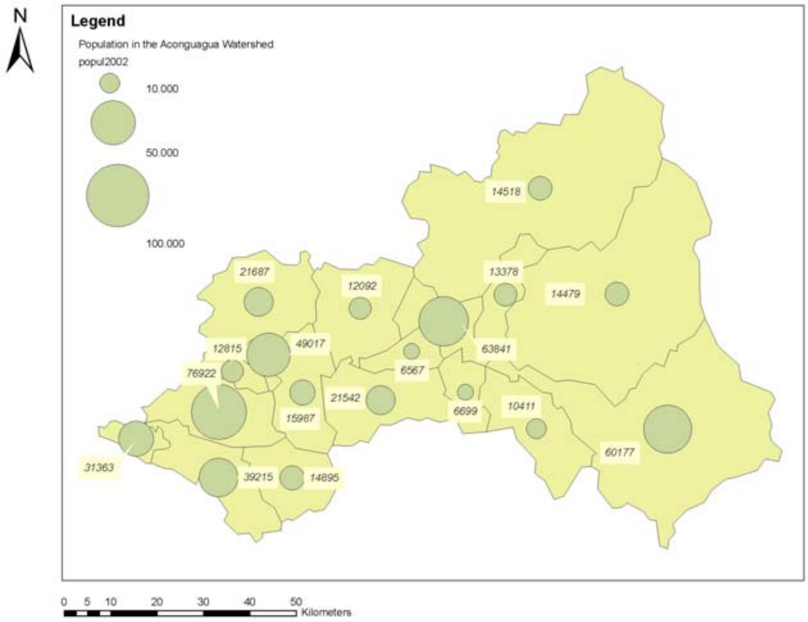


Fig. 13 Number of inhabitants per municipality

source: INE (2002)

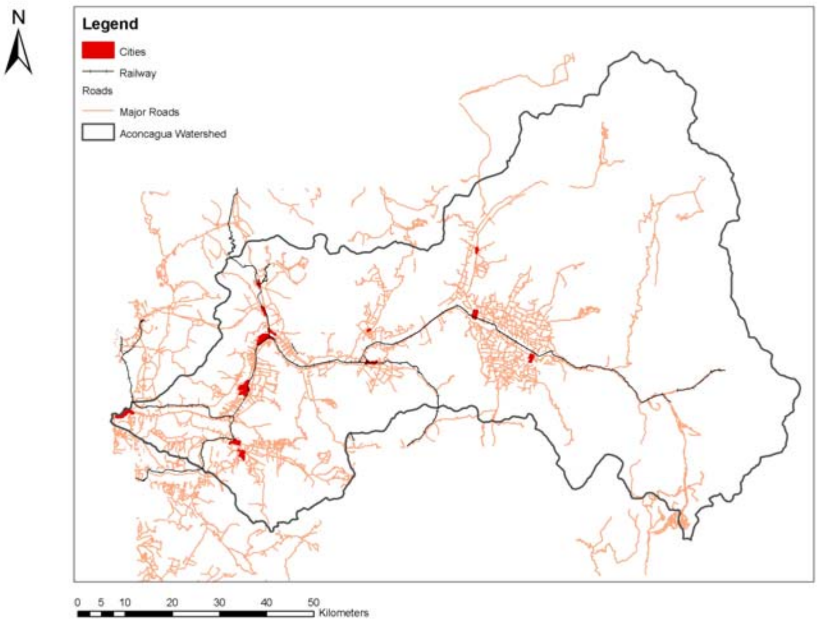


Fig. 14 Roads, railways, and settlements in the Aconcagua Basin

Source SEREMI (2005)

4.2.1.1. Topography and Physical Setting

A digital elevation model (DEM) was build on the basis of digitized maps (1:50,000) with contour lines each 25 m of elevation. For the rather flat areas of the Aconcagua valley maps at the scale 1:10 000 with contour lines every 2.5 m were added to build the DEM. (compare Fig. 15).

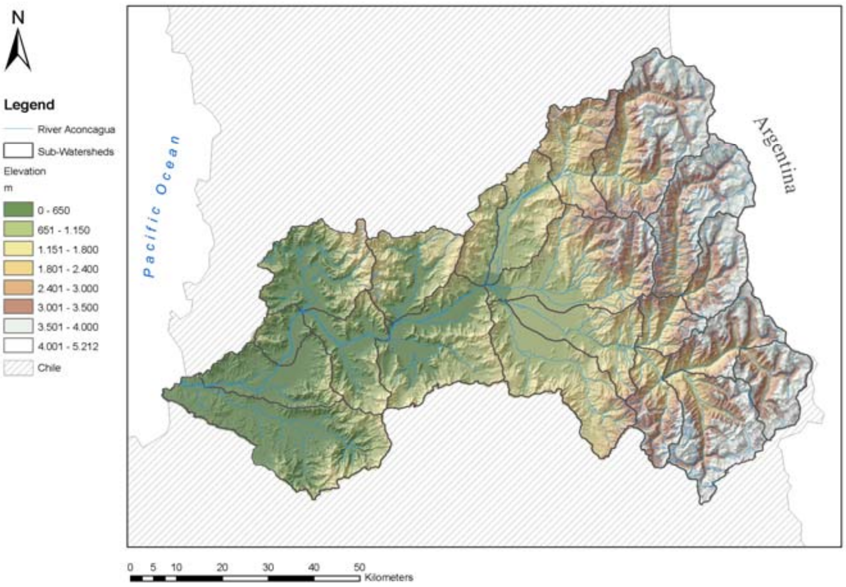


Fig. 15: Topography of the Aconcagua basin, hydrological network and sub-watersheds

This DEM was used to determine the hydrological network and subsequently to divide the watershed into sub-watersheds. These sub-watersheds were chosen according to a) existing discharge stations and b) the spatial distribution of irrigated areas which could be distinguished according to available land use and water abstraction data. The latter is related to the presence of major water intake structures for irrigation.

4.2.2. Climate and Hydrology

The Mediterranean climate of Central Chile during the summer months is related to the South-eastern Pacific Subtropical Anticyclone located at latitude of between 35° to 40° S in summer. Its border changes to the latitude of between 30° and 35° S in winters, which are cool and humid as a consequence of continuous passages of fronts and depressions due to the increased influence of the sub-polar low pressure belt (DIRECCIÓN METEOROLOGICA DE CHILE, 2007).

4.2.2.1. Climatic Zones

The climate in the study area is determined by elevation and distance from the ocean. The driest zones are those in the intermediate valleys situated between the coast and the Andean mountain range, represented by zone 5-06 (compare Fig. 16). Here the average annual precipitation is around 265 mm a^{-1}. In the upper parts of the Andean mountains precipitation is in the range of 1300 – 1500 mm a^{-1} (e.g. zone 5-24) and in the coastal area around 350 - 500 mm a^{-1} (e.g. zones 5-01 and 5-22). In the whole watershed potential evapo-transpiration in the summer months exceeds precipitation (compare Fig. 17). This period can be as long as August – May (climate zone 5-06) or as short as September-March (climate zone 5-24). Average annual temperatures vary from 15 C° in the coastal zones to values around zero or below in the upper mountains. Fig. 16 and

Fig. 17 provide details on the location and parameters of the climatic zones as reported by SANTIBAÑEZ and URIBE (1990).

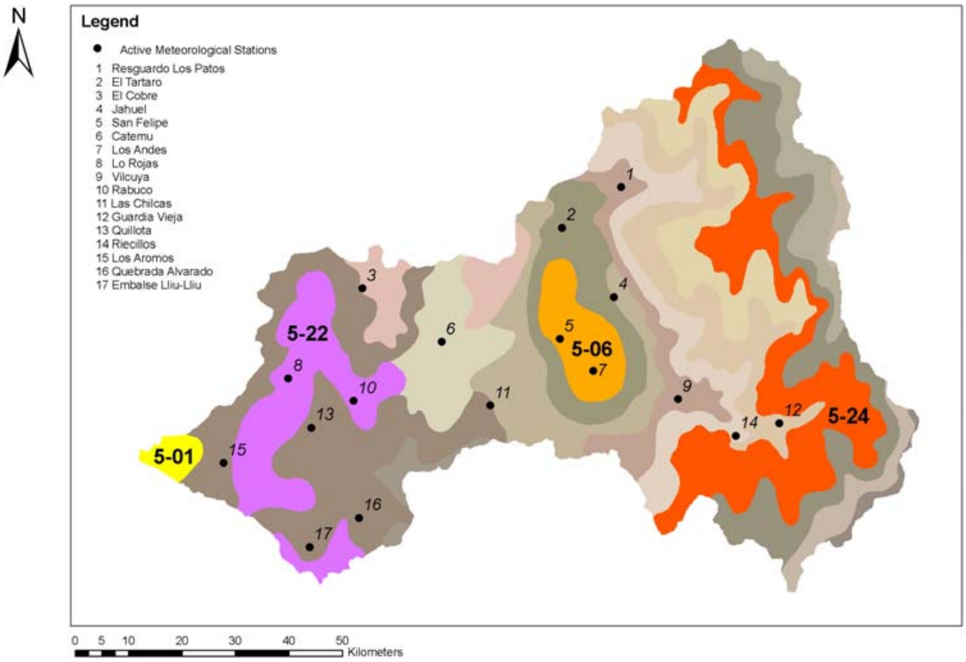


Fig. 16 Climatic zones in the Aconcagua watershed and location of meteorological stations

Source: data based on SANTIBÁÑEZ and URIBE (1990). For four selected climatic zones the climate zone number is provided and the climate diagrams are shown below (Fig. 17)

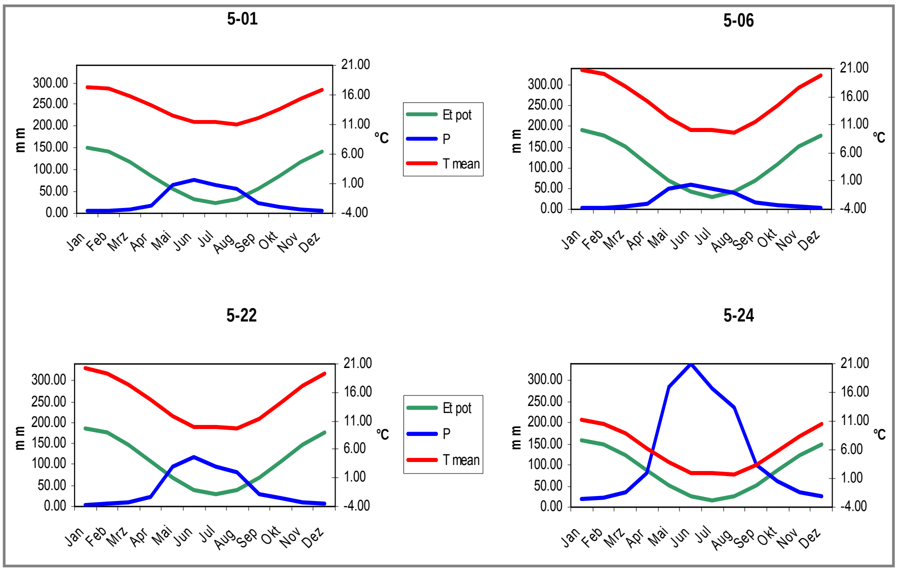


Fig. 17 Climate diagrams of selected Climatic zones

Source: data obtained from SEREMI (2005) ; compare Fig. 16 for location of the four selected climatic zones
P= monthly precipitation, ETpot= potential evapo-transpiration,
Tmean= average monthly temparature

4.2.2.2. Long Term Variation of Precipitation

Next to the seasonal and spatial variation of precipitation which was depicted in the previous paragraph there is also a strong long term variation. In the years with a high ENSO index (El Niño Years) precipitation is above average (1972, 1978, 1982, 1987, 1992, 1997). La Niña Years are significantly dryer than average (1971, 1973-76, 1988-90, 1998-99). All stations in the Aconcagua watershed demonstrate a high correlation among each other regarding long term variability of rainfall. Fig. 18 visualizes the precipitation of three selected stations between 1970 and 2002. A correlation with the Oceanic Nino Index is apparent (Fig. 19). Fig. 20 shows the spatial distribution of rainfall.

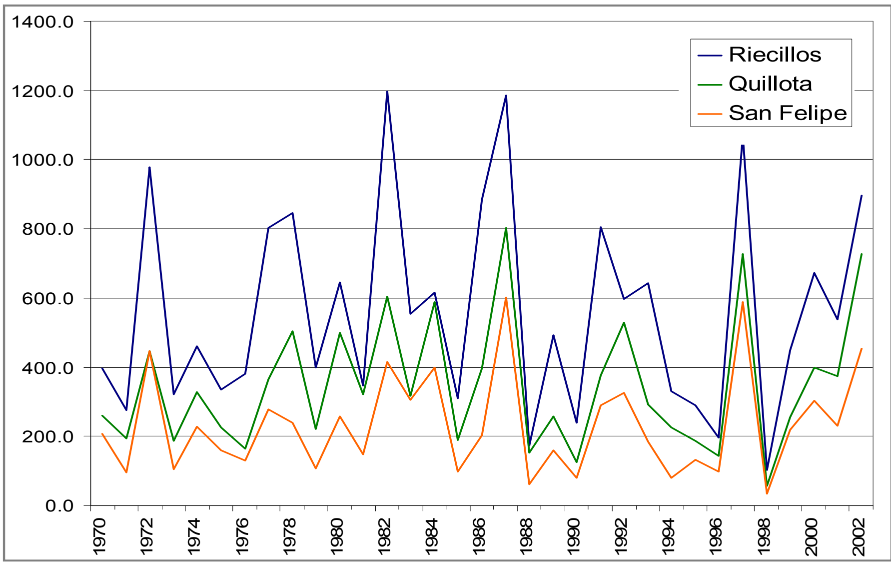


Fig. 18 Long term variation of precipitation at three selected stations (1970-2002).

Note: for location of stations see Fig. 16

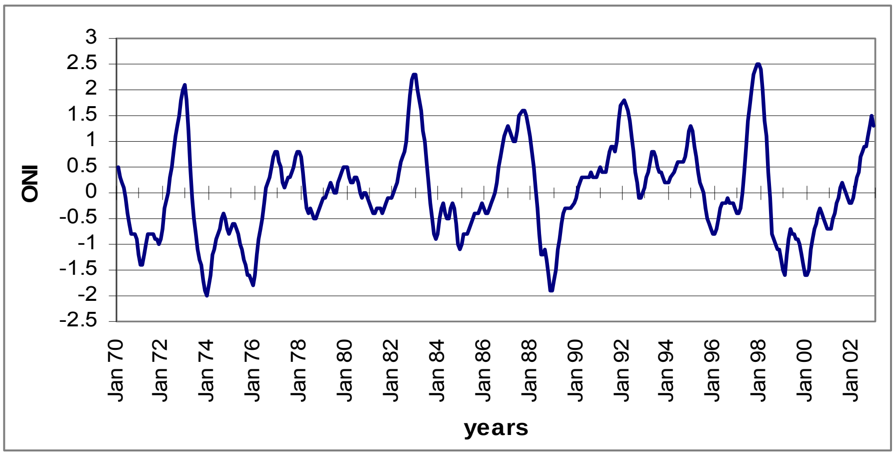


Fig. 19 Oceanic Nino Index (1970 – 2002)

Source of data: Climate Prediction Center (2007)

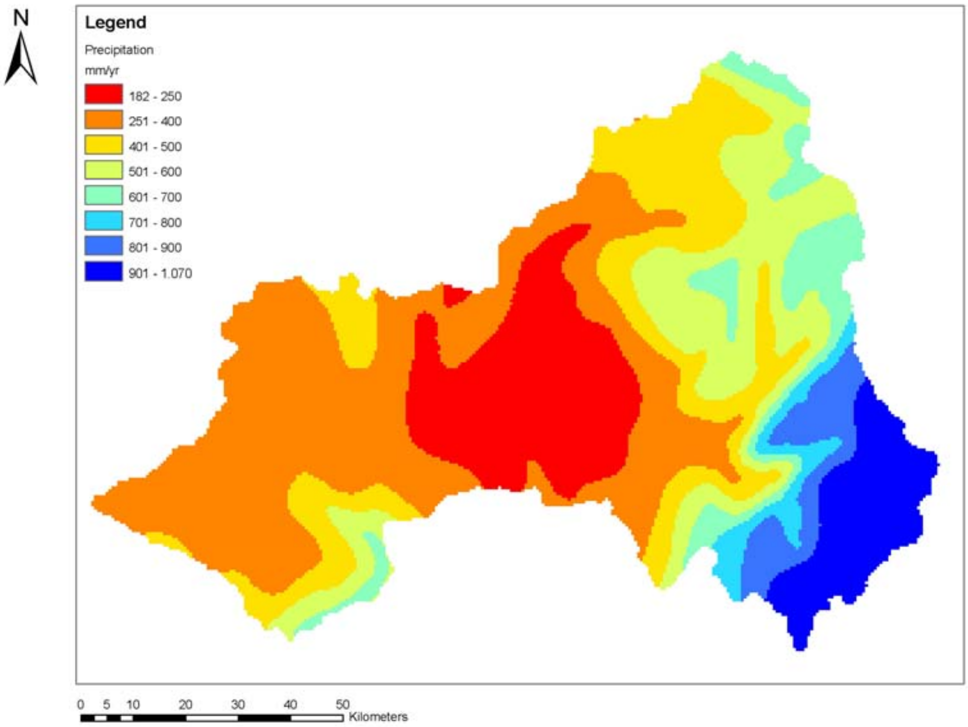


Fig. 20 Spatial pattern of average annual precipitation

Source: interpolation of isohyets (from SEREMI, 2005)

4.2.2.3. Measured Discharges

The upper part of the watershed is characterized through a nival regime. Discharges from snowmelt occur during summer months with peak runoff in January. In the middle and lower part of the sub-watershed discharges peak in the winter during the months of highest rainfall (June-August). Since annual precipitation is much higher in the upper watershed this part contributes to the largest part of annual runoff. The area depicted in blue in Fig. 21 contributes to and estimated 83 % of the total average annual runoff in the watershed; the sub-watersheds related to Chacabuquito station alone contribute to 61 % of the discharge (CICA 1982; DGA/BNA 2007).

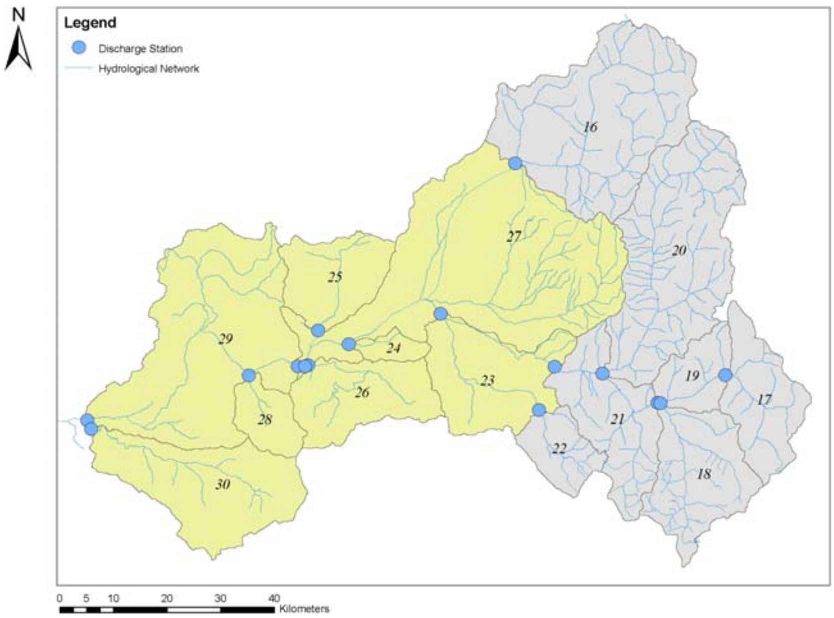
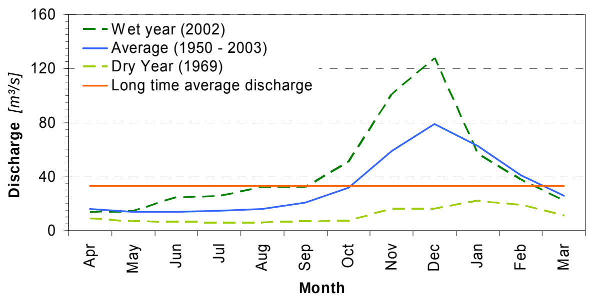


Fig. 21 Sub-watersheds related to discharge measurement stations

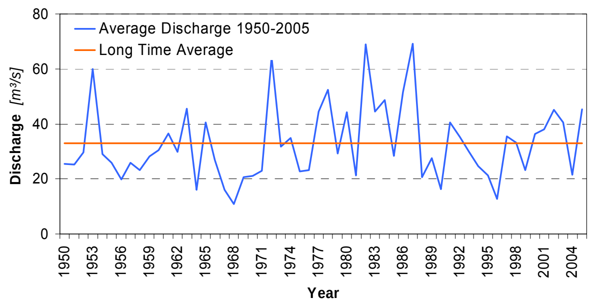
For the watersheds depicted in blue daily values of observed discharges are available through DGA/BNA (2007); for the stations related to watersheds in beige only very sporadic discharge measurements are available; numbers relate to the DGA/BNA coding system

While in the lower watershed discharge measurement are rather sporadic, in the upper watershed long daily data records dating back to the 1950s and beyond are available. Fig. 22 visualizes the average seasonal variation and Fig. 23 the long term variability of discharge at Chacabuquito station.



Data Source. DGA/BNA (2007)

Fig. 22 Seasonal variation of discharge at Chacabuquito station



Data Source: DGA/BNA (2007), values are reported per hydrological year (April-March)

Fig. 23 Long term variation of discharge at Chacabuquito station 1950-1998

4.2.2.4. Discharges of Ungauged Sub-watersheds

No reliable discharge measurements are available to derive a rainfall runoff relationship. One reason is the that measurements are taken very sporadically, another that gauging is quite difficult due to unstable and shallow river beds and a third, perhaps most important, is that irrigation infrastructure transfers irrigation water from the Aconcagua river to the sub-watersheds and runoff from the sub-watersheds to irrigation areas.

The prediction of runoff from ungauged basins is and remains a major challenge in hydrological science (compare SIVAPALAN et al. 2003). For this study runoff from sub-watersheds was modelled based on the Curve Number approach, a method with widespread application used to determine runoff from ungauged basins (compare MISHRA and SINGH 2003). The modelling was realized using the model HEC-HMS. It should be noted that the error in using this simplified approach of runoff estimation may be large, since the actual runoff depends on several other factors like soil saturation, evaporation and local conditions of soil, vegetation etc. However, as described above the ungauged sub-watershed in the middle and lower part of the Aconcagua watershed contributes to an estimated mere 20% of total runoff in the basin, and the errors are not likely to have a major impact on the modelled discharges.

The Thiessen polygon method was applied to derive the relevant impact of the different meteorological stations for each sub-watershed and the relative weight of each rainfall gauging stations was calculated. It should be noted here that the Thiessen method only provides an approximation to the spatially distributed rainfall. Especially in regions with high variations of altitude this method could introduce significant errors.

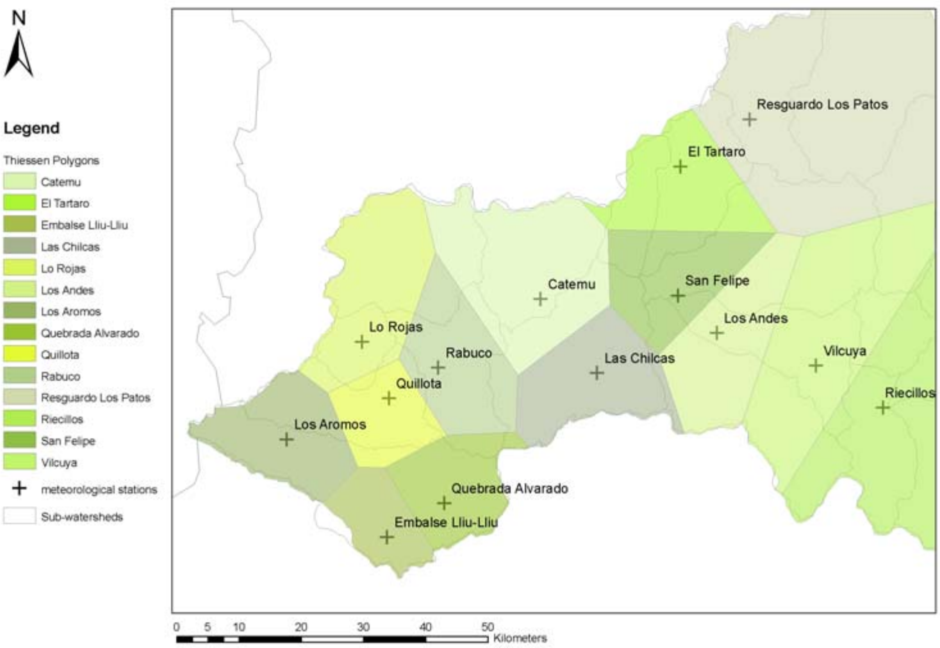


Fig. 24 Thiessen polygons in relation to modelled sub-watersheds

Data gaps in rainfall time series were filled after applying linear regression. Regression results are provided in Tab. 6.

Tab. 6 Linear regression results for daily precipitation time series analysis

Precipitation Station Name	Station Number	Station Acronym	Regression Function	R^2
Catemu	6	CAT	1,0319·LCH+0,0408	0,89
Las Chilcas	11	LCH	0,8719·CAT+0,0326	0,89
Lliulliu embalse	17	LLE	1,021·QAL+0,081	0,89
Quebrada Alvarado	16	QAL	0,9816·LRO+0,1613	0,86
San Felipe	5	SFL	0,8819·LAN-0,0275	0,88
Los Andes	7	LAN		
El Tartaro	2	ELT	0,8227·RLP+0,0234	0,92
Resguardo Los Patos	1	RLP		
Quillota	13	QUI	0,736·LAR+0,1199	0,79
Los Aromos	15	LAR		
Lo Rojas	8	LRO	1,0011·RAB+0,0335	0,91
			0,8764·QAL+0,0231	0,86
Rabuco	10	RAB	0,8743·LRO+0,0924	0,88
Vilcuya	9	VIL	1,1418·LAN+0,1588	0,83

For location and number of meteorological station compare Fig. 16.

4.2.2.5. Runoff Simulation with HEC-HMS

The Hydrologic Modelling System (HEC-HMS, version 3.1.0) was designed by the United States Army Corp of Engineers (USACE) (USACE, 2000; 2006). It simulates the precipitation runoff processes of dendritic watershed systems. The program is a modelling system capable of representing many different watersheds. A model of the watershed is constructed by separating the hydrologic cycle into smaller processes and constructing boundaries around the studied watershed.

In addition HEC-HMS provides a geographic information system (GIS) interface, the GeoHMS 1.1 that allows the definition of numerous physically based parameters and the watershed physical description. This GIS interface was used to calculate the Curve Number Grid as well as the different Parameters needed in the SCS curve number runoff calculation (Basin Slope, Basin Lag, Area, etc…) (USACE, 2003).

The HEC-HMS model allows the utilisation of the SCS curve number method, which was chosen as no runoff or discharge measurements are available in the studied basin. The Curve Number Method was originally developed by the Soil Conservation Service (SCS) (SOIL CONSERVATION SERVICE 1964; 1972) for conditions prevailing in the United States. Since then, it has been adapted to semi arid zones and it is still used in many studies to estimate the depth of direct runoff from the rainfall depth (HAMMOURI AND EL-NAQA, 2007, MARTINEZ DE AZAGRA et al., 2004).

SCS theory is based on the fact that direct runoff (after initial infiltration occurs) depends on land cover, land use, soil type and antecedent moisture conditions of surface soil.

Several accompanying tables had been developed in association with empirical equations (SCS, 1964; 1972).

The SCS Curve Number Method is based on the following equations:

$$Q = \frac{(P_i - I_a)^2}{P_i - I_a + S} \qquad (18)^{1}$$

$$I_a = 0{,}2S$$

As presented by Soil Conservation Service (1964; 1972), the initial abstraction I_a, was found to be 20% of the potential maximum retention S. This value represents an average and could be modified with regard to the region. Then:

$$Q = \frac{(P_i - 0{,}2S)^2}{P_i - 0{,}8S} \quad \text{for } P_i > 0{,}2S \qquad (19)$$

Where:

Q= Accumulated runoff depth [mm]
Pi=Accumulated rainfall depth [mm]
I_a= Initial abstraction [mm]
S=Potential maximum retention

The potential maximum retention can be converted to the Curve Number CN in order to make the calculation more or less linear. This relationship is:

$$CN = \frac{25400}{254 + S}$$

To determine how runoff is distributed over time, a time dependent factor is introduced. The Time of Concentration (t_c) is used in the HEC-HMS Curve Number method. The time of concentration usually refers to the time needed for a particle to travel from the remotest point of a basin to its output. Equation 20 was used to calculate t_c in each sub-basin.

$$t_L = \frac{L^{0,8}\left[(1000/CN) - 9\right]^{0,7}}{1900S^{0,5}}$$
$$and \qquad (20)$$
$$t_c = 1{,}67t_L$$

Where:

t_c is the time of concentration [min]
t_L is the watershed lag [min]
L is the longest flow path [m]
S is the mean slope of the watershed [%]
CN is the curve number of the basin

[1] For all equations adapted to SI units

In the Curve Number Method, the CN parameter is related to land use, land treatment, hydrological condition, hydrological soil group, and antecedent soil moisture condition in the drainage basin.

Land use represents the surface conditions in a drainage basin and is related to the degree of vegetation cover. In this study, land use classification as provided by SEREMI (2005) is used which is displayed in Fig. 31. They are intersected with slope classes provided in Fig. 25.

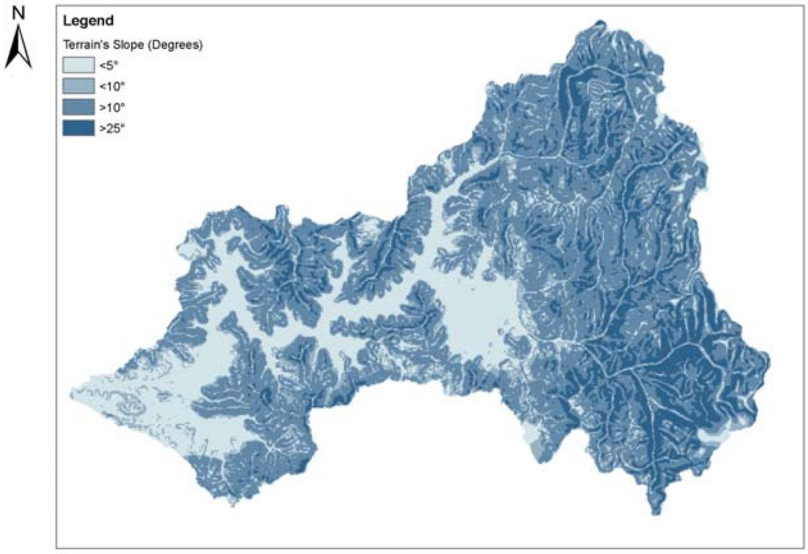


Fig. 25 Terrain's slope in the Aconcagua Watershed

Slope classes derived from the digital elevation model

Soil groups have a heavy influence on runoff. The SCS has classified different soil types in four categories according to the soil runoff potential. The soil runoff potential includes its infiltration rate and its transmission rate. The hydrological soil groups as defined by the SCS (1972) are:

Group A: Soils having high infiltration rates even when thoroughly wetted and a high rate of water transmission.
Group B: Soils having moderate infiltration rates when thoroughly wetted and a moderate rate of water transmission.
Group C: Soils having low infiltration rates when thoroughly wetted and a low rate of water transmission.
Group D: Soils having very low infiltration rates when thoroughly wetted and a very low rate of water transmission.

Unfortunately, with regard to the hydrologic soil conditions, no data was available for the study area. Consequently, soil conditions were related with terrain slope. The watershed was divided in different classes of slopes as displayed in Fig. 25 under the assumption that a slope inferior to 10° (flat and slightly sloping) is considered to represent a soil of hydrological group B when slopes superior to 10° (Highly sloping) will be considered to represent hydrologic soil groups of inferior infiltration capacity like C (<25°) and D (>25°).

MOCKUS AND MOODY (2004) defined several hydrological soil groups for arid and semi-arid watersheds. Consequently, the following soil groups have been attributed to the Aconcagua watershed.

Tab. 7 Hydrological Soil Groups related to Landuse Types

	Hydrological Soil Groups			
Landuse related to SEREMI (2005)	**A**	**B**	**C**	**D**
Urban	89	92	94	95
Agriculture	72	81	90	91
"Matorral"		71	81	89
Forest	35	56	70	77
No vegetation		80	87	93
Water	100	100	100	100

Source: (after MOCKUS AND MOODY, 2004)

Antecedent Soil moisture Conditions

The combination of land use types and hydrological soil groups returns a curve number map defined by the relations determined in Tab. 7.

However, the soil moisture condition in the drainage basin before runoff occurs is another important factor influencing the final CN value. In the Curve Number Method, the soil moisture condition is classified in three Antecedent Moisture Condition (AMC) classes (SCS, 1972):

> AMC I: The soils in the drainage basin are practically dry (i.e. the soil moisture content is at wilting point).
>
> AMC II: Average condition.
>
> AMC III: The soils in the drainage basins are practically saturated from antecedent rainfalls.

Since the Aconcagua watershed is considered to be particularly dry, the assumption is made that in the watershed, most of the time, could be assimilated to the Antecedent Moisture Condition class I. Consequently, the Curve Number as determined above should be adjusted according to Tab. 8.

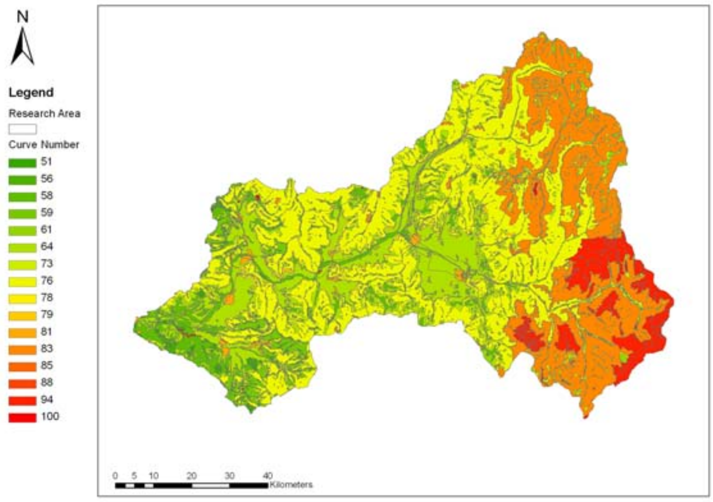
Tab. 8 Curve Number Adjustment to Antecedent Soil Moisture Conditions

Original Curve Number	70	75	77	82	83	84	85	86	87	89	90
Adjusted Curve Number (AMC I)	51	56	59	66	67	68	70	72	73	76	78

Source: (SCS, 1972)

Once this relationship is defined, curve number polygons are derived from the land use maps and the soil use map (here derived from the terrain slope DEM). Curve numbers are then calculated for each watershed using an area weighted average method as displayed in Fig. 26. Here the calculated curve numbers for the whole Aconcagua watershed are depicted, even though merely for the middle and lower parts runoff was calculated.

Fig. 26 Curve Number polygons in the Aconcagua Watershed



Physical Parameters Estimation

All parameters were calculated with the help of the GeoHMS module (USACE, 2003).

The following Tab. 9 describes the parameters selected for the HMS simulation. All parameters are physically based and derived from the Digital Elevation Model.

Tab. 9 Physical Parameters Estimation

Catchment Name	Longest Flow Path *[m]*	Mean Basin Slope *[%]*	LagTime *[min]*
1	15671	6,27	40
2	65444	23,76	159
4	50407	13,77	134
5	39293	12,67	97
6	24416	15,62	62
7	18250	14,65	46
8	31896	20,33	87
9	14733	13,04	36
10	20485	22,22	61
11	21913	23,69	61
12	8008	15,47	24
13	28830	21,62	79
14	44538	22,15	116
15	29584	26,2	84
16	14471	27,64	54
17	21162	30,9	64
19	15885	17,63	46
20	14988	27,04	47
24	46061	21,33	120
25	41122	16,35	96
26	40150	20,82	96
27	6194	23,35	24
28	12939	10,75	31

For location of watersheds compare Fig. 27

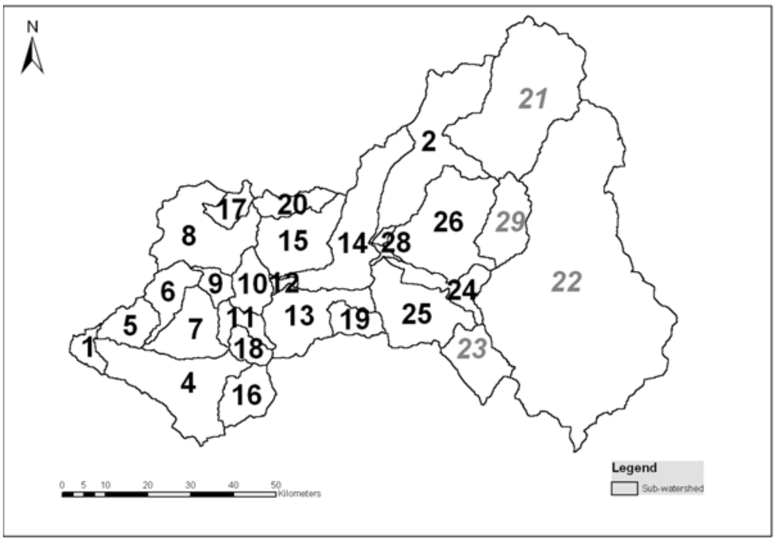


Fig. 27 Location of modelled sub-watersheds in HEC-HMS

Simulation Results

Tab. 10 provides the average runoff per sub-watershed calculated from the daily modelled values (1986 – 2006). The sum of the runoff of these watersheds located in the middle and lower part of the Aconcagua basin is 12.4·m³ s^{-1}. The total discharge of gauged stations in the upper, Andean, part of the Aconcagua watershed (watersheds 21-23 and 29 in Fig. 27) is 45.2·m³ s^{-1} at average for the same period (1986-2006).

These runoff time series were entered into the watershed model described in chapter 6. Fig. 28 provides an example of a time series for sub-watershed no. 4 (Lower Limache).

Tab. 10 average runoff per sub-watershed for the simulated period 1986-2006

SWS No		1	2	4	5	6	7	8	9	10	11	12
average Runoff	m^3s^{-1}	0.13	2.93	1.51	0.56	0.32	0.28	0.86	0.15	0.27	0.38	0.04

SWS No		13	14	15	16	17	19	20	24	25	26	28
average Runoff	m^3s^{-1}	0.49	0.50	0.44	0.5	0.1	0.1	0.2	1.20	0.62	0.83	0.05

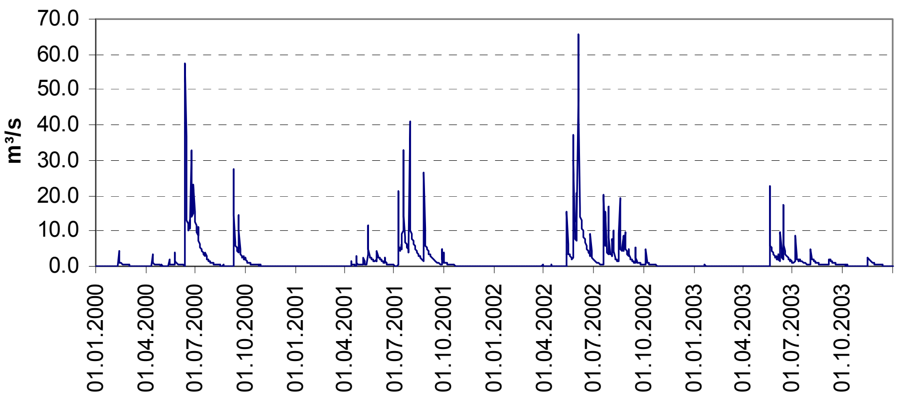


Fig. 28 Example of runoff time series created for the lower Limache watershed (years 2000-2003)

Sub-watershed number 4, compare Fig. 27; daily values

4.2.2.6. Groundwater

Groundwater availability is of major interest in the Aconcagua River, due to the necessity to determine how many groundwater abstraction rights can be issued on a sustainable basis. Thus the Chilean Water Authority (DGA) conducted several studies on the long term groundwater availability in the different aquifers of the Aconcagua Watershed. A basic study of a groundwater balance was provided by the DGA (2001) with subsequent additions (DGA, 2002; DGA, 2004_a).

The map in

Fig. 29 depicts the location of the ten main aquifers which are described in Tab. 11. Fig. 30 provides the long term water balance for five groundwater units as reported in DGA (2001). Each groundwater unit comprises several aquifers which were joined for the groundwater balance model.

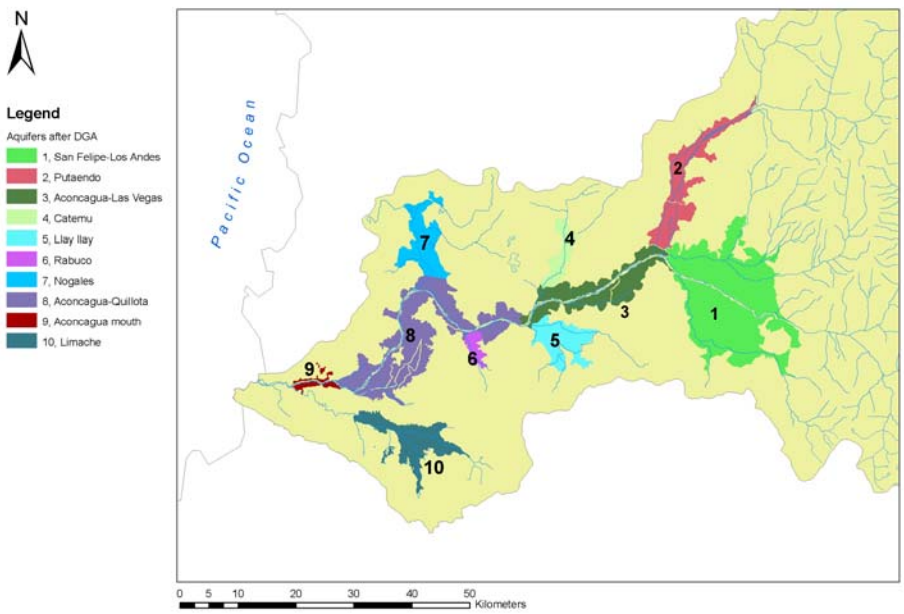


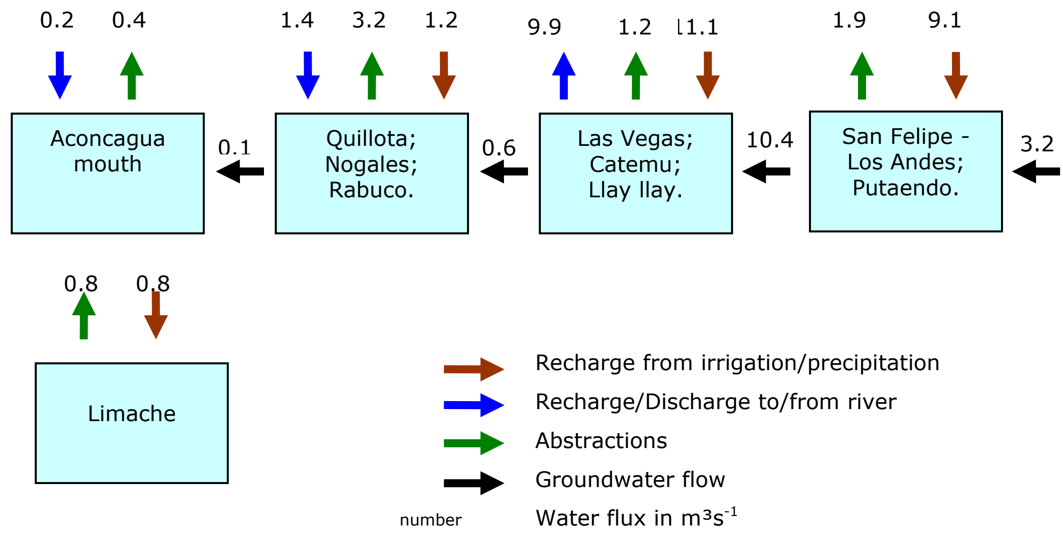
Fig. 29 Location of the ten principle aquifers in the Aconcagua watershed

All major aquifer systems except the one in San Felipe - Los Andes and Putaendo are shallow alluvial aquifers. An important element in the system is the groundwater discharge occurring downstream of San Felipe from the San Felipe/Los Andes Aquifer. An estimated 9.94 $m^3\ s^{-1}$ is discharged to the main Aconcagua River adding to the base flow of this stretch of the Aconcagua (DGA 2001) and providing a safe yield of water resources to the second irrigation section. This groundwater stems from percolation of the Aconcagua River and of the irrigation system upstream in the sector of Los Andes-San Felipe. Since no data on temporal dynamics of groundwater were available the groundwater fluxes were considered as constant over time in the subsequent modelling (chapter 6).

Tab. 11 Description of aquifers and groundwater balance

Section Name (Number)	Major Features
San Felipe – Los Andes (1)	Phreatic level rather deep (> 30 m), thickness less than 70 m in the western and up to 100 m in the central-eastern part. *Total area: 300 km²*
Putaendo (2)	Sediments of course structure. Aquifer with thickness of > 150 m. Very deep phreatic level around 130 m. The thickness of the aquifer decreases towards the mouth of the Putaendo to 70 m with phreatic levels at around 20 m. *Total area: 90 km²*
Rio Aconcagua – Las Vegas (3)	Very shallow aquifer (phreatic level around 1,3-3.8 m), thickness > 50 m. significant discharges of aquifer to the river. *Total area: 100 km²*
Catemu (4)	No detailed information available. *Total area: 35 km²*
Llay llay (5)	Complex system of at least five different sediment layers, some of them from paleo-lacustrine origin. *Total area: 55 km²*
Rabuco (6)	Thickness of aquifer between 30 m (upper part) and 100 m (lower part), *Total area: 15 km²*
Nogales (7)	Thickness up to 80 m. Increasing towards the centre and south of the aquifer. *Total area: 62 km²*
Aconcagua-Quillota (8)	Thickness varies between 50 m (upper part), 90 m in the middle part (Ocoa) and 30 m in the lower part (City of Quillota) *Total area: 200 km²*
Aconcagua Mouth (9)	One phreatic and one confined aquifer. Both are separated through a clay layer. The confined aquifer occurs at a depth of > 30 m the unconfined is less than 10 m deep. Both aquifers are around 1500 m wide. *Total area: 10 km²*
Limache (10)	This aquifer has its sink in the Reservoir "Embalse los Aromos"; it is not connected with aquifers in the Aconcagua valley. Thickness from 60 m to 100 m. *Total area: 75 km²*

Source: DGA (2001)



Notes:

- *Data on fluxes were obtained from DGA (2001), using the reported values for the base scenarios.*
- *Water balances may not add up to zero due to some additional inflows and storage values which were not reported here.*
- *The Limache aquifer is not connected to the other aquifers in the system.*

Fig. 30 Schematic view of water balance of aquifer units in the Aconcagua watershed

4.2.3. Land Use

The predominant vegetation in the watershed is "matorral" (s. Fig. 32) characterized through sparse shrub vegetation. In the upper part of the watershed bare rocks, snow or glaciers are the typical land cover. In the lower part, few natural and planted forests are present. The major land use in the valleys and alluvial plains is irrigated agriculture determined by the presence of fertile soils and by water availability. In these areas the major settlements are found as well. Fig. 31 visualizes the general spatial distribution of land use and land cover.

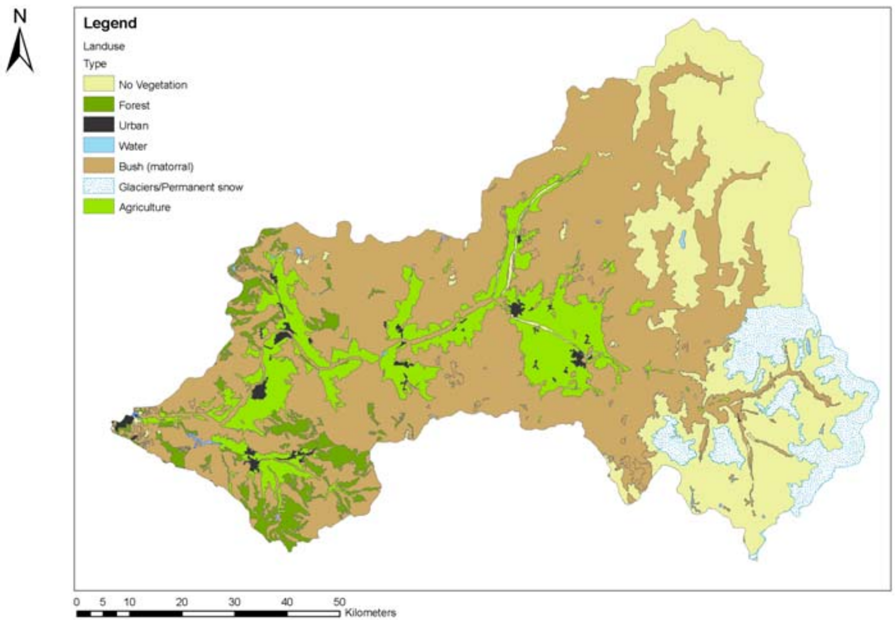
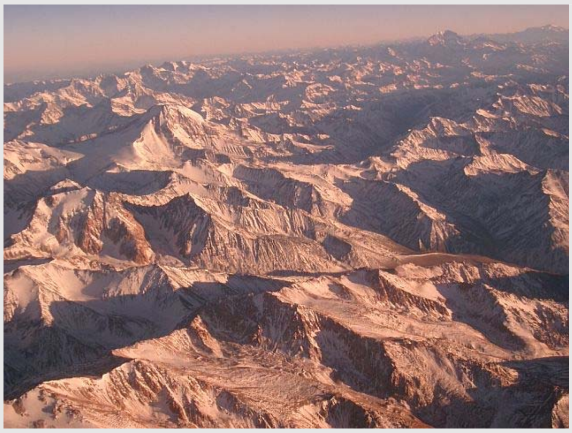


Fig. 31 Major land uses in the Aconcagua watershed

Source: SEREMI (2005)

"Matorral" vegetation on slopes, in the central part of the watershed



Snow covered mountains, upper Aconcagua

Photographs by Lars Ribbe

Fig. 32 Typical land cover features in the watershed: matorral and snow covered mountains

4.2.3.1. Land Use Statistics

The statistical Institute of Chile (INE) conducted a detailed agricultural census in 1976 and in 1997. Land use data is being reported on basis of municipalities and provinces. Tab. 12 shows the major agricultural land uses per municipality in the Aconcagua region according to the census of 1997. Fig. 33 visualises the spatial distribution of major crop groups.

Tab. 12 Agricultural land use (ha) in the municipalities of the Aconcagua Watershed in 1997

Municipality	Avocado and Citrus	Other Fruits	Grapes	Annual Crops	Horticulture +flours	Pasture	Total
Los Andes	13	504	638	240	34	257	***1685***
Calle Larga	44	908	1252	322	92	400	***3017***
Rinconada	62	446	1079	188	70	190	***2036***
San Esteban	38	1124	1882	595	170	479	***4289***
Quillota	1590	198	0	65	2773	736	***5362***
Calera	408	26	0	32	219	16	***701***
Hijuelas	1131	328	43	344	1674	360	***3879***
La Cruz	1677	348	0	1	379	32	***2438***
Limache	376	368	25	132	1181	667	***2748***
Nogales	530	418	36	706	802	633	***3126***
Olmué	371	225	8	31	300	115	***1050***
San Felipe	231	1175	2017	446	313	798	***4979***
Catemu	202	209	323	682	1091	1195	***3702***
Llaillay	318	511	488	502	1505	690	***4013***
Panquehue	639	253	806	546	513	616	***3373***
Putaendo	50	1268	385	450	173	304	***2629***
Santa María	163	1430	1856	212	102	257	***4020***
Total	**7842**	**9738**	**10835**	**5496**	**11390**	**7742**	**53044**

Source: INE, 1997 for locations of municipalities see Fig. 12; all figures reported in hectare

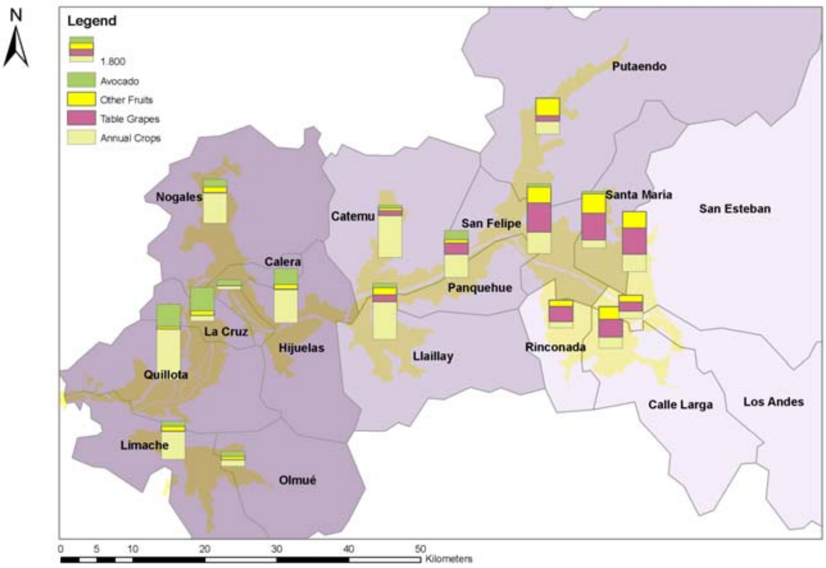


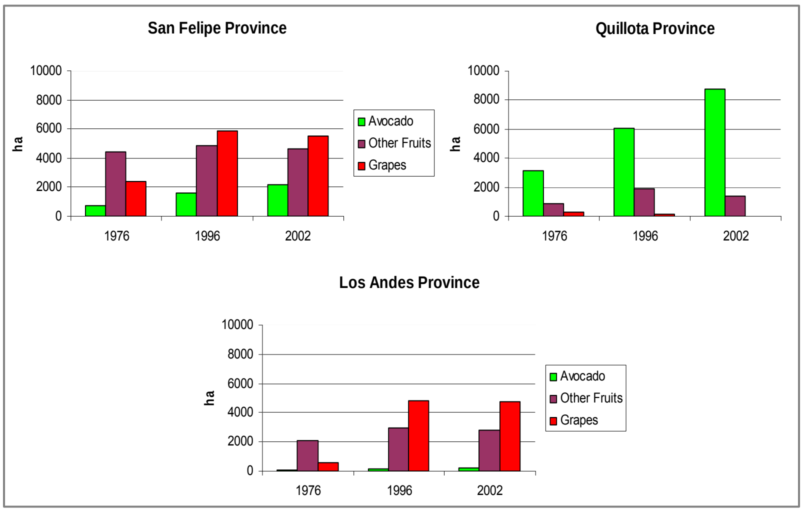
Fig. 33 Major crop groups in the municipalities of the Aconcagua watershed.

Source: of data: INE 1997, municipalities shaded in colours according to affiliation with the three provinces

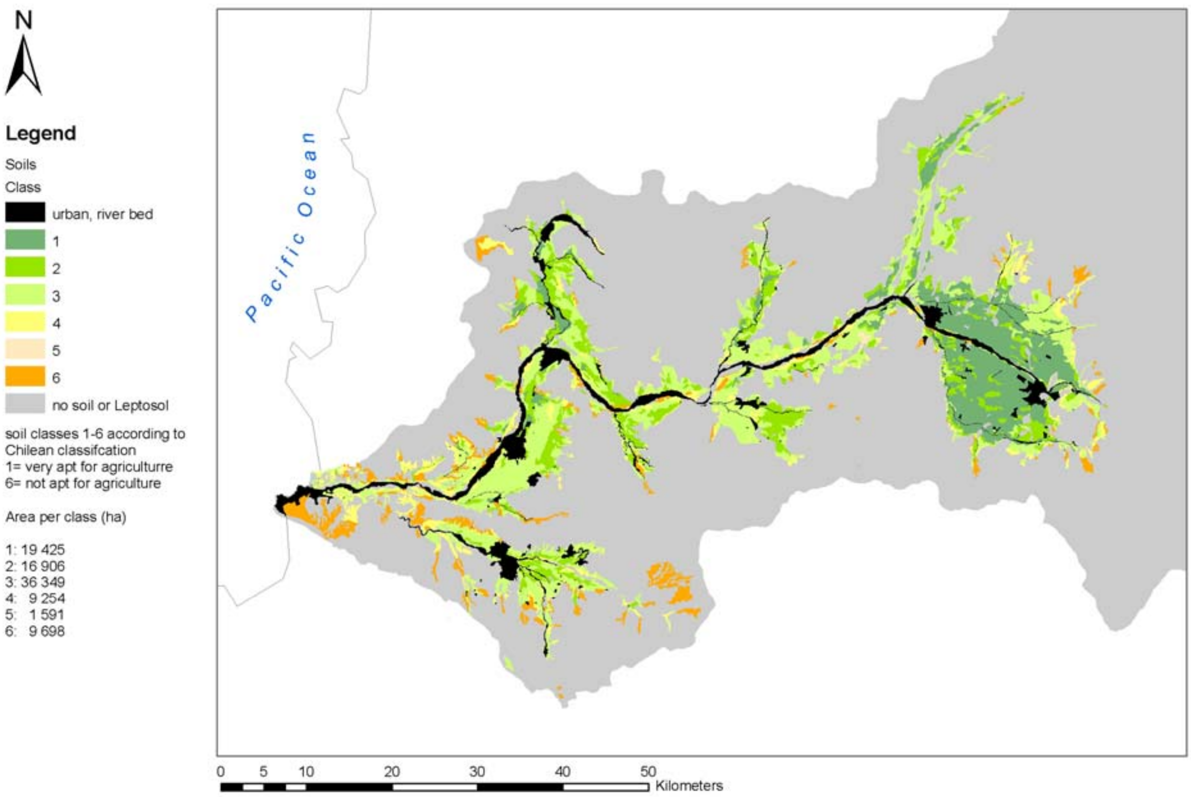
Since 1997, major land use changes occurred in the region, especially in the province of Quillota where the growing prices of Avocado and the easier access to the US market triggered a conversion of annual crops to Avocado plantations. Fig. 34 compares the temporal development of fruit trees in the three provinces San Felipe, Quillota, and Los Andes. For the area planted with fruit trees a cadastre of CIREN (2002) was used for comparison. A strong increase in surface planted with fruit trees can be observed, especially in the case of Avocado between 1997 and 2002. A similar development occurred for Grapes between 1976 and 1997 in the provinces of San Felipe and Los Andes.

Fig. 34 Area planted with fruit crops in the Aconcagua Watershed 1976 – 2002

Sources: INE (1976), INE (1997) CIREN (2002)



Agriculture in the watershed almost exclusively depends on the availability of irrigation water, since during the vegetation period in summer almost no rainfall occurs. The total area with soils of a very good to moderate potential for agriculture, is 81,925 ha (compare Fig. 35, classes 1-4). These lie almost entirely beneath channel level i.e. they are potentially irrigable. In 1997, 53.044 ha were under irrigation (agricultural census 1997, INE), in 1976 this area was 56.870 ha (INE 1976). In the past decades, total irrigated area stayed rather stable. Nevertheless, land use dynamics can be observed since irrigated agriculture is in competition with settlement development as the alluvial plains are also the most favourable sites for new rural settlements and urban sprawl. On the other hand, the high expected economic returns, especially related to Avocado in the recent years led to the development of irrigated areas above channel level – typically at the slopes of the foothills – which are irrigated by pumping water to the elevated areas.



Source: SEREMI (2005)

Fig. 35 Soils according to classes of agricultural capacity

4.2.3.2. Landsat Image Interpretation

MOSTAGHIM (2004) conducted a supervised interpretation of land uses of the whole Aconcagua basin based on Landsat images of 2000 and 2003. For the purpose of this study, the results of the classification of the agricultural area was adopted from MOSTAGHIM (2004). In addition, land uses other than agriculture and urban areas in the valleys are known (SEREMI 2005) and not subject to major changes in the last decades. Fig. 36 shows the result of this agricultural land use classification allowing to distinguish not only irrigated from non-irrigated land but also permanent (avocado and citrus) from deciduous fruit trees (mainly stone fruits), grapes, horticulture and pasture. Half of the ground data was used for the supervised classification; the other half was used for validation. Tab. 13 gives details on the accuracy of the Landsat ETM image interpretation in form of a confusion matrix showing how the pixel of the validation plots were classified. The overall accuracy of 80.5 % shows that the classification is reliable while an uncertainty remains. With the current classification it is difficult to distinguish grape from deciduous fruit trees and horticulture from meadow, which may introduce errors into the derived land use distribution.

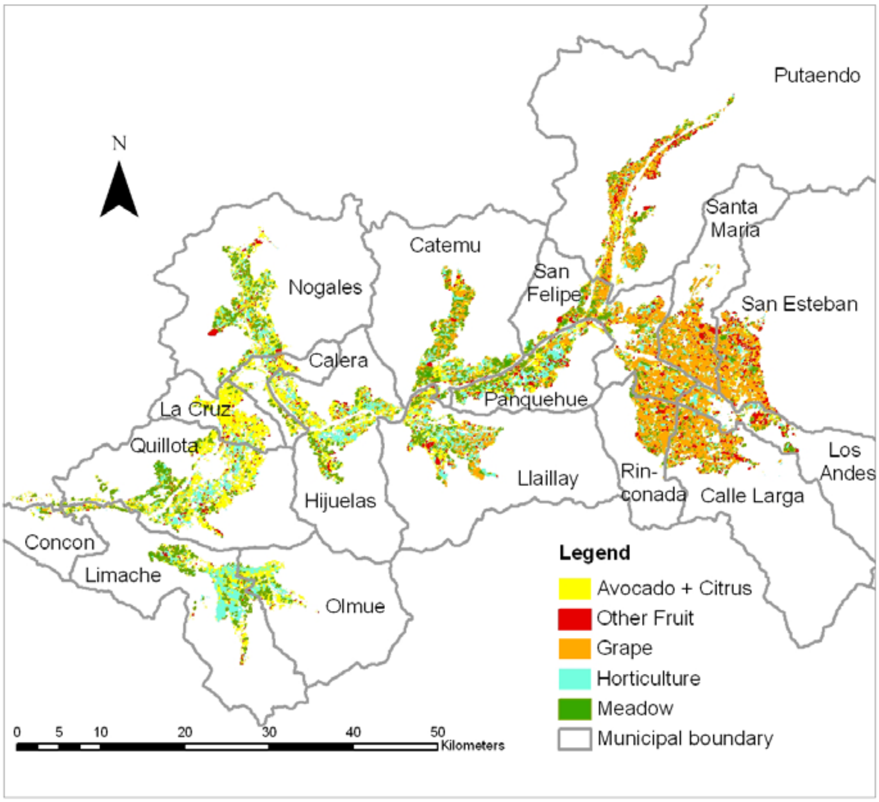


Fig. 36: Agricultural land use as determined by the Landsat ETM 2003 interpretation

based on data by Mostaghim (2004)

Tab. 13 Confusion matrix comparing classification with ground truthing data

	Ground Truth (validation)					
Class	**Avocado Citrus**	**Decidious Fruit Trees**	**Grape**	**Horticulture**	**Pasture**	**% of Total**
Avocado Citrus	88.4	3.3	2.2	7.2	7.1	*26.8*
Decidious Fruit Trees	0	72.1	10.4	2.6	4.5	*15.5*
Grape	1.7	19.6	84.9	2.9	5.8	*30.8*
Horticulture	7.3	5.1	2.4	69.1	3.2	*16.0*
Meadow	2.6	0	0.0	18.2	79.4	*11.0*
Total	100	100	100	100	100	

Figures show classification of pixel of ground truthing ROI in % ; Overall accuracy = 1403/1742 = 80.5 %. based on Landsat 7ETM+, 19.01.2003; Scene 233/83.

In order to compare land use with the census of 1976 and 1997, the land use was related to municipal boundaries. Tab. 14 shows the land use per municipality as classified for 2003 and Fig. 37 visualizes the changes of major crop groups aggregated per province (the province *Valparaiso* was excluded since it is represented by only one municipality, Concón, where almost no agriculture takes place).

Tab. 14 Agricultural land use (ha) in the municipalities of the Aconcagua Watershed in 2003

Municipality	Avocado and Citrus	Other Fruits	Grapes	Annual Crops and Horticulture	Pasture	Total
Los Andes	56	215	814	363	133	1581
Calle Larga	90	837	1501	429	215	3072
Rinconada	163	481	1039	348	222	2253
San Esteban	88	1188	1746	677	222	3921
Quillota	2120	111	32	2689	562	5514
Calera	688	89	35	155	44	1012
Hijuelas	1235	178	87	1814	244	3557
La Cruz	2154	96	21	200	30	2500
Limache	560	299	39	1502	596	2996
Nogales	910	252	77	1043	607	2889
Olmué	430	15	7	525	104	1081
San Felipe	447	814	2048	784	688	4783
Catemu	354	185	273	1654	1080	3547
Llaillay	417	481	584	2346	451	4280
Panquehue	862	474	718	1103	348	3504
Putaendo	92	999	460	511	407	2469
Santa María	259	978	2134	407	163	3941
Total	**10925**	**7691**	**11616**	**16551**	**6117**	**52900**

Source: Landsat image classification 2003

The increase of Avocado plantations in the Quillota province is obvious and it compares well with the data of the fruit cadastre reported by CIREN (2002), (compare Fig. 34).

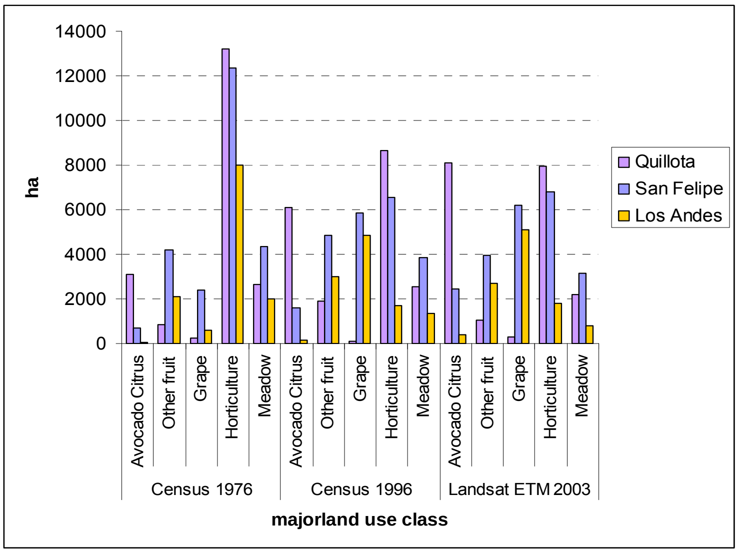


Fig. 37 Changes of agricultural land use between 1976 and 2003 in the three provinces

4.2.3.3. Accounting for temporal changes of land uses

While land uses evidently changed during the study period, nothing is known regarding the rate of change between the years 1976, 1997 and 2003. In order to create time series of water and fertilizer use, land use for each year per irrigation sector or municipality is necessary. For this purpose a linear development process between the three dates with classified land use was assumed and related to each municipality of province of the watershed.

4.2.4. Water Uses

Dominant water use within the watershed is irrigation accounting for approximately 84 % of the total consumption (excluding water used for hydro- and thermal power generation, which are non-consumptive uses). Drinking water supply accounts for 7.5 % (2.9 m³/s) and industrial water supply for 6.6 % (2.5 m³/s) the rest is used for mining (1.5 %, 0.6 m³/s); (DGA 1996).

The most important abstraction of drinking water, "Dren Las Vegas"; is right below the Romeral monitoring station, located in the centre of the watershed, for the purpose of supplying water to the cities of Valparaíso and Viña del Mar with municipal water. Here around $45 \cdot 10^6$ m³a^{-1} (1.44 m³s^{-1}) are abstracted at average. The detailed time series with daily values of abstraction is available and incorporated in the subsequent modelling of the river basin. In addition, the cities Los Andes and Concón and some smaller communities are supplied with surface water from the Aconcagua River. The rest of the settlements and industries are supplied by groundwater from the alluvial aquifers (VON IGEL GRISAR 1999).

Tab. 15 gives an overview of the spatial distribution of water uses as related to the different sections (for description of irrigation sections see Fig. 39, chapter 4.2.4.2) of the river system. Since section four is not very significant in terms of surface area and water uses, it is generally treated together with section three.

In the third (and fourth) section industrial and domestic uses are quite significant representing almost 30% of total demands whereas in the second section almost the entire water is used for irrigation (99%). This is due to the fact that the valley here is very narrow not providing adequate space for bigger settlements or industrial activities.

Tab. 15 Water supply and demands in the five mayor irrigation sections

	Section 1		**Section 2**		**Section 3 & 4**		**Putaendo**		**Total**	
Year	*1995*	*2025*	*1995*	*2025*	*1995*	*2025*	*1995*	*2025*	*1995*	*2025*
Water Availability (Average)	1055		1182		922		273		**3432**	
Agricultural Demand	365	381	228	247	324	314	108	102	**1025**	**1044**
Domestic Demand	9,8	18,9	0,3	0,5	81	144	0,3	1	**81**	**145**
Industrial Demand	15	29	1,2	2,3	64	121	0	0	**79**	**150**
Mining	13	19	0,7	1,1	4	6	0,2	0,2	**17**	**25**
Total Demand	**403**	**448**	**230**	**251**	**474**	**586**	**109**	**103**	**1202**	**1364**

Data source: DGA (1996). (All figures in 10^6 m³ a^{-1}; $1 \cdot 10^6$ m³ a^{-1} = 0.03171 m^{3}s^{-1})

Fig. 38 shows the temporal distribution of water uses during an average year. The peak of water demand (Nov-Feb) almost coincides with the peak of water availability (Nov-Jan). This peak demand is due to irrigation water uses. Industrial and domestic demands stay more or less the same throughout the year. The long term evolution of water demands is discussed in later chapters.

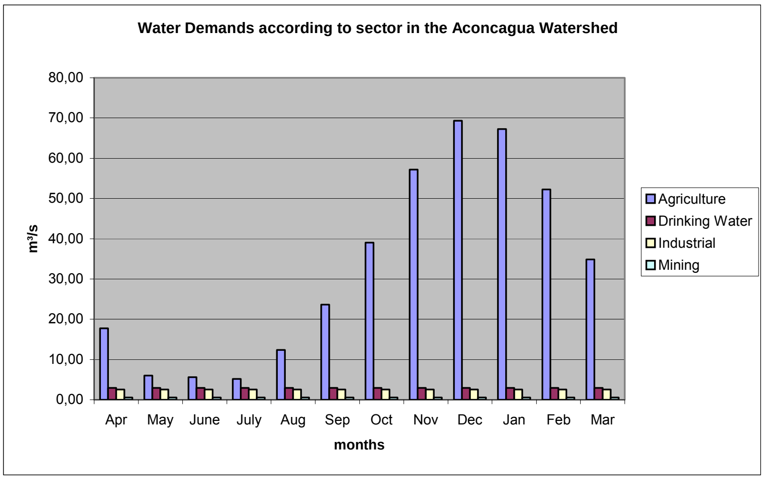


Fig. 38 Annual distribution of water demands (1995)

Source: DGA (1996)

4.2.4.1. Water Rights and Allocation Principles

In order to develop temporal time series for water abstractions, the water allocation and water rights system next to water availability is a very important factor. In the Aconcagua River, each of the five sections uses the water rather independently of the other sections. Within each section, water is distributed to the different channels according to established water rights. These water rights are granted on the basis of the available flow that is guaranteed in 85 % of the years (Q 85). This means that at average in 15 % of the years irrigators receive less water than their water rights permit. In those years of water scarcity, each channel (typically organized by a channel association) experiences the same drop in percentage of available water as the other channel located in the same section. Prior appropriation does not occur within a given irrigation section. The other sections manage their water distribution according to the water availability. Between the sections, however, there is no coordination regarding water allocation. Each section abstracts all the water according to their established water rights. This leads to situations were at the end of one section, the water flow in the river is merely constituted of the irrigation return flows of the upstream section and groundwater discharges or discharges of tributaries which enter the Aconcagua River. Reuse within a section is another important water source. Next to permanent water rights each section also possesses contingent water rights. These can be utilised in years of above-average flow.

4.2.4.2. Irrigation and Drainage

The irrigation system in the Aconcagua Watershed has a long tradition. There is even evidence of irrigation water use in pre-Columbian times. While the region is inhabited at least since 800 BC, there is no information on the existence of pre-Incan irrigation infrastructure in the Aconcagua Valley (GAY, 1862). After the arrival of the Inca to the "Norte Chico" and Central Chile about 1490, small and medium sized irrigation channels were constructed in the valleys of Central Chile, among them the Pocochay Canal but the total irrigated area in the central valley between the rivers Aconcagua and Cachapoal did not exceed an area of 3.000 ha. The major irrigation channels and infrastructure were built in the 19th century. The irrigation system as it is seen today, however, has been fully developed in the early and mid 20th century (JERIA, 2003).

The four irrigation sections in the Aconcagua are related to the hydrographical conditions of the Aconcagua River, which is by far the most important source of irrigation water. At the upper part of each section are points, where abstraction of water is especially favourable. From here, water is conveyed to the regions with fertile soils in the lower parts of the Aconcagua valley or of the valleys of tributary streams. Taking advantage of the slope of the terrain water is transferred even to the upper parts of the valleys of tributary streams. Fig. 39 shows the irrigation sections and the major irrigation channels. The drainage system is developed well and either surface or land tile drainage systems are in place in the whole region.

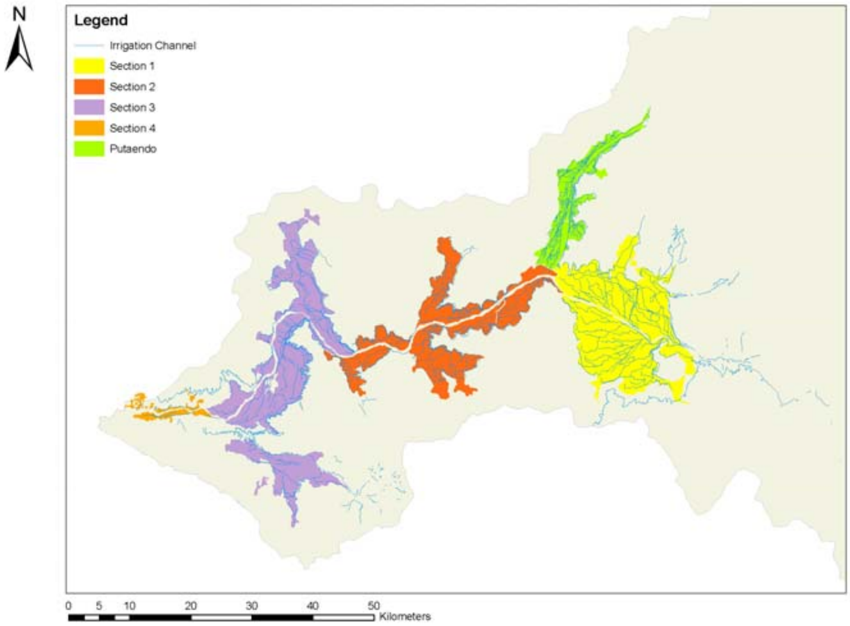


Fig. 39: Location of main irrigation sections

Source: SEREMI (2005)

4.2.4.3. Irrigation Abstractions and Return Flow

At the beginning of the irrigation season (September), channels are opened and convey the water from the main river to the fields. Part of this water is returned to the surface water system as return flow.

The overall water abstraction for irrigation depends on the crop water demands (see Tab. 16) on the established water rights (Tab. 17) and on the available water in the Aconcagua River. For the first irrigation section and the Putaendo section, information on water availability is provided as measured data from the upper Andean watersheds. For the other sections of the river, water availability results from the subsequent water balance of the river which is determined by irrigation and municipal return flow and inflows from tributaries and groundwater.

Tab. 16 Water requirements (mm) for selected crops

Section Putaendo	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
Avocado	141	126	100	56	0	0	0	0	36	80	115	138	792
Grape	149	132	93	29	0	0	0	0	26	82	120	146	776
Horticulture	207	138	0	0	0	0	0	0	5	75	170	207	801
Pasture	217	177	125	51	0	0	0	2	56	127	180	216	1151
Section 1	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**	**Total**
Avocado	150	134	106	60	0	0	0	0	38	85	122	147	841
Grape	149	132	93	28	0	0	0	0	26	82	120	146	776
Horticulture	224	141	0	0	0	0	0	0	6	76	173	210	829
Pasture	217	177	125	51	0	0	0	2	56	127	180	216	1150
Section 2	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**	**Total**
Avocado	149	133	105	59	0	0	0	0	37	84	121	146	835
Grape	140	124	88	27	0	0	0	0	25	77	113	137	729
Horticulture	210	140	0	0	0	0	0	0	5	76	173	210	815
Pasture	217	177	125	51	0	0	0	2	56	127	180	216	1150
Section 3+4	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**	**Total**
Avocado	136	106	72	42	0	0	0	0	35	78	109	133	711
Grape	136	106	64	21	0	0	0	0	24	75	109	132	667
Horticulture	200	114	0	0	0	0	0	0	5	57	155	191	724
Pasture	199	142	86	35	0	0	0	0	53	118	162	196	991

Source: CICA 1982, based on average climatic conditions in the four irrigation sections; calculations on basis of Potential Evapotranspiraiton using the Penman-Monteith formula.

Crop Water Demands

Crop water demands are decreasing from irrigation section 1 to 3 due to the prevailing climatic conditions (Evaporation and Precipitation). CICA (1982) reports the crop water requirements for all major crops for the four major irrigation sectors (1-3, Putaendo); Tab. 16 shows irrigation water demands for some selected crops for the respective zones.

The net and gross irrigation water requirements per irrigation section were calculated according to the following formulas (compare chapter 3.3.2.2) using the parameters provided in Tab. 17:

$$NIWR = \sum_i CWR_i \cdot A_i \qquad (21)$$

NIWR = Net Irrigation Water Requirement ($m^3\ a^{-1}$)
CWRi = Crop Water Requirement of Crop i (m)
Ai = Area of Crop i (m^2)

$$GIWR = \frac{NIWR}{Ef \cdot Ec} \qquad (22)$$

GIWR = Gross Irrigation Water Requirement
Ef = Field Efficiency
Ec = Conveyance Efficiency

Tab. 17 Characteristics of irrigation sections (1997)

Irrigation Section	**A** [(1)] *Irrigated Area Below Channel Level* [ha]	**QC_{max}** [(2)] *Maximum Channel Capacity* $[m^3\ s^{-1}]$	**Ef** [(2)] *Field Efficiency*	**Ec** [(2)] *Conveyance Efficiency*	**NIWR** [(3)] *Net Irrigation Water Requirement* $[m^3\ s^{-1}]$	**GIWR** [(4)] *Gross Irrigation Water Requirement* $[m^3 s^{-1}]$
Putaendo	2630	7.9	0.41	0.90	0.7	1.9
Section 1	20027	40.2	0.44	0.94	5.5	13.2
Section 2	14969	27.1	0.42	0.88	4.2	11.4
Section 3	15424	29.2	0.48	0.89	3.7	8.7

Sources: 1) INE (1996); 2) DGA (2001) p. 38 ff; 3) based on CWR (CICA, 1982) and crop distribution per section based on INE (1996); 4) see text for explanations

Time series of gross irrigation water requirements (GIWR)

In order to describe the spatio-temporal behaviour of the water system, time series need to be developed for the gross irrigation water demand. Actual abstractions are lower than GIWR in certain periods of dry years and in certain parts of the river according to actually available water in the Aconcagua River. This water availability is a function of discharges and upstream water abstractions which vary from year to year.

The time series is developed with monthly values of water demand for each irrigation section according to equations *21 and 22* taking into account the cropping pattern of each section. Land use changes are accounted for in the sense that a linear dynamic is assumed for the land use changes from 1976 to 1997 and from 1997 to 2003; the linear trend of 1997 to 2003 is being extrapolated to 2006 (compare 4.2.3).

Fig. 40 shows the temporal development of irrigation requirements. The highest water requirements are observed in the month of January. Peak water demand decreases over the years as land use shifts from horticulture towards more fruit crops which have a more balanced water demand distribution over the year. Total water demands show a slight decrease due to a reduction of total irrigated area between the 1980s and today.

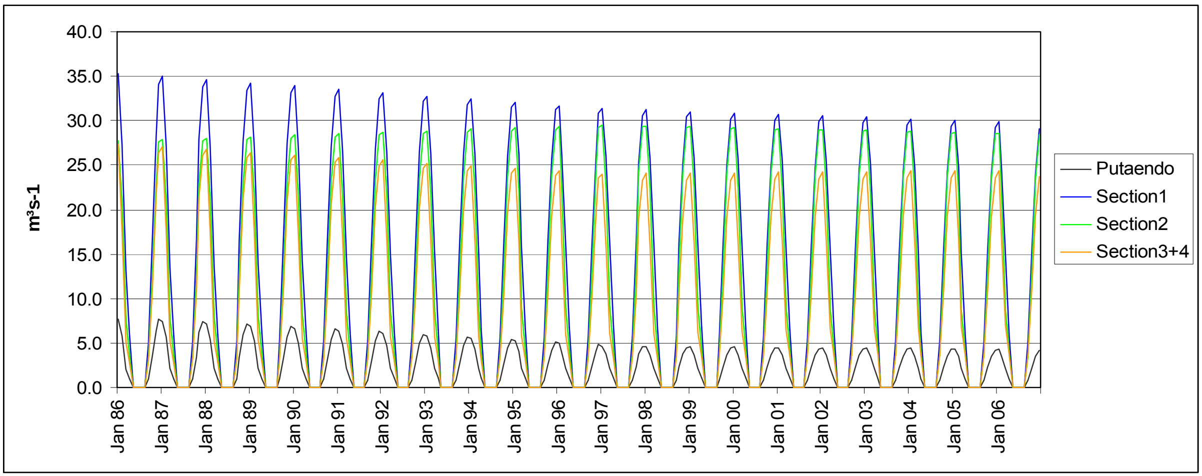


Fig. 40 Monthly gross irrigation water requirements (GIWR) for the four irrigation sections

Irrigation return flows

Irrigation return flow is the fraction of the water applied to an irrigation section, which is flowing back through surface or sub-surface drainage to the recipient stream or river.

DGA (2004_b) determined the return flow fractions for all irrigation sectors of the Aconcagua, subdivided into 20 irrigation districts. Tab. 18 summarises these values for the four main sections. These values were employed to calculate return flow as fractions of applied irrigation water in the water balance presented in the next chapter.

Tab. 18 Return flow fraction for major irrigation sectors

Irrigation Section	$C_{RS,O}$ Over Land Return Flow Coefficient	$C_{RF,S}$ Seepage Return Flow Coefficient
Putaendo	0.13	0.46
Section 1	0.17	0.38
Section 2	0.22	0.37
Section 3	0.19	0.32

source DGA 2004_b

4.2.4.4. Municipal and Industrial Water Uses

Municipal water abstractions were estimated by the population of the settlements in the watershed as described in chapter 3. The temporal development of municipal water demands can be based on the development of population numbers including information on the change of per capita water demands. Regarding the latter, ESVAL provides data for some years, which were extrapolated to the past through polynomial population growth functions, which were determined based on population data of the recent censuses (INE 1982, INE 1992 and INE 2002) for each municipality. The result of this calculation for the three main urban agglomerations is shown in Fig. 41.

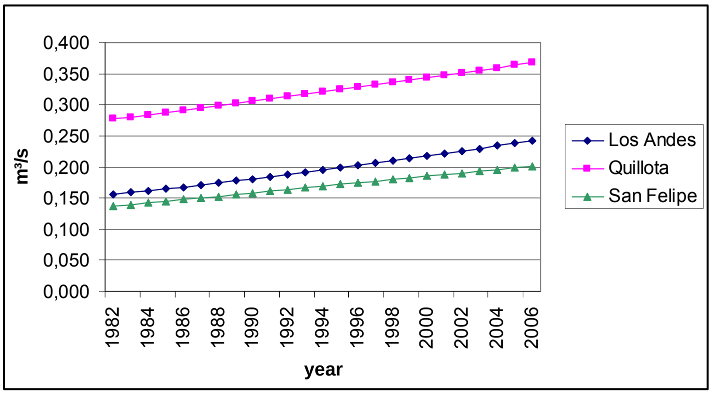


Fig. 41 Temporal development of municipal water abstraction

Note: "Quillota" includes the municipalities Hijuelas, Quillota, Calera, Artificio, Limache. San Felipe includes San Felipe and El Almendral.

No historic data on industrial water use is available. A constant water use is assumed here, based on the studies provided by Kristal (1996) and SISS (2005). The latter recently established a monitoring process providing information on the industrial wastewater emissions. Major abstractions are realized by the company Algas Marinas (100 l s^{-1}), Sobraval (50 l s^{-1}) and Pentzke (150 l s^{-1}). In addition, there are two thermoelectric power plants downstream of Quillota (San Isidro), each taking a volume of 450 l s^{-1} from the river. Other industrial abstractions as for example for mining activities or for hydropower generation were not investigated further since they usually take place in areas above those discharge stations which serve as input to the model of this case study, they are either non-consumptive water uses or they are simply too small to be considered for the purpose of this study.

4.2.5. Nitrogen Sources of Pollution

There are point and diffuse pollution sources which affect the water quality of the Aconcagua River. The point sources are subdivided into sources from municipal and industrial waste water, the diffuse pollution into sources from agricultural and storm water run off. These sources need to be quantified and time series for the period of 1986 to 2006 need to be developed.

4.2.5.1. Municipal Wastewater

Until 2003, municipal wastewater of all major communities in the Aconcagua basin was either treated by aerated or facultative lagoons or – the major part – only with primary treatment technologies.

Tab. 19 lists all relevant settlements in the Aconcagua watershed and shows the treatment method, the recipient water body and the nitrogen produced by the population. The data is calculated on the basis population figures (available for all communities based on the population census of 1982, 1992 and 2002).

It is important to note that the loads reaching surface water are less, depending on the treatment and disposal methods. The effluents of the facultative lagoons in the watershed have nitrogen (Total Kjeldahl N) concentrations between 29 mg l^{-1} and 45 mg l^{-1} (Tab. 20), depending on the abstracted volume of water for domestic supply.

Between 2002 and 2004, three major wastewater treatment plants were constructed joining the wastewater of a) Los Andes and surrounding settlements, b) San Felipe and surrounding settlements, and c) Quillota, La Calera, Limache and other surrounding settlements (Tab. 21). Fig. 42 visualises the location of communities, their wastewater production and the location of the outfalls of recently (2003) constructed waste water treatment plants.

Tab. 19 Wastewater production and nitrogen loads before 2003

Community	Treatment Method pre 2003	Nitrogen Produced [Kg/D] 1986	Nitrogen Produced [Kg/D] 2002	Recipient
Calle Larga	no	93	104	Aconcagua
Catemu	aereated lagoon	150	187	Catemu
Con - Con	marine outfall	133	323	Ocean
Hijuelas	no	127	160	Aconcagua
La Calera	no	403	495	Aconcagua
La Cruz	no	98	129	Aconcagua
Limache	no	421	533	Limache
Llay-Llay	aereated lagoon	179	216	Las Vegas/ Los Loros
Los Andes	no	407	602	Aconcagua
Nogales	facultative lagoons	163	216	El Litre
Putaendo	aereated lagoon	119	146	Putaendo
Quillota	no	593	759	Aconcagua
Rinconada	no	49	67	Pocuro
San Esteban	facultative lagoons	110	144	Aconcagua
San Felipe	no	447	641	Aconcagua
Santa María	facultative lagoons	97	128	SanFranciso/ Quilpue

Nitrogen loads based on per capita production of 10 g N d^{-1}. source: ESVAL 2007

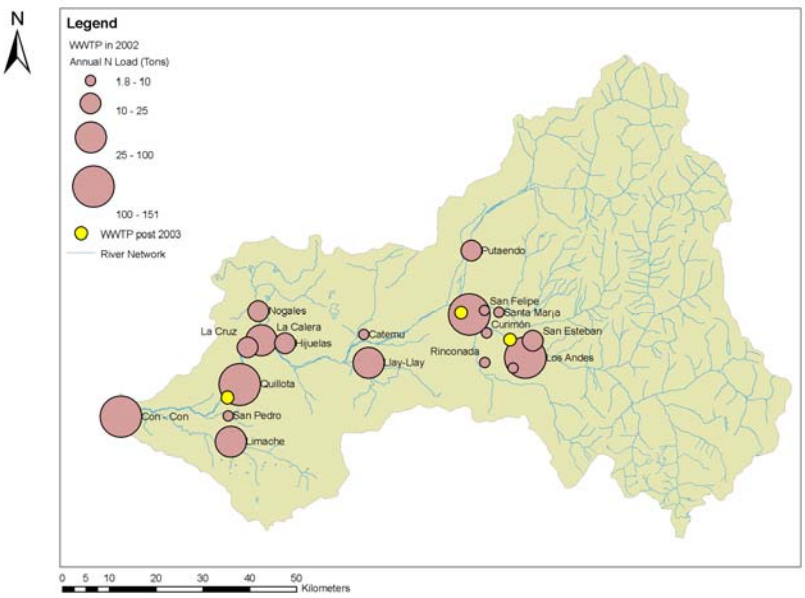


Fig. 42 Location and quantification of wastewater sources in the Aconcagua watershed (2002)

wwtp post 2003: wastewater treatment plants constructed in 2003, started operation in 2004

Tab. 20 Examples of effluent composition of aerated lagoons in the Aconcagua Watershed

Name of community	BOD	TSS	Total Nitrogen (Kjeldahl)	Phosphorus
	[mg l^{-1}]	*[mg l^{-1}]*	*[mg l^{-1}]*	*[mg l^{-1}]*
Catemu	57	46	38	3.7
Santa María	118	174	29.6	8.7
San Esteban	308	592	43.4	14.1
Putaendo	142	215	34.4	8.8
Placilla			45	

BOD. Biological Oxygen Demand, TSS: Total Suspended Sediements
Sources: ESVAL (2004); for treatment plant Placilla: SALGADO et al. (2005)

Tab. 21 Characteristics of wastewater treatment plants which started operation in 2004

New Treatment Plant	Communities Connected	Population Served (Capacity)	Technology	Average TKN Concentration Of Effluent (Measured)	Nitrate Concentration (Estimate[1])	N-Load
				[mg N l^{-1}]	*[mg N l^{-1}]*	*[Kg d^{-1}]*
Los Andes	Los Andes San Esteban Calle Larga	75 000	Secondary treatment via oxidation ponds	1,6	10	29
San Felipe	San Felipe El Almendral	75 000	Secondary treatment via oxidation ponds	1,9	10	30
Quillota	Quillota La Calera Hijuelas Artificio La Cruz Limache	200 000	Secondary treatment, activated sludge	10,3	10	311

Notes: average TKN (total Kjeldahl nitrogen) concentration: based on weekly sampling of ESVAL between Oct 2004 – Dec. 2006; Source: ESVAL (2007)
[1] Estimated nitrate concentration for biological wastewater treatment without denitrification step (Metcalf & Eddy, 1991).

Developing time series for wastewater nitrogen emissions

No exact data about the wastewater production before 2003 is available since only simple treatment facilities were in place and discharges were not measured, except in some isolated studies (e.g. KRISTAL 1996) or in recent years by ESVAL (2007). For this reason the approach described in chapter 3 (equations 9 and 10) was applied to estimate nitrogen loads which were hindcasted back to the year 1986. While water consumption per capita has changed, it is assumed that waste loads per capita stayed stable. After the construction of modern wastewater treatment plants in 2003/2004 their wastewater production as monitored by ESVAL was taken into account for the creation of the time series of the period 2004-2006 (compare Tab. 21). The time series for TKN loads (Kg TKN per day) for the period of 1986 – 2006 is shown in Fig. 43. The sharp drop of TKN emissions in 2004 is attributed to the start of operation of modern waste water treatment plants in that year. It is important to note that the wastewater treatment significantly reduces ammonium and organic nitrogen (expressed as sum parameter TKN) of the wastewater but part of the ammonium is transferred to nitrate via nitrification. A modern treatment plant using the activated sludge technology, like the three constructed in the Aconcagua Watershed in 2003/2004, have residual nitrate values of around 10 mg l^{-1}. These N-inputs were added to the effluent time series for the modelling described in chapter 6.

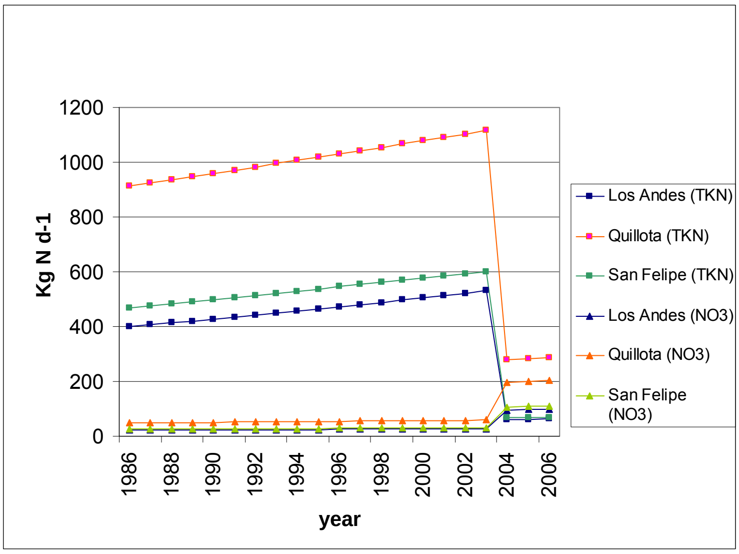


Fig. 43 Temporal development of TKN and NO_3 loads for three major municipality groups

Note: The sharp drop in 2004 is due to the construction of waste water treatment plants; TKN = Total Kjeldahl nitrogen, the sum of organic nitrogen, ammonium and ammonia. NO_3=Nitrate

4.2.5.2. Industrial Pollution

There are seven industries that are direct emitters to the river. Other industries discharge to the wastewater network managed by ESVAL and their discharges reach the river via the public sewerage system.

Tab. 22 Location, type and N-loads of industrial effluents

Name	Location of discharge	Type of Industry	BOD load [Kg d^{-1}]	N-load [Kg d^{-1}]
Pentzke	San Felipe	Canning	1847	67
Algas Marinas "Algamar"	La Calera	Fish processing	4861	438
BASF	Concón	Chemical	no data	375

Source: Kristal Consultoria, 1996; Average value of two sampling campaigns (Nov. 1994, May 1995)

A study conducted on behalf of the Chilean Environmental Agency (CONAMA) analysed the contaminant load of all industries present in the watershed (Kristal, 1996). Only three of the industries discharging directly to the river have significant nitrogen loads, they are listed in Tab. 22. Due to lack of information, the temporal behaviour of food processing discharges are considered constant over the modelled time span (1986 – 2006).

4.2.5.3. Agricultural Pollution Sources

The major source of nitrate pollution to streams stems from fertilizers applied to agriculture. In the context of this study it is important to characterize the spatial and the temporal distribution of fertilizer applications. The spatial distribution of fertilizer application can be calculated based on the land use distribution. For each municipality the cropping pattern is known. Fertilizer used per crop and hectare were determined through a specially designed survey (compare chapter 5). Thus, for each municipality the fertilizer application can be quantified. Tab. 23 shows details of the result of calculation of fertilizer application for the year 1997.

Tab. 23 Fertilizer applied to agricultural land per municipality (1997)

Municipality	Horticulture [ha]	N [Kg]	P [Kg]	Fruits [ha]	N [Kg]	P [Kg]	N tot	P tot
Calera	151	22063	5271	627	125322	39476	147385	44747
Calle Larga	89	13009	3108	2123	424500	133718	437509	136826
Catemu	1070	156696	37436	814	162790	51279	319486	88715
Hijuelas	1252	183403	43817	2041	408108	128554	591511	172371
La Cruz	285	41767	9979	2280	455920	143615	497687	153593
Limache	708	103766	24791	740	147952	46605	251718	71395
Llaillay	1502	219984	52556	1798	359562	113262	579546	165818
Los Andes	33	4893	1169	1019	203802	64198	208695	65367
Nogales	739	108234	25858	1283	256514	80802	364748	106660
Olmué	206	30238	7224	475	94982	29919	125220	37143
Panquehue	501	73338	17521	1544	308706	97242	382044	114763
Putaendo	172	25198	6020	1592	318482	100322	343680	106342
Quillota	2408	352699	84263	2706	541176	170470	893875	254733
Rinconada	70	10226	2443	1603	320674	101012	330900	103455
San Esteban	169	24788	5922	3009	601850	189583	626638	195505
San Felipe	311	45503	10871	3453	690652	217555	736155	228426
Santa María	102	14899	3560	3108	621640	195817	636539	199376

Source of land use data: INE (1997), fertilizer use per crop: agricultural survey in Pocochay area (compare chapter 5).

The temporal behaviour of nitrogen fertilizer is estimated based on fertilizer sales numbers. Since no data per municipality or geographic region was available, the same dynamic was assumed for all municipalities. The application of organic manure is considered to be constant and not very significant since the number of cattle has always been very low in the study region (INE 1997, INE 1976). Fig. 44 visualizes the general trend of fertilizer application where the base year of the survey (2005) is set to a value of 1.

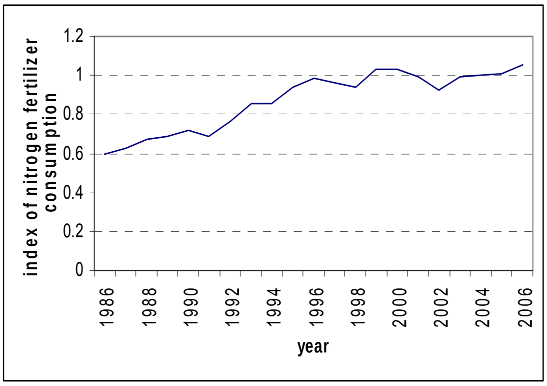


Fig. 44 Time series of fertilizer application

Sources: FAO (2007), Donoso (1999)
Graph shows relative development of N-fertilizer consumption related to the reference year 2005 which is assigned a value of 1

Applying this trend together with spatial distribution and temporal dynamic of cropping patterns (compare 4.2.3) and related fertilizer applications the actual total N-fertilizer application was calculated per municipality and aggregated area (province, irrigation section). Tab. 24 and Tab. 25 show the calculated fertilizer applications per irrigation section for the years 1990 and 2000 as examples.

Tab. 24 fertilizer applications calculated for the year 1990

	Avocado Citrus	Other fruit	Grape	Horticulture	Pasture	Sum
Putaendo	4,517	110,296	30,377	268,934	41,873	**455,996**
Section 1	44,603	599,188	731,594	967,566	177,122	**2,520,074**
Section 2	200,519	128,998	145,190	1,219,181	206,532	**1,900,419**
Section 3 + 4	473,676	146,195	15,009	1,452,726	162,814	**2,250,420**
Sum	**723,315**	**984,677**	**922,170**	**3,908,406**	**588,341**	**7,126,910**

Tab. 25 Fertilizer applications calculated for the year 2000

	Avocado Citrus	Other fruit	Grape	Horticulture	Pasture	Sum
Putaendo	11,251	179,817	67,017	141,286	36,618	**435,988**
Section 1	131,187	801,044	1,428,111	721,933	207,232	**3,289,507**
Section 2	409,135	207,672	263,456	1,716,553	256,726	**2,853,542**
Section 3 + 4	936,940	193,869	22,239	1,587,346	213,300	**2,953,693**
	1,488,513	**1,382,401**	**1,780,822**	**4,167,118**	**713,876**	**9,532,730**

With the overall temporal development of fertilizer consumption and the information on land use changes for each municipality (compare chapter 4.2.3), time series of fertilizer applications can be generated. The accumulated fertilizer use for the whole Aconcagua is presented in Fig. 45. While until 1996 an increase of N-fertilizer application can be observed, the consumption remains rather stable for the past 10 years.

For the subsequent modelling fertilizer time series were developed for each municipality which were later distributed according to sub-watersheds in the subsequent watershed nitrate model (chapter 6).

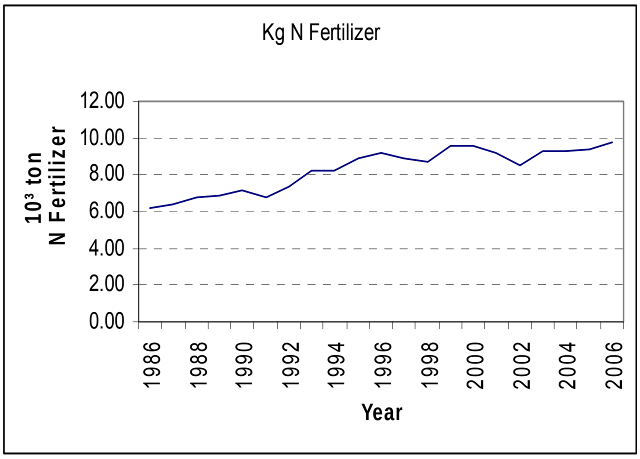


Fig. 45 Total N Fertilizer Application within the Aconcagua Watershed

Export of fertilizers to surface water

As described above, estimates for nutrient input to agricultural areas can be estimated according to the spatial and temporal distribution of land uses. The crucial question for modelling nitrate concentrations in surface water is which fraction of this applied fertilizer is being exported to drainage and streams and according to which temporal behaviour. In order to make assumptions on the fertilizer export, detailed data on soil type, and amount of harvest, irrigation and fertilizer application timing should be known. Since this is not feasible for the region and scale, a three year study was conducted in one sub-watershed in order to determine nitrogen export coefficients. This assumes that the export behaviour of nitrogen is similar in all irrigation sectors of the Aconcagua watershed. The results of this specific study in order to determine export coefficients are presented in chapter 5.

4.2.5.4. Urban Stormwater Runoff

During and after rainfall events, urban runoff adds an additional amount of contaminants to the river. Since urbanisation is not very advanced in the Aconcagua basin itself, this does not represent a major source of pollution. Stormwater accumulation is a function of average slope, imperviousness and size of the urban area. The average slope of urban areas in the Aconcagua is rather low since the majority is built in the alluvial plains; imperviousness is rather low, as typical for smaller cities. However, details are not known. The estimated area of settlements in the watershed is provided on basis of the Landsat interpretation. Since for Chile no storm water pollution data is available, it needs to be estimated from studies of other regions. In an extensive review paper LIN (2004) reports export coefficients combining studies from EPA and USGS (total of 178 urban sites in the US). The median value for Total Nitrogen export from urban areas was 7.5 Kg N ha-1 (25 percentile: 5 Kg N ha^{-1} a^{-1}, 75 percentile: 9.7 Kg N ha^{-1} a^{-1}). This value was distributed over the year according to rainfall amounts as the most important pathway to introduce nitrogen to surface water is via drainage. The precipitation for each urban area was determined after applying the Thiessen polygon interpolation. The results of the estimates for nitrogen export for the urban areas within the watershed are presented in Tab. 26. It should be noted that the overall impact of urban runoff on nitrogen loads from urban areas is not very significant in comparison to irrigation or wastewater loads. For this reason, estimates of nitrogen export by export coefficients related to precipitation, is considered sufficient in order to estimate nitrate concentration variability. Therefore, an empirical study merely designed to improve calculation of storm-water N-export from cities is not necessary. Here, no attempt was made to ask the question if Chilean cities show significantly different N-export than the ones reported in the studies summarized by Lin (2004). Also *first flush* effects, attributing a higher N-load to the drainage of rainfall events after a prolonged dry season, were not considered.

Tab. 26 Urban stormwater runoff

Name of urban area	**Surface** [Km²]	**N-Load** [Kg N a^{-1}]
Los Andes	7.9	6083
San Felipe	8.2	6314
La Calera	5.2	4004
Quillota	9.4	7238

Urbanized area according to Landsat ETM image interpretation (MOSTAGHIM 2004)

Using precipitation data (after the Thiessen polygon interpolation), time series for stormwater runoff were produced for the four urban centres and later added to the watershed nitrate model (chapter 6). Since all urban areas count with a drainage system with an outlet to the Aconcagua River, it is assumed that the complete storm water runoff reach surface water. As mentioned in chapter 3 the share of nitrate in stormwater is set to 70 %.

4.2.6. Reported River Water Quality Data

4.2.6.1. River Water Temperatures

For the modelling of nitrogen compounds in the Aconcagua River, estimates of temperature are important as they influence the nitrification and denitrification rates (compare chapter 3). The following Fig. 46 shows results of average river temperature.

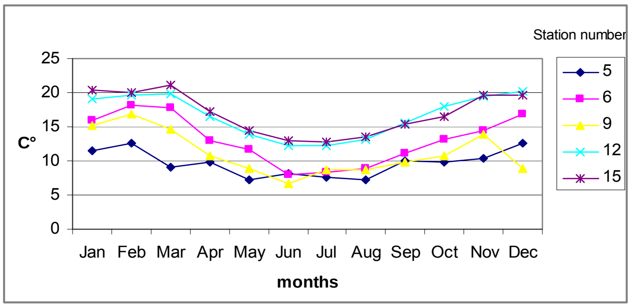


Fig. 46 Average temperatures in the Aconcagua River at five stations.

Note: average temperature values were determined on the basis of measured values by DGA (1981-2006). A total of 73-83 temperature measurements were available per station (period 1981-2006). For location of stations see Fig. 47.

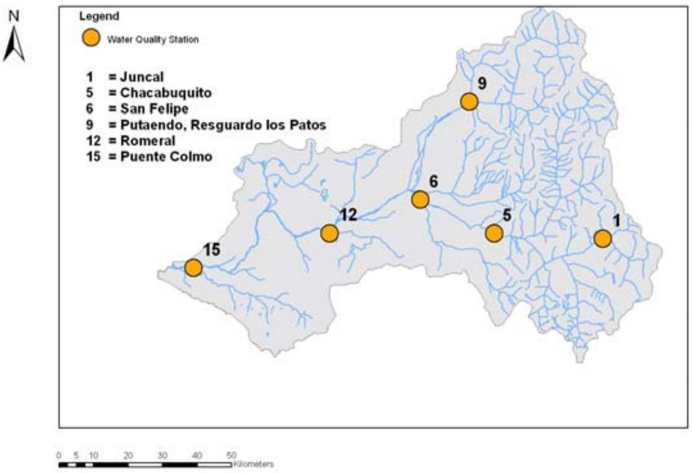
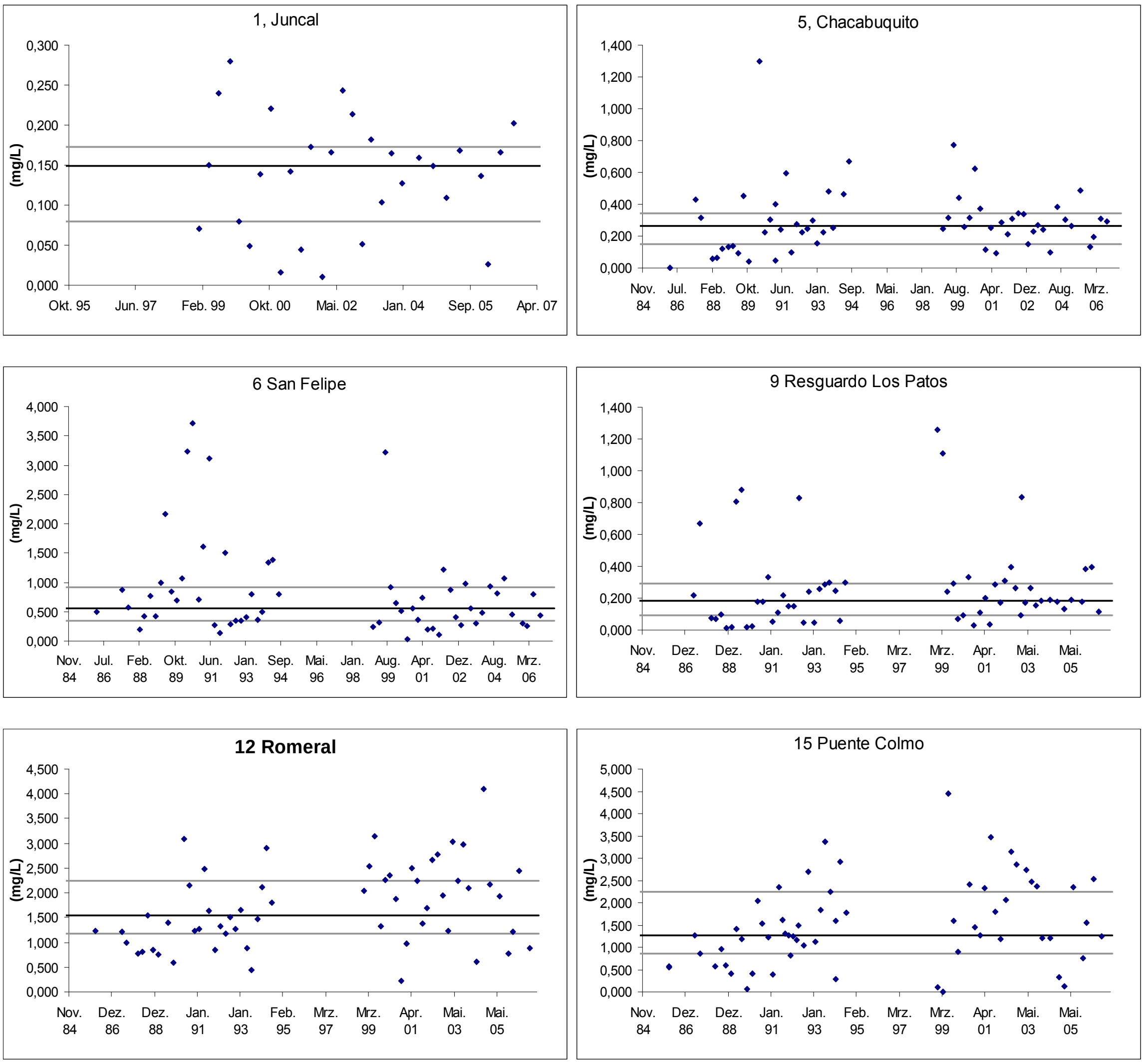


Fig. 47 Location of water quality stations of the DGA in the Aconcagua and Putaendo River

4.2.6.2. Reported Nitrate Values

In the current program of the DGA, nitrate was measured up to four times a year. The following graphs represent the monitoring results. For each station a line representing the median and other lines representing the 25th and 75th percentile is presented. Later these data where used to calculate background N concentration and in order to validate modelling results.



For location of monitoring stations see Fig. 47

Fig. 48 Reported nitrate concentrations in six stations in the Aconcagua river

4.2.6.3. Background Concentrations of Nitrate

According to the measured nitrate values at the upstream stations Juncal and Resguardo Los Patos, where no human activities are reported upstream, average background concentration of nitrate were determined (measurements of other N components are not available). Tab. 27 shows the result of the calculation including estimates of nitrogen deposition based on these figures. The calculated annual N depositions for the two sub-watersheds are 1.1 Kg N ha^{-1} and 0.8 Kg N ha^{-1} respectively (Godoy et al. 2003 report an average NO_3 deposition for central Chile of 1.2 Kg N ha^{-1}).

Important to note is that total N-deposition is higher since other nitrogen components than nitrate were not considered in this estimate and transformations between N-deposition and export to the surface water, like denitrification, may take place. For the subsequent modelling of nitrate in the Aconcagua watershed, however, N-deposition was not modelled specifically but the average values of background NO_3 concentrations were rather entered into the headwater streams.

Tab. 27 Calculated nitrate background concentrations based on the stations Juncal and Resguardo los Patos

Station	Number of Measured Values	Average NO_3–N Concentration	Range	Standard Deviation	Average Discharge[2]	Related Area[1]	Estimated N-Deposition
	[n]	*[mg l^{-1}]*	*[mgL^{-1}]*		*[m^3 s^{-1}]*	*[km^2]*	*[Kg km^{-2} a^{-1}]*
Juncal (station 1)	29	0.18	0.01–0.28	0.07	6.1	307	113
Resguardo los Patos (station 9)	51	0.27	0.01–1.26	0.28	8.75	886	84

[1] Own calculation based on DEM; [2] average of daily values 1984-2005; all data from DGA/BNA (2007).

4.2.7. Conclusions

Water availability and water demand in the Aconcagua Watershed is characterised through pronounced seasonality and long term variability. The runoff in the Aconcagua River is determined through snowmelt with peaks from December to January. In addition, a smaller peakflow is being observed during the winter months when precipitation reaches its maximum. Water demands are high during the irrigation season in the summer months from October to March. The highest water deficit is usually observed in January when snowmelt declines and irrigation demands peak.

The watershed hydrological cycle is extremely impacted by human intervention. Water from the main rivers is conveyed to irrigation areas, which are often located in alluvial plains of tributaries to the Aconcagua. This leads to a reduced flow in the main river and higher discharges in the tributaries, due to irrigation return flow.

Important nitrogen inputs stem from domestic wastewater. Industrial discharges and storm water runoff contribute rather insignificantly to total nitrogen loads.

A major source for nitrogen inputs to the hydrological system are irrigation return flows. While the N-fertilizer inputs to the irrigated areas can be estimated based on the land use analysis there are rather large methodological difficulties to estimate the nitrogen discharges stemming from irrigated areas, especially if clear statements are needed regarding the exact quantities and the temporal behaviour of nitrogen transfer from irrigated areas to the surface water system. Since these N-inputs are very significant, a special study was designed to quantify these inputs in one of the Aconcagua sub-watersheds, the Pocochay, which is presented in the subsequent chapter.

5. Pocochay Sub-watershed Analysis

In order to quantify the impact of irrigated agriculture on surface water a special study was designed in the Pocochay area, one of the major irrigated areas of the Aconcagua watershed.

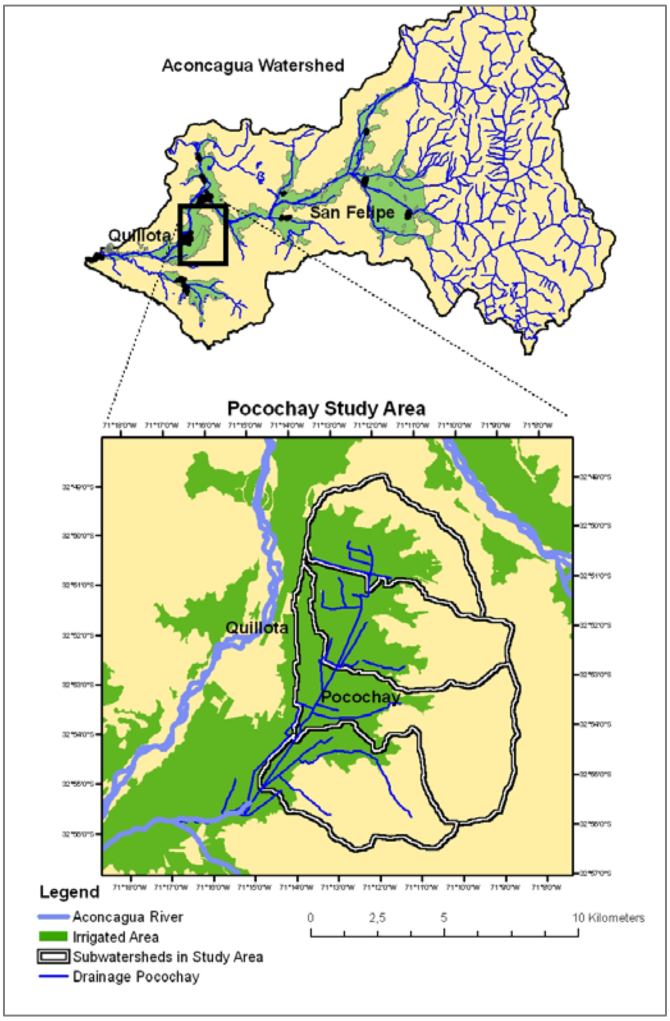


Fig. 49: Location of Pocochay watershed

The Pocochay is a small stream within the Province of Quillota, Valparaíso Region (see location in Fig. 49). From its origins close to the community of La Cruz until its confluence with San Pedro River, tributary to the Aconcagua, it drains around 30 km² of irrigated land on a length of 14 km. Within the drainage area of Pocochay stream, totalling around 90 km², there are neither major settlements nor industrial sites.

This fact makes the area ideal to study the impact of agriculture on water quality since other pollution sources are negligible. Some individual farms do dispose their human excreta to cesspits from where pollutants may leach to the shallow ground water and later may reach surface water, but the total population in the area is less than 5000 and this equals a quantity of less than 15,000 Kg N a^{-1} (compared to around 600,000 Kg a-1 of fertilizer N applied in this region, see below).

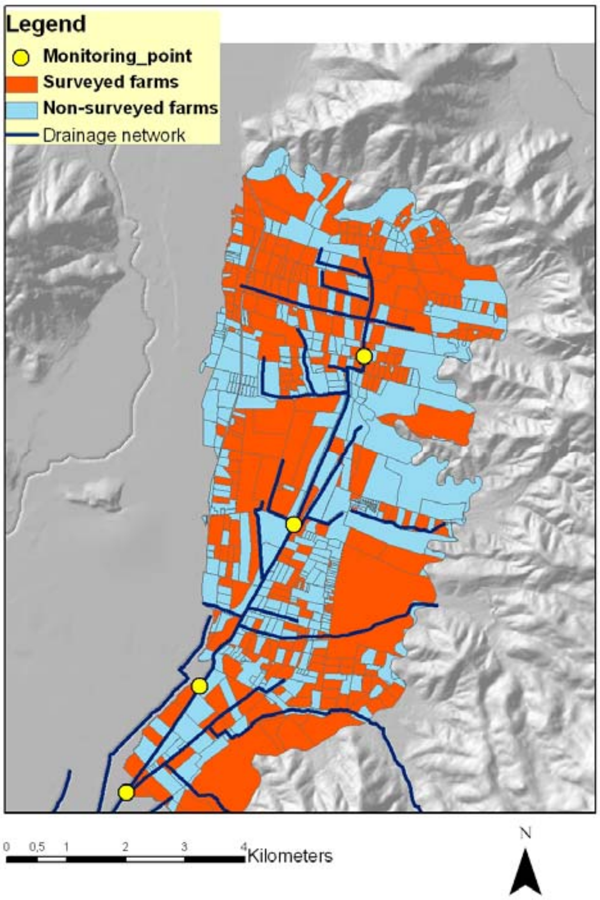
In addition, a large part of the settlements are connected to the wastewater collection system of La Cruz, evacuating wastewater towards the Aconcagua River, and since 2004 to the treatment plant of Quillota.

The study area resembles typical features of other areas under irrigation in the major tributary watersheds to the Aconcagua. The climatic conditions and the pattern of irrigation water applications are comparable. The planted crops may differ, and this has to be accounted for when estimating the amount of fertilizer leached to surface water bodies when the results from this watershed are used for up-scaling purposes. However, in the Pocochay just as in the rest of the Aconcagua valley, fruit trees are the dominant crops. Details on the study design are published by RIBBE et al. (2008).

5.1. Land and Fertilizer Use

The study area comprises 592 agricultural properties. A total of 356 farms in the study area were surveyed, representing 60 % of all farms and 66 % of the total irrigated area. For each farm the actual land and fertilizer use was collected for the agricultural period 2004/2005. Fig. 50 shows the surveyed and non-surveyed plots in the watershed.

For those farms where no survey could be performed, the land use was determined based on the Landsat ETM image interpretation of 2003. The survey was used to verify land use changes, which occurred between 2003 and 2005. The survey was designed by the author and conducted by the Catholic University of Valparaíso (School of Agronomy) culture. The results were transferred to spreadsheets; the subsequent analysis was performed by the author.



Total cultivated area in the surveyed farms was 2352 ha. The land use is dominated by fruit trees; among these Avocado plantations are the dominant crop with a total of 1352 ha. Other fruit trees are citrus (152 ha) and custard apple (125 ha). In the middle section of the watershed horticulture plays an important role. Major crops are sweet corn, tomato and cabbage. Another land use form is greenhouses. Tab. 28 provides the details of the land use according to the surveyed areas.

Fig. 50 Surveyed farms in the Pocochay sub-watershed

Tab. 28 Major crops in the four micro-watersheds (in hectares) according to the 356 surveyed plots

	Micro-watershed			
Crop Class	***La Cruz***	***La Palma***	***Los Indios***	***San Isidro***
Fruit Trees	853	240	243	321
Horticulture	44	202	162	61
Greenhouse	45	28	110	48
Total	*942*	*470*	*515*	*430*

5.1.1.1. Land Use Based on Satellite Interpretation

In order to determine the land use of the non-surveyed areas, remote imagery (Landsat ETM7+, 19.01.2003) was interpreted on the basis of a supervised classification applying 30 test areas and 18 validation areas within the study region. For the non-surveyed land uses, average fertilizer application rates as determined by the agricultural survey for each major crop class, were assumed. Fig. 51 shows the result of the land use classification based on remote imagery.

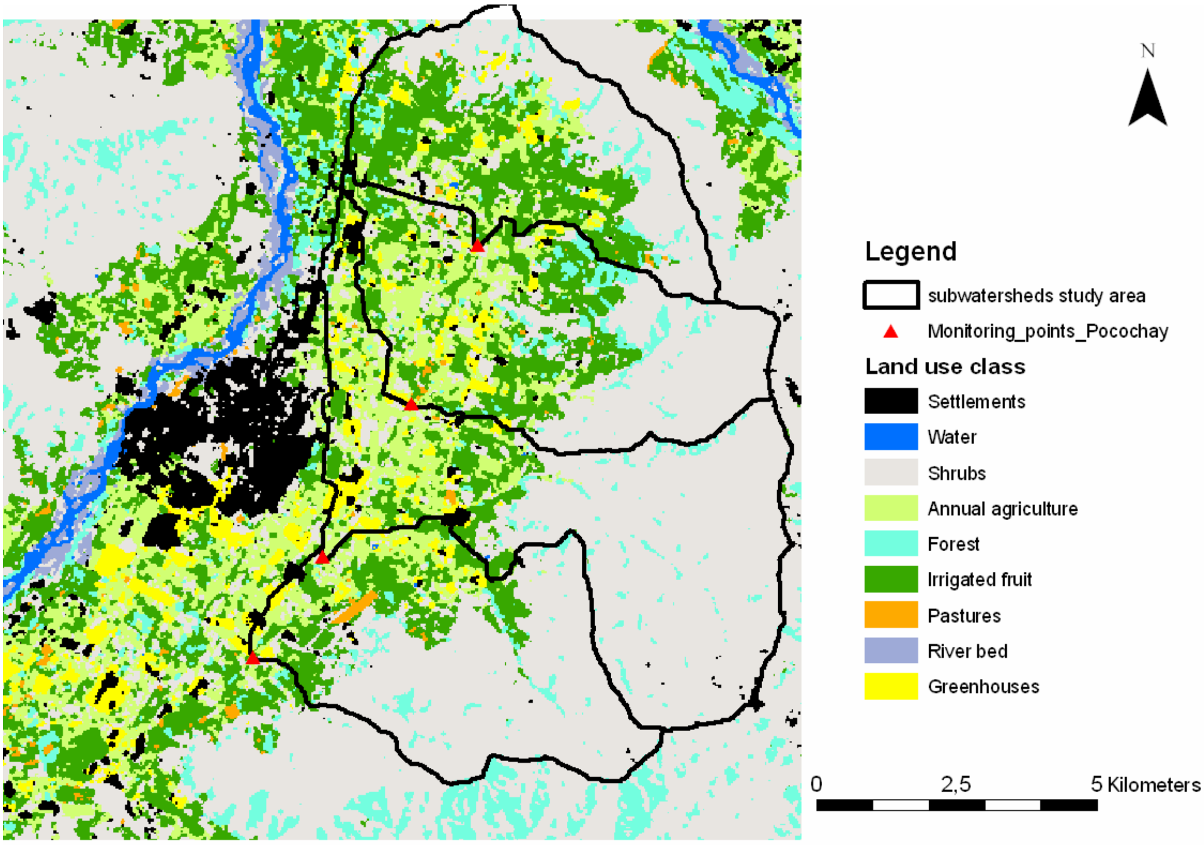


Fig. 51 Results of LANDSAT image based interpretation of land use

The combined results of the Landsat image interpretation and the land use survey are shown in Tab. 29. Here the three major crop classes are reported. The results show that dominant crops in the study area are fruit trees covering 70 % of the agricultural area.

Tab. 29 Major agricultural land uses in the micro-watersheds (ha) of the Pocochay

	Micro-watershed				
Crop Class	***La Cruz***	***La Palma***	***Los Indios***	***San Isidro***	***Total***
Fruit Trees	1,047	480	514	474	*2,515*
Horticulture	50	289	237	90	*666*
Greenhouse	55	75	188	74	*392*
Total	*1,152*	*844*	*938*	*638*	*3,572*

Land use determined on basis of the agricultural survey in 2005 in combination with satellite image interpretation (2003)

5.1.2. Fertilizer Applications

The survey provided reliable data on fertilizer amounts for a total of 235 agricultural plots (in other cases farmers did not provide data or data which could not be quantified). Data provided by the farmers in Kg or tons of applied fertilizer per ha were converted to Kg of nitrogen according to the type of fertilizer. Of the estimated 294,000 Kg N applied to the whole surveyed area Urea is the most common fertilizer, followed by nitrates (Saltpeter, KNO_3, $NaNO_3$, NH_4NO_3), guano and composite fertilizers (Ultrasol, Soquimich) – compare Tab. 30. Hence, around 80 % of the applied fertilizers are easily soluble mineral fertilizers. Guano is almost exclusively used in horticulture, and its use is positively correlated to small farm size.

Tab. 30 Amount and type of fertilizer applied in the surveyed plots

Fertilizer (type)	**Amount N** *[Kg]*	**%**
Urea	130374	44
Nitrates	89684	31
Guano	59360	20
Composites	14269	5
Total	*293686*	*100*

Total surveyed area: 1690 ha

In order to estimate the N applications to those agricultural plots that were not surveyed or where no reliable data was available, the average N application per crop type was calculated and applied to the plots with no fertilizer application data. For this purpose the median values of N application per crop type were used. The median was used due to the fact that the surveyed N application rates (Kg/ha/crop) do not follow a normal distribution (a few farmers apply extremely high rates of fertilizer). Tab. 31 shows the results of fertilizer applications grouped according to major crop classes.

Tab. 31 Fertilizer applications per crop classes according to survey

	Number of Surveyed Fields	***Surveyed Area*** *[ha]*	***Median N Application*** *[Kg/ha]*	***Fertilizer Type Applied*** *In % of total N*	
Avocado and Citrus	160	1433	154	Urea Nitrates Guano Composites	52 34 12 4
Horticulture and Greenhouses	94	257	242	Urea Nitrates Guano Composites	25 22 49 8
Average / Sum	*254*	*1690*	*167*		

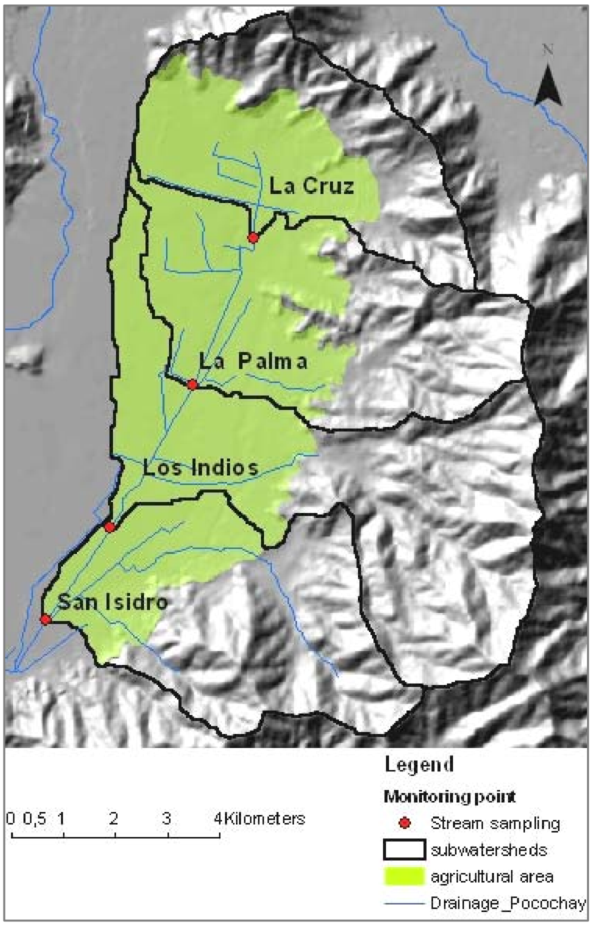
The surveyed data together with the median of N-applications allows estimating the N inputs to each micro-watershed. The result is provided in Tab. 32.

Tab. 32 N applications related to the four micro-watershed of the Pocochay area

Sub-watershed	**Total N application** *[Kg]*	**Average Nitrogen Fertilizer Applied per Hectare** *[Kg/ha]*
La Cruz	182,443	158
La Palma	139,931	166
Los Indios	167,837	179
San Isidro	106,924	168
Total / average	*597,135*	*167*

5.2. Water Quality and Discharge Measurements

5.2.1. Monitoring Points



Along the Pocochay stream four monitoring points were determined in order to monitor water quality and discharge of the drainage waters. The monitoring sites were placed on locations that were easily accessible (bridges) and led to division of the Pocochay in parts of more or less equal length. A *Digital Elevation Model* was built on the basis of contour lines with 2.5 m spacing (SEREMI 2005). The drainage network was digitalized and together with the DEM, the corresponding watershed to each monitoring point was calculated (see Fig. 52).

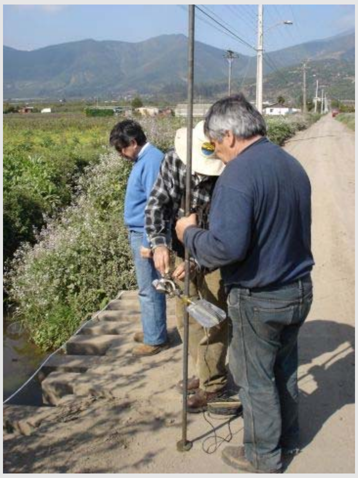
Fig. 52: Topography, irrigated area, monitoring points and related micro-watersheds in the Pocochay

5.2.2. Measurement Methods

Water quality analysis for the parameters *N-, and P-species Temperature, Electric Conductivity* and discharge analysis was realized at two monitoring points (La Cruz and Los Indios) between January 2004 and December 2006. Initial sampling was on a weekly basis; from mid 2005 on, it was biweekly but two additional points were monitored (La Palma, San Isidro); Compare Fig. 53 for location of monitoring points.

Conductivity and temperature were measured in situ. At each point two samples were taken and analysed separately in the laboratory. If the two analytical results differed by more than 20 %, the analysis was repeated for each sample. The nitrogen species *nitrate, ammonium, and nitrite* were analysed; after November 2004 total nitrogen was analysed additionally. Chemical analysis was performed using the following spectro-photometric standard methods: Nitrate - dimethylphenol, nitrite - diazotization, ammonium - salicylate, total nitrogen - persulfate digestion. Spectrophotometer model Hach Odyssey DR/2500 and prepared test solution by Hach UniCell™ vials were employed for analysis.

Discharge was measured using a flow meter (model *Gurley 622*; at 20 and 80 % depth and 30 cm horizontal intervals) at La Cruz and Los Indios stations from the beginning and for the other stations from October 2005 onwards. Discharge was correlated to water level taken from staff gages installed at each monitoring station. Water level was determined and in addition the flow velocity and profile was determined. Based on these measurements the discharge was calculated. A stage discharge relation (rating curve) was established allowing substituting velocity and wetted perimeter by just reading the water level. At each station a staff gauge was installed for this purpose.



Preparation of Flow Meter

Staff Gauge

Flow Measurement

Photographs by Ribbe

Fig. 53 Photographs of discharge measurement

5.2.3. Nitrogen Loads and Export Coefficients

Nitrate, nitrite, ammonium, and total nitrogen were determined in the stream samples. Below only nitrate values are reported since they represent over 98 % of inorganic N species in the samples. Nitrite-N was found in concentrations ranging from 0.005-0.055 mg l^{-1} (average 0.016 mg l^{-1}); Ammonium-N concentrations ranged from 0.002 to 0.621 mg l^{-1} (average 0.054 mg l^{-1}); Nitrate-N ranged from 1.25 – 10.07 mg l^{-1} (average 4.5 mg l^{-1}); total nitrogen ranged from 1.65 – 10.15 mg l^{-1} (average 4.9 mg l^{-1}).

Measured nitrate concentrations showed higher values during the rainy season than during irrigation season. The time series graph of nitrate concentrations presented as monthly averages is shown in Fig. 54.

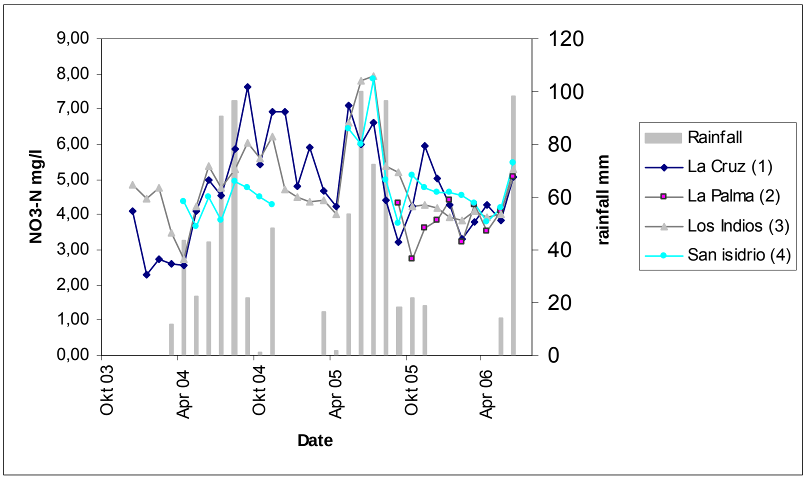


Fig. 54 Measured nitrate concentration at the four stations

Monthly N-loads were calculated for each sampling on the basis of nitrate concentration and discharge. For each micro-watershed, loads of the upstream monitoring stations were subtracted in order to estimate the contribution of each individual micro-watershed to N-loads emitted to the receiving stream. Fig. 55 shows the results of monthly N-loads per hectare. Some higher peaks in July 2004, July 2005 and April 2006 relate to the monitoring during or shortly after rainfall events. As this relationship is evident and significant, specific rainfall events were monitored in winter 2006 in order to establish a relationship between amount of rainfall and N-export.

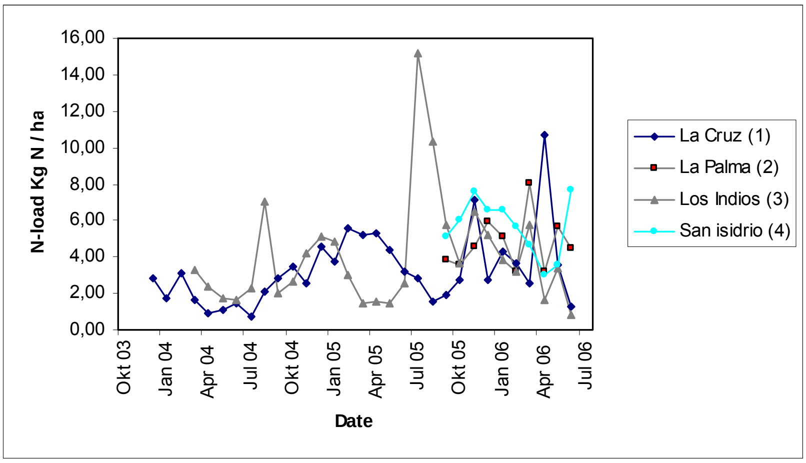


Fig. 55 N-loads related to the four micro-watersheds

During the months of May-August, irrigation is reduced and pronounced nitrogen export occurs during and after rainfall events. In this context, nitrogen discharges were observed during three rainfall events in intervals of two hours. Results of these measurements are shown in Tab. 33.

Tab. 33 Nitrate exports related to three rainfall events in 2006 at La Palma Station

Event 1			Event 2			Event 3		
Date	**P** *[mm]*	**N-load** *[Kg N day^{-1}]*	**Date**	**P** *[mm]*	**N-load** *[Kg N day^{-1}]*	**Date**	**P** *[mm]*	**N-load** *[Kg N day^{-1}]*
7.6.2006	5	no data	6.7.2006	20.5	no data	10.7.2006	33	420
8.6.2006	20	890	7.7.2006	18	780	11.7.2006	42.5	1922
9.6.2006	0	758	8.7.2006	0	820	12.7.2006	0	1697
10.6.2006	0	606	9.7.2006	0	415	13.7.2006	0	842
Total	71	2254		38.5	2015		75.5	4881
N- load Base flow *(1)*		259			268			415

Notes: P=precipitation, N-loads determined as nitrate loads
All measurements taken at station "La Palma"; total drained agricultural area: 1996 ha
(1) Base flow: N-loads determined as N-loads of last measurement before the rain started

Tab. 34 Export of N related to amount of rainfall and applied fertilizer in three rainfall events

		Event 1	**Event 2**	**Event 3**	**average**
Kg N exported per mm rainfall in the micro-watershed "La Palma"	*[Kg N mm^{-1}]*	27.8	31.5	42.6	34.0
Kg N exported per mm rainfall per hectare of irrigated area	*[g N mm^{-1} ha^{-1}]*	13.95	15.76	21.37	17.0
% of total annual applied fertilizer exported per mm of rainfall		0.009	0.010	0.013	0.011

Note: Base for calculation 162 Kg N fertilizer applied per ha in the contributing watershed for "La Palma" Station

As displayed in Tab. 34, for each mm of rainfall, between 0.009 % and 0.013 % (average 0.011%) of the fertilizer applied annually is exported to surface water. Tab. 35 shows the average amount of nitrate export calculated on the export coefficient for rainfall and the actual measured precipitation per month.

Tab. 35 Precipitation related N-export per month (average)

		Jan	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**	**Tot.**
P related N-export (C_{ep})	*[Kg ha^{-1}]*	0.00	0.00	0.16	0.26	0.51	1.32	2.10	1.41	0.25	0.41	0.17	0	6.58

After reducing the calculated contribution of precipitation induced nitrogen export the remaining loads were calculated as base flow for each month. Tab. 36 provides the average amount of nitrogen that is being exported from irrigated areas per hectare per month for the total study area of the Pocochay watershed and the whole study period in absolute numbers and as percentage of applied N-fertilizer, which was 167 Kg ha^{-1}at average.

Tab. 36 Base flow related average N loads exported from the irrigated area in the Pocochay area per month

		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
[Kg ha^{-1}]		4.30	3.70	3.64	3.44	2.69	1.48	1.60	2.89	4.95	2.89	3.33	4.90	39.3
% of annual Fertilizer exported as base flow	C_{eb}	2.57	2.22	2.18	2.06	1.61	0.89	0.96	1.73	2.96	1.73	2.00	2.93	23.8

Average N application in the agricultural area of Pocochay: 167 Kg ha^{-1}

5.2.4. Interpretation of Results

The empirical study presented above determined that at average 27.7 % of the fertilizer applied to the irrigation perimeters in the Pocochay watershed is exported to surface water of these 23.8 % are attributed to base flow and 3.9 % to precipitation events. These are average values which result from a measurement campaign in four micro-watersheds, two of them being observed during the period of one year and the other two for two and a half years. Export coefficients could be determined for each month which allows estimating nitrate export from other agricultural areas as a function of fertilizer inputs to agriculture.

The overall export coefficient for nitrate of 0.28 compares well to other studies on export coefficients related to irrigated agriculture, where comparable amounts of fertilizer were used and similar climate conditions prevail (BASSO 1994, CAUSAPÉ et al. 2004, KLOCKE et al. 1999, CAVERO et al. 2003). These authors determined export coefficients for areas irrigated with surface methods between 0.17 and 0.56 with values between 0.23 and 0.3 being reported more frequently (compare also chapter 3.1.3).

It is assumed that the other irrigation areas in the Aconcagua Watershed show a similar behaviour of nitrogen export regarding amount and temporal pattern; This assumption is based on the fact that the other irrigation sectors of the Aconcagua show many similarities in terms of soil (prevailing are Entisols and Inceptisols of alluvial origin with depth of around 1 – 1.5 m, of clayey loam type and having good to very good drainage properties), slope (1-3 °), drainage (all watersheds are equipped with artificial drainage) and crops (mixed cropping with fruit crops dominating). A region which is significantly different from the conditions in the Pocochay is the first irrigation sector since here soils of higher natural drainage capacities are present and table grape are much more frequent than in other sections. It would have been adequate to conduct a second N-export study in this region. The difference in nitrogen fertilizer application for grapes can be accounted for, the nitrate leaching and export behaviour, however, is assumed to be like in the Pocochay sub-watershed.

6. Modelling Nitrate Variability in the Aconcagua River

In the previous chapters the data which are necessary in order to model the concentration of nitrate in the Aconcagua watershed were analysed and calculated. Now these data need to be interpreted with regard to the *objective number 4* of this study to quantify the spatio-temporal variability of nitrate in the Aconcagua River. For this purpose a model representing the watershed by sub-watersheds, water users and polluters is established and populated with the data analysed above. As modelling software "Mike Basin" (DHI 2005) was chosen, which models the flow of water and substances in a watershed according to a network model consisting of nodes and branches. Branches represent individual stream sections while the nodes represent confluences, locations where certain water activities may occur, or important locations where model results are required.

Inputs to the model in form of time series are runoff, water abstractions, point and non point sources and return flow from water users. Area related parameters like specific runoff or diffuse nutrient loads are connected to the network model via catchments which can be delineated in the required resolution. The discharges or loads of a catchment are added to the river network at the next downstream node.

Outputs of the model regarding nitrate are concentrations or loads at any node of the network. Time scale for any input or output parameter is variable and can be daily, monthly or annual. Thus, it is an adequate tool to implement the conceptual model presented in chapter 3.3, where the different timescales for various processes were presented. Details on the model are provided in the Mike Basin User Manual (DHI, 2005).

The river flow is modelled using the measured runoff from the main tributaries coming from the Andes as an input to the system. Here, daily discharge values are available. Subsequently, the various water abstractions and return flows are considered and their water demands are subtracted from the providing river stretch and return flow is added to the system again. This way the flow pattern for the whole Aconcagua River downstream of Chacabuquito is represented over a period of 21 years (1986-2006). Time series of irrigation and other water demands were calculated and presented in chapter 4.

Based on the hydrological model the various sources of nitrate, namely agriculture, municipalities and industries are added to the system in order to quantify nitrate along the course of the Aconcagua River. Here, temporal variations of nitrogen input were considered, as described in chapter 4. Regarding agricultural pollution the results of the case study of the sub-watershed Pocochay were employed in order to estimate nitrate export of the other sub-watersheds which have similar characteristics. Non point loads are calculated by the load calculator based on GIS layers containing the land use polygons and related load attributes. For each type of land use individual nitrate loadings (fertilizer inputs) and export coefficients can be determined.

In the following chapter, settings and data of specific relevance to model nitrate concentrations with Mike Basin are provided.

6.1. Model Set up and Inputs

6.1.1. Determine the Hydrological Network

First, the network of streams was defined on the basis of the watershed topography; in a second step, sub-watersheds were delineated. This involved the following steps and data:

1. Based on the DEM (25 m resolution), the river network (SEREMI 2005) was burned into the DEM to create a modified DEM ("AgreeDEM") using the Arc Hydro extension (Version 1.1, ESRI 2005; applied values were: vector buffer = 5 cells, smooth drop = 10 m sharp drop = 10m);
2. Fill sinks command (using Arc Hydro) was used to clean the DEM of sinks which would create discontinuities in the flow direction calculation;
3. Flow direction was determined (with Mike Basin option);
4. River flow and the hydrological network were calculated and digitized using "river tracing" option in Mike Basin. (Compare result in Fig. 56).

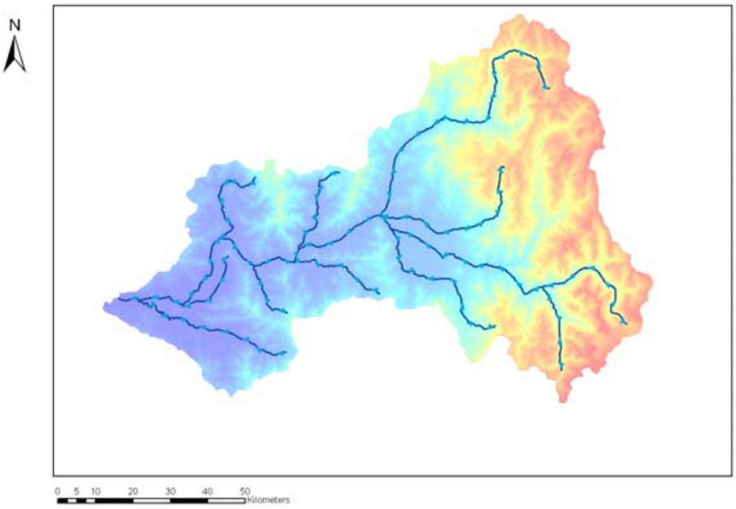


Fig. 56 River network as basis for the *Mike Basin* model derived from digital elevation model

6.1.2. Aconcagua Network and Catchment Model

The network model was based on the hydrological network, catchment nodes were placed at confluences, discharge station, and water quality stations; the latter two for model validation purposes. Catchments were automatically delineated for each catchment node according to the DEM.

Water users were added wherever an abstraction is taking place (municipal, industrial or irrigation scheme). Municipal abstraction nodes relate to the major municipal centres. Smaller municipalities and villages in the vicinity were lumped together with the main municipalities in order to simplify the model; industrial water users were added separately, resulting in four municipal and three industrial water users. At Romeral station, in the middle of the watershed, water is abstracted for an inter-basin transfer – here an additional user was added. Irrigation areas were lumped together for each major irrigation section, resulting in four irrigation water users. The resulting set up of the model including nodes, water users and catchments is demonstrated in Fig. 57.

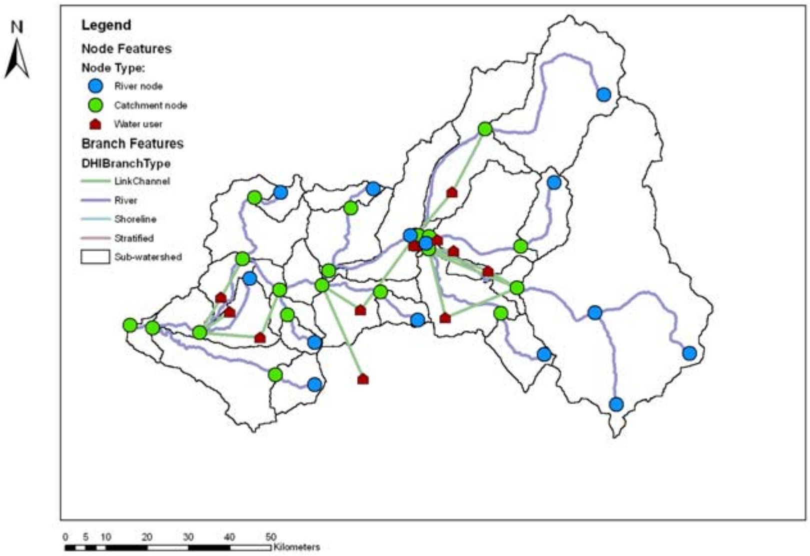


Fig. 57 Basic set up of the Mike Basin model for the Aconcagua river

6.1.3. List of Data Inputs

The data for the input to the model are derived from the Aconcagua watershed and Pocochay sub-watershed studies, described in chapters 4 and 5. In particular they are:

- Time series of measured discharge from upper watersheds (daily data 1986-2006);
- Time series of modelled discharges of the lateral, ungauged sub-watersheds (daily data 1986–2006);
- Time series of irrigation abstractions for four irrigation sections (monthly data, 1986-2006);
- Time series of water abstractions by municipalities and industries (annual, 1986–2006);
- Return flow fraction for municipalities, irrigation areas and industries;
- Recharge coefficients for precipitation and irrigation applications on catchments with groundwater defined;
- Spatial distribution of agricultural land use defined by major crop type;
- Associated fertilizer uses per crop type, and time series to account for long term change of fertilizer use (annual data 1986–2006);
- Export coefficients to account for fraction of applied fertilizer which is being exported to surface waters (C_{eb} and C_{ep}, as defined in chapter 3.3 and determined through the Pocochay study in chapter 5).

The data input formats are shapefiles and related attribute tables, direct input of data via the Mike basin interface and input of time series using the special extension "Temporal Analyst" (DHI 2005b). The original time series were prepared in Excel and later converted to the specific data format dfs0 used by Mike Basin Temporal Analyst.

6.1.4. Water Users

In order to describe the water balance of the Aconcagua River, next to catchment runoff, all major water users abstracting from and recharging to the river where located and time series of water use were associated. Tab. 37 summarises water users considered in the model; several municipalities and irrigation districts were lumped together where suitable. Smaller municipalities were aggregated to bigger ones. After 2003 these were also physically aggregated with the construction of new wastewater treatment plants. (Compare chapter 4.2.4 for detailed analysis and data regarding water users).

Tab. 37 Water users described in the model

Name	Type	Remark
Los Andes	Municipal	98 000 inhabitants
San Felipe	Municipal	109 000 inhabitants
Quillota	Municipal	184 000 inhabitants
Limache	Municipal	55 000 inhabitants
Romeral/Las Vegas	Water abstraction	basin transfer, at average 1.44 $m^3 s^{-1}$
Putaendo	Irrigation	2630 ha
Section 1	Irrigation	20027 ha
Section 2	Irrigation	14969 ha
Section 3+4	Irrigation	15424 ha
Pentzke	Industry	food processing, canning
Algas Marinas	Industry	food processing
Stormwater Los Andes	Urban stormwater	17 km^2
Stormwater San Felipe	Urban stormwater	24 km^2
Stormwater Quillota/Calera	Urban stormwater	38 km^2

At Las Vegas water is abstracted for the supply of Valparaiso Metropolitan Region. A time series for abstraction was available. Since no seasonality, trend or other pattern in abstraction is evident, data gaps were filled using the average abstraction calculated for the time span 1978 and 2001 (1.44 $m^3 s^{-1}$).

6.1.5. River Reaches

The hydraulic properties of each river stretch determine the travelling time of river water. In order to define the retention time of water per river stretch, the velocity was estimated based on the slope and hydraulic radius (derived from SAG 2003 for most reaches, others were estimated based on visual inspection) with the Manning formula. A Manning coefficient of 0.05 was chosen as the Aconcagua River in the middle part is a braided stream frequently with pebble beds and vegetation (CHOW et al. 1988)

Tab. 38 Reach properties of the main Aconcagua River

Reach number	Reach name	slope	length *[Km]*	flow time *[days]*
05414	Resguardo los Patos – San Felipe	0.017	35.8	0.29
05410	Chacabuquito – San Felipe	0.012	28.0	0.28
054221	San Felipe- Catemu	0.009	24.8	0.29
054222	Catemu - Romeral	0.004	4.5	0.07
05423	Romeral - Rabuco	0.006	12.4	0.16
54232	Rabuco - Calera	0.005	13.7	0.19
05425	Calera - Quilota	0.005	26.1	0.36
05426	Quillota- Puente Colmo	0.003	13.7	0.24

Reach number according to DGA classification; slope determined on basis of DEM; lenght determined on basis of river shapefile provided by DGA.

The rate coefficients for **reactive transfers** were set to 0.15 for nitrification (K_{nit} , 20 °C) and to 0.09 for denitrification (k_{denit}, 20 °C) according to values recommended in literature (CHAPRA 1997; LINDENSCHMIDT 2005). The rate coefficients for nitrification and denitrification are temperature-dependent and for each reach average temperatures were determined based on measured data of DGA/BNA (2007). For reaches where no temperature estimates based on measured values are available, they were adopted from neighbouring reaches. Monthly average temperatures of monitored stream reaches are shown in Fig. 46 (chapter 4).

6.1.6. Agricultural Non-point Pollution

Catchment N-Loads were modelled using the overall applications of fertilizers as described in section 4 and the results of nitrogen export coefficients of the Pocochay study which were used for irrigated areas in the whole basin.

The applied fertilizer was calculated per municipality considering the temporal development of cropping pattern and fertilizer application (compare chapter 4 where annual values are reported). The land use data per municipality were based on agricultural census and Landsat interpretation data (chapter 4). A shapefile was created by intersecting the actually irrigated area (derived from land use layer) with municipal boundaries. Mike Basin automatically calculates the share of nutrient input each municipality has within catchment boundaries according to the area, if one municipality is shared by more than one catchment. Fig. 58 shows the municipal boundaries as compared to the catchment boundaries.

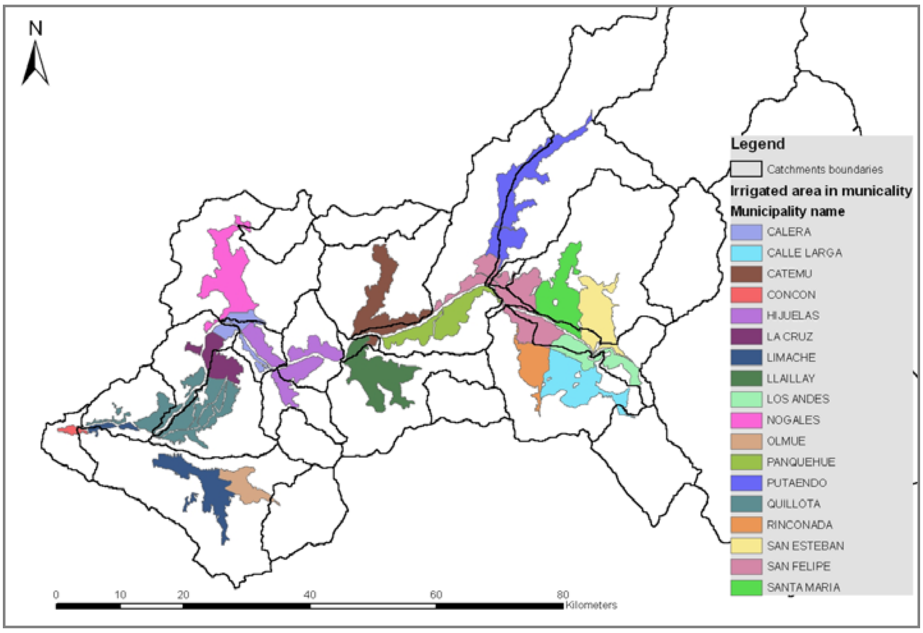


Fig. 58 Irrigated area within municipal-boundaries (coloured) and sub-watershed boundaries

6.2. Modelling results

Subsequently, the results of modelling for the period 1986-2006 are shown first for water quantity then for nitrate concentration. For the presentation of results three locations were chosen which also serve as water quality and discharge stations of the Chilean water service (DGA). These stations are (compare Fig. 59):

- San Felipe
- Romeral
- Puente Colmo

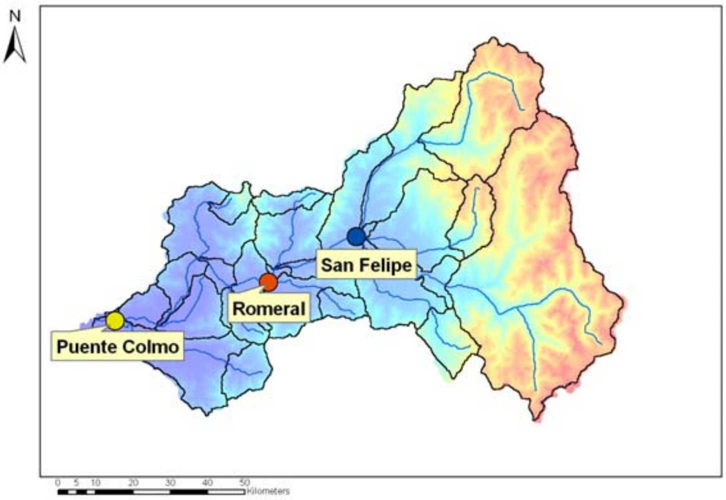


Fig. 59 Selected stations to report modelling results

6.2.1. Discharge Data and its Validation

Discharges are modelled for each node of the network. For three stations in the upper, middle and lower part of the basin modelling results are reported. Only the station at San Felipe has long term daily data records which can be used for validation. For the Romeral station only several months of data were available, at Puente Colmo discharge is not measured at all. Fig. 60 and Fig. 61 show the modelled and the measured discharge at San Felipe. Between 1990 and 1994 no reliable discharge data were available. The visual interpretation shows that modelled values represent the observed values quite well. The Coefficient of Determination and the Nash-Sutcliffe Model Efficiency Index confirm this (Tab. 39).

The good fit of modelled versus observed data is not surprising since a major part of the river flow is determined by the observed discharge data at Chacabuquito station upstream of San Felipe. During low flow conditions the model tends to underestimate the discharge, however, in general the modelled abstractions and discharges downstream of Chacabuquito (mainly irrigation abstractions and some sub-watershed discharges) lead to a good fit of the discharge at San Felipe station.

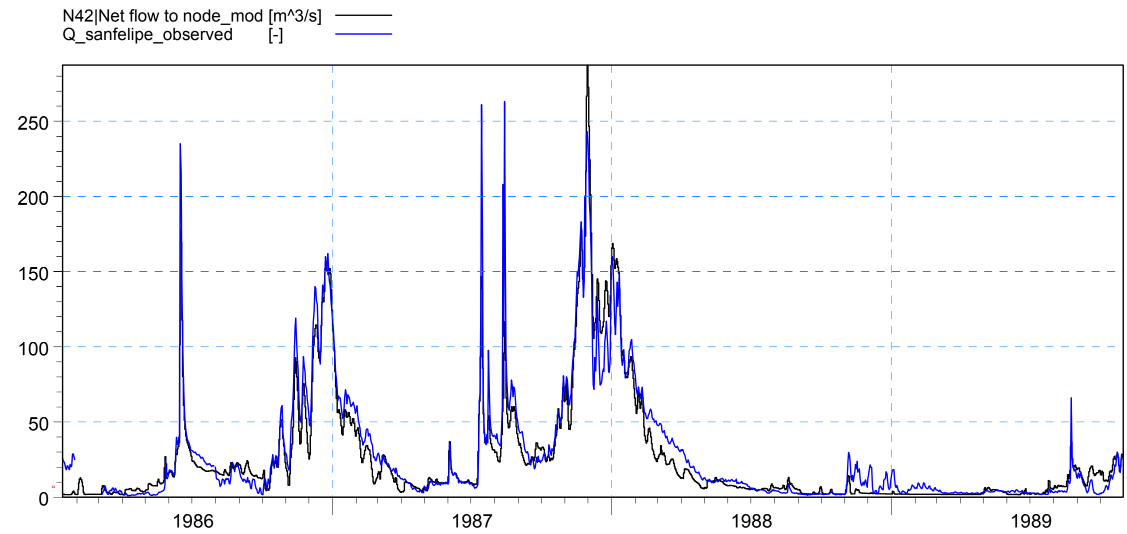


Fig. 60 Modelled versus observed discharge at San Felipe Station (1986-1989)

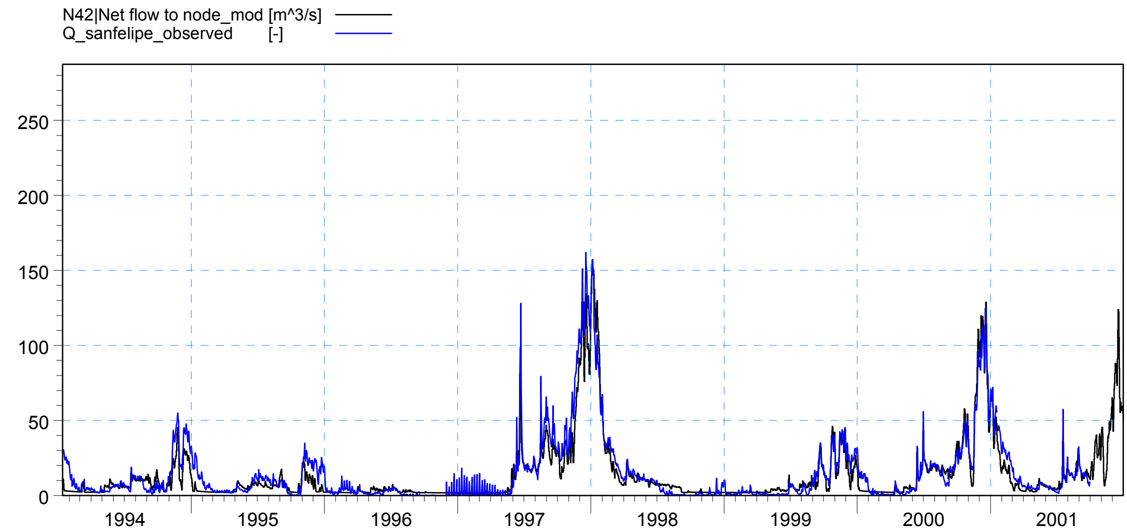


Fig. 61 Modelled versus observed discharge at San Felipe Station (1994-2001)

As discussed by KRAUSE et al. (2005) the Nash Sutcliffe Model Efficiency Estimator *E* tends to overestimate the impact of high peak flows. To reduce the sensitivity to extreme values, *E* can be calculated for the logarithms of observed and predicted values (KRAUSE et al. 2005). The results show that ln*E* especially for the period 1994 – 2001 when many low flow years are observed is significantly lower (Tab. 39).

Tab. 39 Measures of efficiency for modelled discharge at San Felipe

Evaluation Period	average (obs)	average (modelled)	R^2	E	lnE
1986-1989	28.6	26.5	0.91	0.90	0.83
1994-2001	14.5	13.0	0.90	0.88	0.60

R^2 = coefficient of determination
E=Nash-Sutcliffe efficiency index (According to NASH AND SUTCLIFFE, 1970)
ln E = Nash Sutcliffe efficiency index calculated with logarithm of observed and predicted values

The modelled discharges for Romeral and Puente Colmo Station are provided in the following figures (Fig. 62 and Fig. 63). Peak flows are related to the snow melt driven discharges in wet hydrological years (1987/1988 and 1997/98); other peak flows are observed after heavy winter rainfall in 1987, 1997, 2002, 2006. In summers of dry hydrological years the modelled discharge is close to zero (see for example January of 1989, 1991, and 1999).

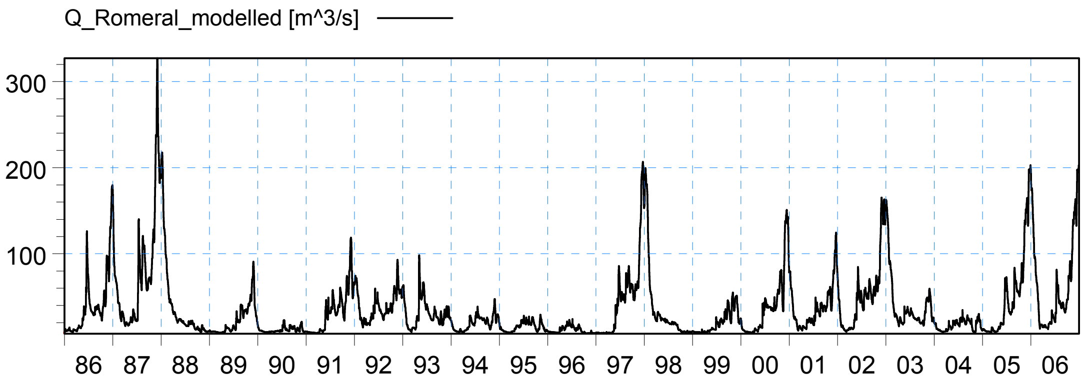


Fig. 62 Modelled daily discharge at Romeral station (1986–2006)

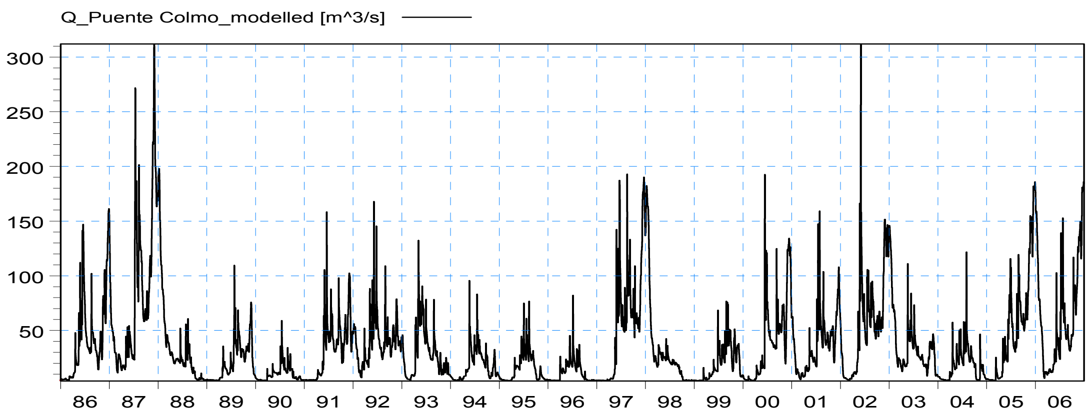


Fig. 63 Modelled daily discharge at Puente Colmo station (1986–2006)

6.2.2. Modelled Nitrate Concentration and its Validation

Nitrate is measured at the three stations in the Aconcagua main river up to four times a year. The following graph shows the modelled daily nitrate values as black lines and the observed values as blue dots (Fig. 64). All stations have a data gap between 1994 and 1999, when the Chilean Water Service (DGA) did not analyse nitrate.

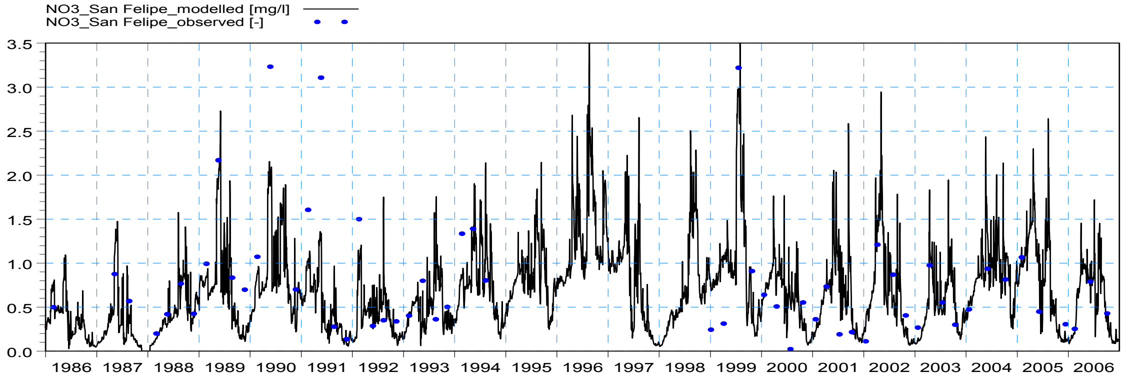


Fig. 64 Modelled versus observed nitrate-N concentration at San Felipe station (1986-2006)

The following figures (Fig. 65 and Fig. 66) show details for the period 1986-1994 and for 1999–2006. Here only those modelled values are reported which correspond to the observed values. The visual interpretation suggests that the general trend of observed nitrate concentrations is represented well by the modelled values.

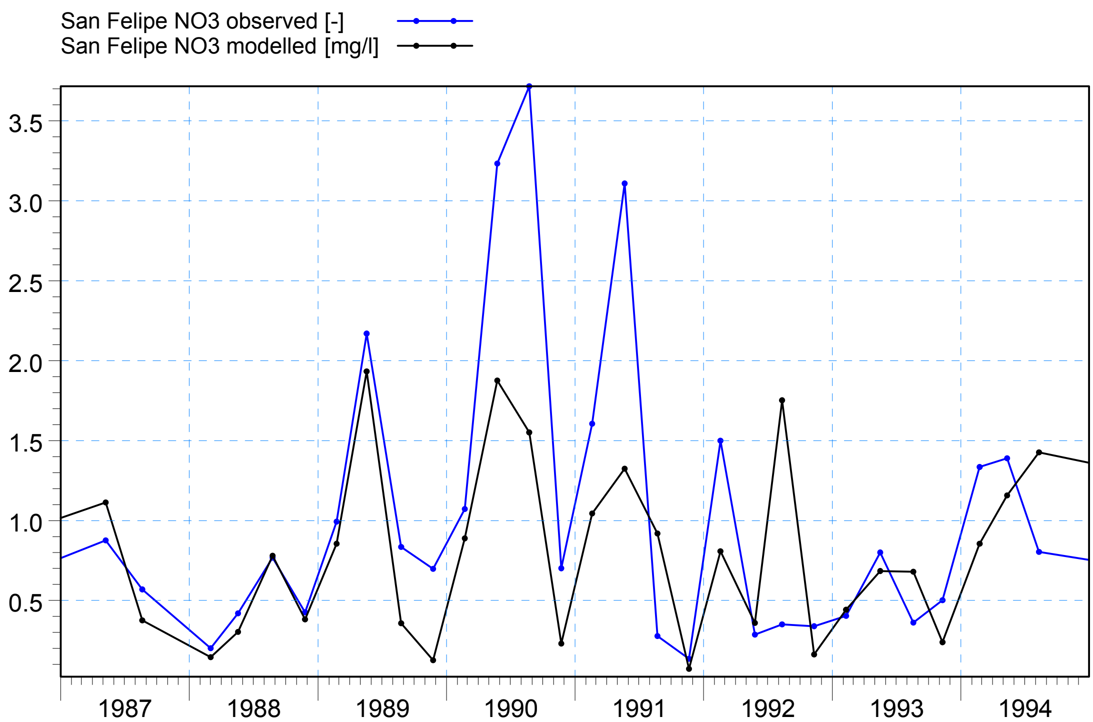


Fig. 65 Modelled and observed nitrate-N concentrations at San Felipe 1987 – 1994 for selected days

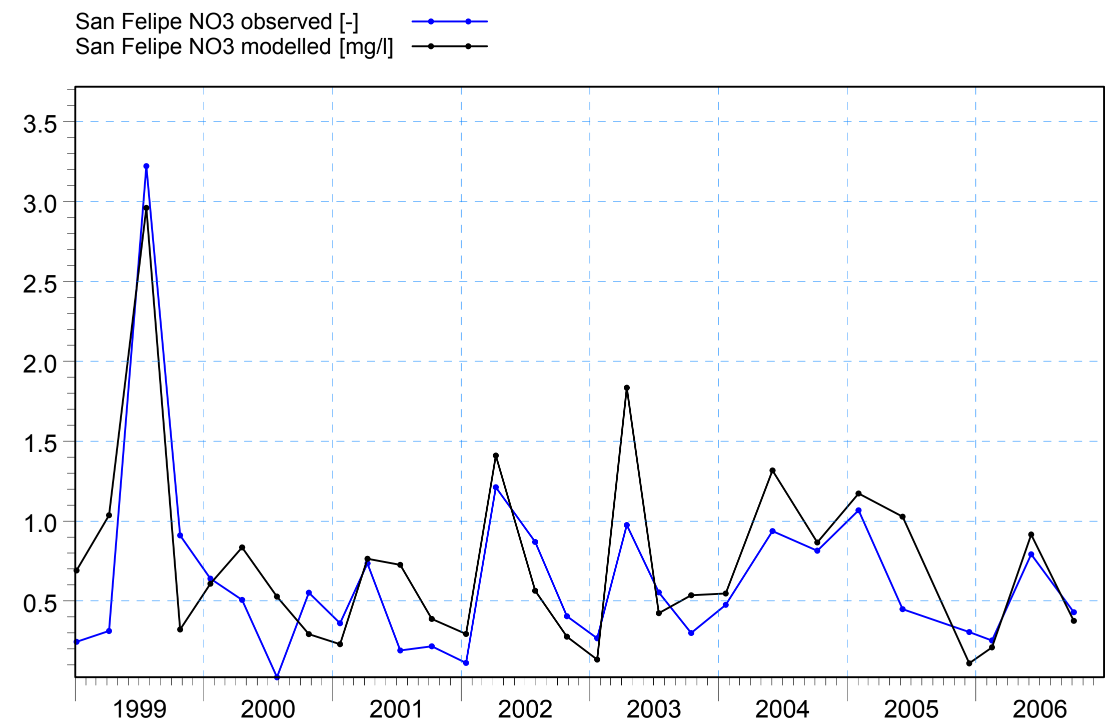


Fig. 66 Modelled and observed nitrate-N concentrations at San Felipe 1999 – 2006 for selected days

The following Fig. 67 shows the modelled and observed data for the next downstream station "Romeral" while Fig. 68 and Fig. 69 show details only for those days where observed data were available. Here also a good fit of the modelled versus observed values is found with the exception of some outliers.

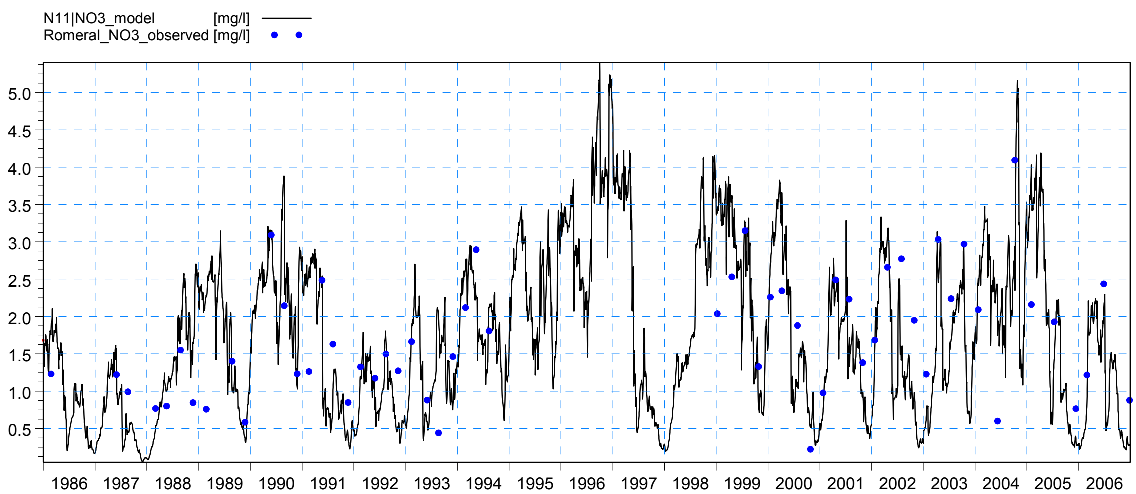


Fig. 67 Modelled and measured nitrate-N concentrations at Romeral station (1986-2006)

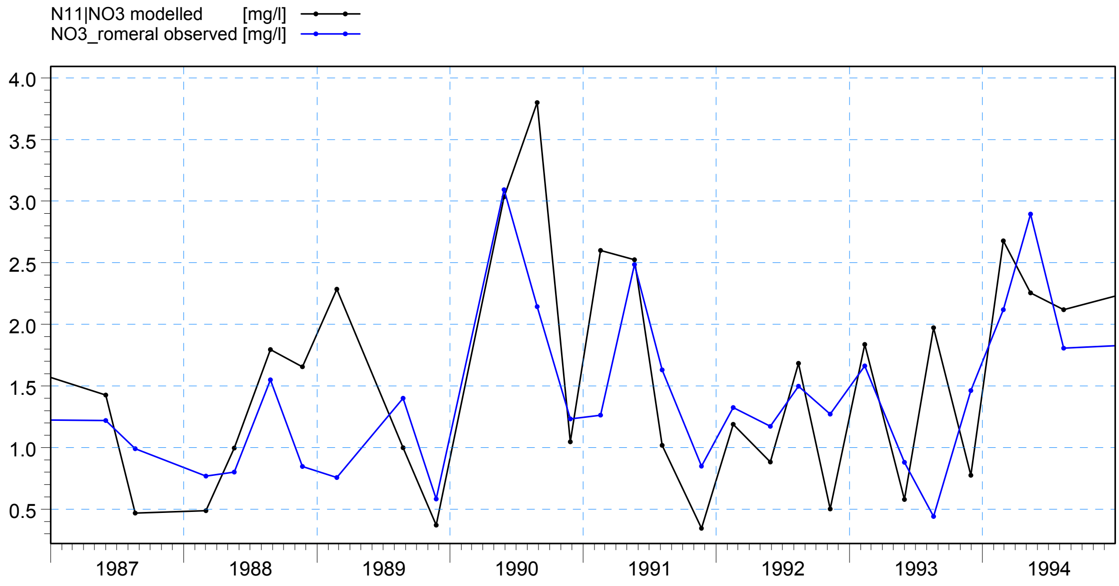


Fig. 68 Modelled versus measured nitrate-N concentration (1987-1993) at Romeral station for selected daily values

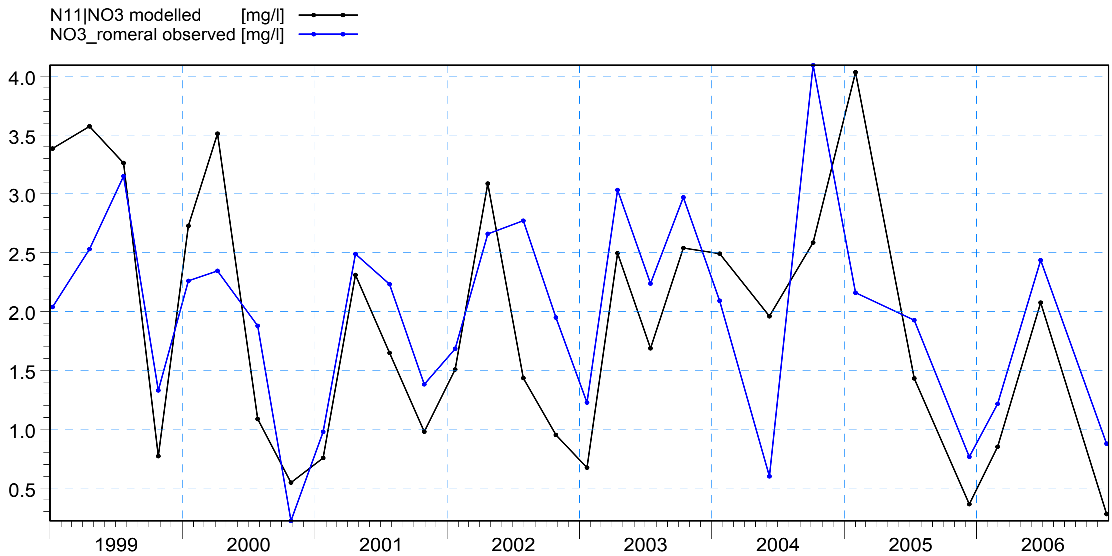


Fig. 69 Modelled versus measured nitrate-N concentration (1999-2006) at Romeral station for selected daily values

The following Fig. 70 shows the modelled and observed data for the downstream station "Puente Colmo". In Fig. 71 and Fig. 72 again details only for those days where observed data were available are shown. In this case no good fit can be observed. In general the model tends to overestimate the observed values. In addition the overall temporal tendency of the observed data is not well represented by the model.

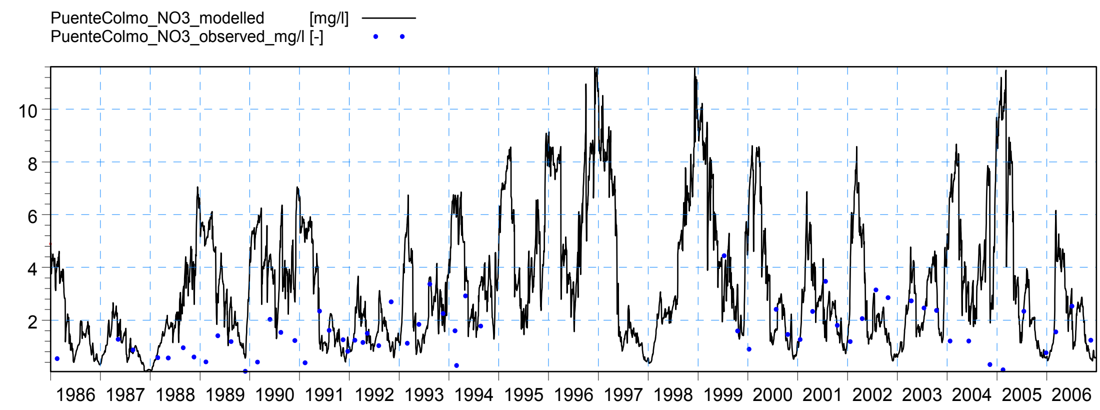


Fig. 70 Modelled versus observed nitrate-N concentration at Puente Colmo

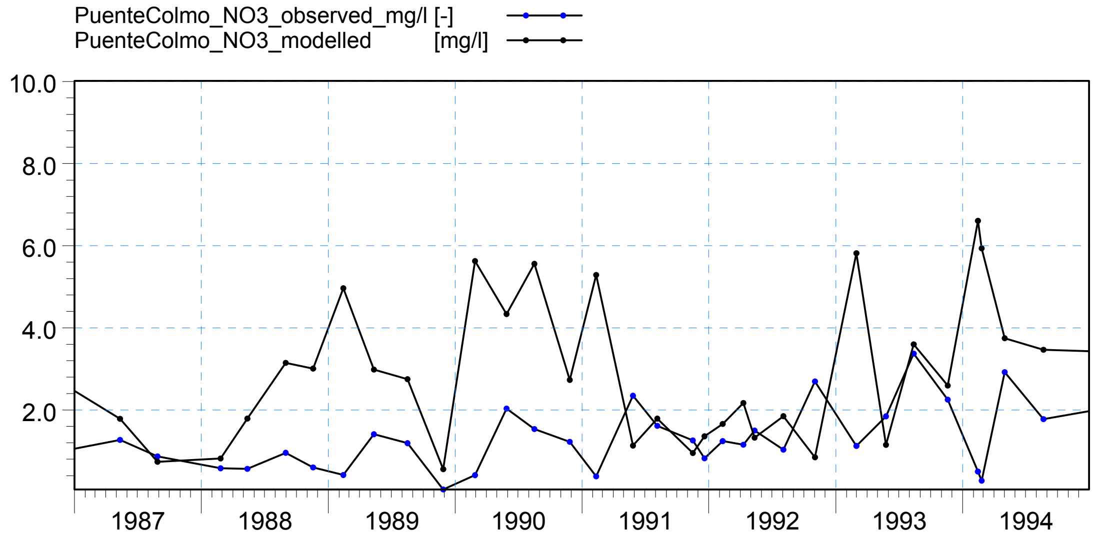


Fig. 71 Modelled versus observed nitrate concentration Puente Colmo 1987-1994

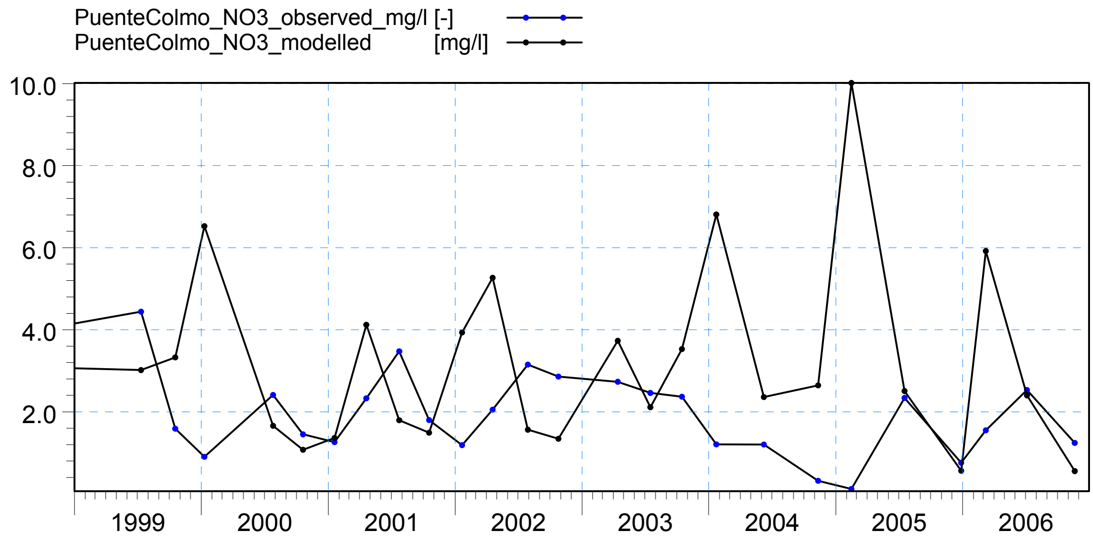


Fig. 72 Modelled versus observed nitrate concentration Puente Colmo 1999-2006

6.2.2.1. Interpretation of Results and Potential Errors

The comparison of the modelled with observed nitrate values is summarized in Tab. 40. It indicates that the general trend and the averages of nitrate concentrations are modelled well for San Felipe and Romeral stations. R^2 values between 0.4 and 0.69 suggest that the correlation of the modelled versus the measured values is not very high but significant. This is supported by the efficiency index of Nash and Sutcliffe (*E*) for the San Felipe Station. For Romeral station this model efficiency indicator is lower but still significant. The Nash Sutcliffe efficiency index is determined for the whole modelling period as for data sets with few values, single outliers have a relative high influence on *E* as McCuen et al. (2006) discuss in detail. The results of *E* for San Felipe and Romeral both are acceptable in terms of model efficiency. Compared with other studies where Nash-Sutcliffe efficiency indicators are reported for water quality parameters (Moriasi et al. 2007), the model fit can be considered as good.

Tab. 40 Comparison of modelled and observed nitrate values at the three selected stations

Station	time span	observed value	Average (observed)	Average (modelled)	R^2	E
San Felipe	1987 - 1993	30	1.02	0.79	0.47	0.49
San Felipe	1999 - 2006	29	0.63	0.74	0.69	
Romeral	1987-1993	28	1.54	1.41	0.40	0.12
Romeral	1999 - 2006	29	1.90	1.98	0.44	
Puente Colmo	1987 - 1993	33	1.26	2.90	0.04	-0.29
Puente Colmo	1999 - 2006	25	1.90	3.18	0.11	

R^2 = coefficient of determination; E = Nash Sutcliffe efficiency index

For Romeral station this efficiency indicator is lower. In general there is a trend of lower modelling quality towards downstream. At the station Puente Colmo, modelled results do not correlate well with the observed data. Puente Colmo is a station close to the river mouth and this stretch of the river is braided, flat and wide. It might be that here ecological conditions prevail which favour N-removal from the stream like denitrification or incorporation of nitrate into organic material and subsequent settlement. It may also be that significant errors are attached to the observed data. Measured data are never error free. Within the period of observations (1987-2006) the sampling and laboratory methods most likely have changed, and there are further potential errors added in data analysis and reporting. Especially at Puente Colmo station it is very difficult to take representative samples due to the hydro-morphological conditions described above (compare also Fig. 73), while the other monitoring stations are located at places where the river is narrow and channelled. The current sampling practice of the DGA at Puente Colmo is to take samples from the river bank which leads to non-representative sampling at this river stretch. Thus, at Puente Colmo station the observed values for nitrate are not very reliable.

Photograph by Ribbe

Fig. 73 Puente Colmo station

The errors related to nitrogen inputs from wastewater treatment plants are probalby relatively low since the treatment technologies are known and the long term nitrogen exports will certainly be in the range of the estimated values as they are based on population number and per capita nitrogen production. Nitrogen emissions of wastewater treatment plants occur predominantly in the form of ammonium. In-stream nitrification is not very significant due to low residence times in the different river segments. Even from the most upstream wastewater emissions to the river mouth, the mean calculated residence time is only 1.6 days allowing to transform approximately 20 – 25 % of the ammonium to nitrate. Considering in-stream nitrification and nitrification taking place within the treatment plants, the overall impact of domestic wastewater on nitrate concentrations is lower than 166 10^3 Kg a^{-1} in 1986 and 225 10^3 Kg a^{-1} in 2006. This compares to nitrate exports from irrigated agriculture of an estimated 1640 10^3 Kg a^{-1} (1986) and 2620 10^3 Kg a^{-1} (2006).

This makes irrigated agriculture by far the largest source of nitrate inputs to the surface water. Uncertainties in estimating the input from irrigation schemes to surface waters have an important impact on nitrate concentrations estimates. As discussed in chapter 5 the major uncertainties lie in the question of how well the export coefficients can be transferred to years of extreme hydrological events and to other irrigation sections than the Pocochay. The modelling results presented above suggest that the assumption of applying the same nitrate export coefficients to all irrigation sections in the Aconcagua watershed was correct as the observed nitrate values are represented well by the modelling results in the upper Aconcagua watershed, whereas the nitrate export coefficients were determined in the lower part of the watershed.

6.2.3. Deriving Information on the Variance of Nitrate Concentrations

The main objective of modelling nitrate concentrations was to develop estimates on their variance. Tab. 41 summarizes the average nitrate concentration, average discharge and variance calculated per hydrological year (April – March).

Tab. 41 Summary of modelling results for nitrate concentration and discharge

Hydrological year	Average NO3 conc.	Average Q	Variance
	mg l^{-1}	*m^3 s^{-1}*	
1986/1987	0.73	52	0.18
1987/1988	0.56	90	0.19
1988/1989	1.79	15	0.33
1989/1990	1.68	23	0.59
1990/1991	2.45	11	0.30
1991/1992	1.02	40	0.44
1992/1993	1.09	36	0.27
1993/1994	1.49	28	0.45
1994/1995	1.99	19	0.45
1995/1996	2.53	15	0.53
1996/1997	3.54	11	0.79
1997/1998	1.14	69	1.14
1998/1999	2.67	15	0.93
1999/2000	2.41	20	0.85
2000/2001	1.39	44	0.71
2001/2002	1.67	35	0.54
2002/2003	1.19	66	0.60
2003/2004	1.98	25	0.56
2004/2005	2.69	17	0.76
2005/2006	1.28	68	1.03
Average	**1.76**	**34.9**	**0.58**

If we plot nitrate concentrations versus discharge a clear relationship can be established (Fig. 74) showing that low flow years are usually related to higher nitrate concentrations. Between the variance of nitrate concentration and average discharge or nitrate concentration no clear relationship can be observed (Fig. 75).

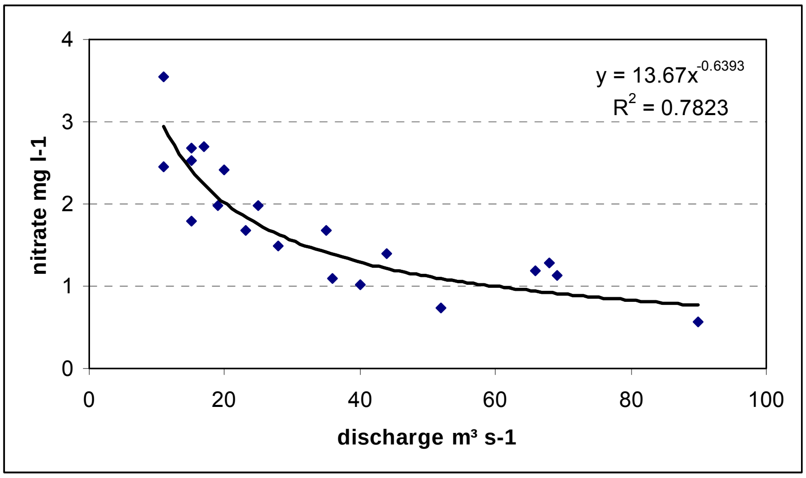


Fig. 74 Average nitrate concentration versus discharge for modelled data

Romeral station, 1986-2006

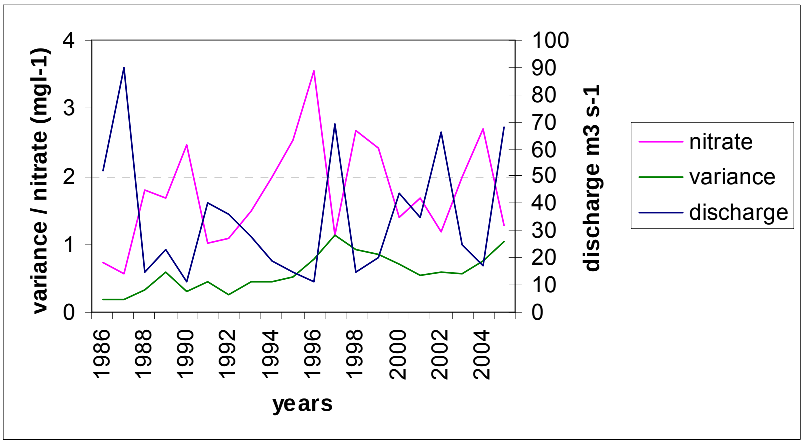


Fig. 75 Average nitrate concentration, discharge and variance for modelled data

Romeral station, 1986-2006

6.3. Discussion

The method employed in this study -modelling variability of nitrate based on nitrogen export coefficients and daily discharge data- is adequate for the situation in the Aconcagua River where the availability of data required for process-based nitrate models is low.

Several factors make the method adequate for the Aconcagua and similar watersheds. One is the dominance of irrigated agriculture. In (large) irrigation schemes nitrate discharges during irrigation season are quite constant and predictable due to the controlled input of water and fertilizer. The export from individual fields may be subject to high temporal fluctuations but the export from large irrigation schemes is much more constant over days and weeks. In watersheds with prevailing rainfed agriculture nitrate export will be much more difficult to be estimated by a simple monthly export coefficient.

The export coefficient method has certain drawbacks which should be considered. A first disadvantage is that fertilizer input and rainfall are the only determinants of the modelled nitrate export. This does not permit to model the behaviour of nitrate in catchments as a function of other factors like soil type, irrigation or cultivation techniques. Second disadvantage is the fact that cause-effect interpretations are not possible. The export coefficient quantifies the N-export from irrigated areas but can not explain why this amount is being exported. Thus the contribution towards enhancing the knowledge on nitrogen dynamics in watersheds is lower than in physically based models. If for a watershed under study sufficient data is available to describe the processes of nitrate export and transport based on deterministic models this should be the preferred mode of simulation. A promising approach in this context is that of defining "Chemical Response Units" (BENDE-MICHL 1999), where areas with similar characteristics regarding the export and dynamics of nutrients are derived on the basis of GIS analysis and are used to parameterize a physically based model. This approach is based upon the Hydrological Response Unit concept widely applied in hydrological modelling (FLÜGEL 1995).

7. Application of Results for Monitoring Design in the Aconcagua River

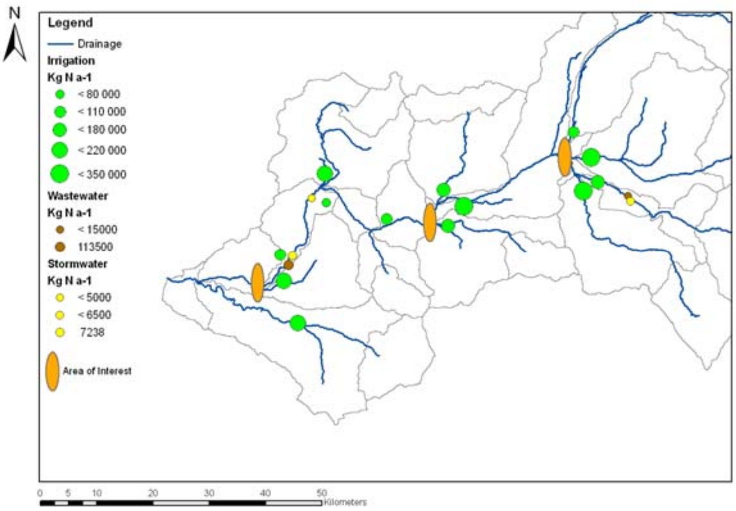
In line with *objective number 5* of this dissertation, in this section the results of the Aconcagua watershed analysis of *chapter 4* and especially of the nitrate concentration modelling of *chapter 6* are employed to exemplify the application for monitoring design. First, the conclusions regarding the selection of adequate monitoring station location will be discussed and second the selection of optimum monitoring frequencies. Important to note that the system under study for monitoring design is limited to the perennial part of the Aconcagua river. Monitoring of intermittent streams impose significant methodological difficulties on the design process which are not discussed further here. The major tributaries to the Aconcagua River rarely fall dry since there is always a baseflow from the irrigation areas. However, they serve as major points of discharges of the irrigation schemes and can not be considered ambient streams but rather artificial drains.

7.1. Monitoring Site Location

Monitoring sites should be located at places where sensitive water users are located downstream. In addition, the location of monitoring stations should consider the likelihood of water quality impairments. Only if both, potential deterioration and significant water uses, are present, the location of a monitoring station can be justified. Whereas the location of water users can be obtained easily from geo-referenced data, the question related to the magnitude of water quality impairment at potential monitoring locations can be answered by the results of the modelling of the previous chapter. Before analysing the likelihood of water quality impairments, important analysis and modelling results of the previous chapters are summarized and a general decision matrix for sampling station location is being developed.

7.1.1. Location of potential polluters and monitoring sites

Important fluxes of N-loads into the Aconcagua can guide the overall decision on adequate monitoring location. Based on modelling results of the previous section, Fig. 76 shows the location and magnitude of nitrogen discharges to the Aconcagua main river stemming from irrigation, wastewater and municipalities. Three areas are defined where major nitrogen sources enter the Aconcagua.



N-loads determined on basis of modelling results (chapter 6)

Fig. 76 Location of N-sources discharged into the Aconcagua River.

These areas should be considered as potential monitoring sites. They refer to the stations "San Felipe", "Romeral" and "Puente Colmo" analysed in the previous modelling of chapter 6.

7.1.2. Decision Matrix

The priority of stations can be expressed numerically if the different indicators of relevance of monitoring sites are weighted and summed. The next table shows a decision matrix for prioritizing monitoring locations. Here the two aspects "downstream water uses" and "likelihood of impairment" are related with numbers. The weights are set according to subjective decision, and need to be discussed among decision makers and other stakeholders. The definition of "downstream" refers to the river reach downstream of the proposed monitoring station, until significant tributaries reach the river. The water users could further be quantified according to number of people supplied with water, annual industrial production value ($), irrigated area (ha), protected area (ha) or level of protection. For example, if the maximum population number (*Pop*) attributed to any stretch in the river basin is one million the matrix value for downstream uses for domestic water supply could be determined with the formula $v_{dr} = 0.036 \ln Pop + 0.5$. This would assign a value of at least "0.5" if there are any drinking water uses at all and a value of "1" for one million inhabitants supplied with water.

In Tab. 42 a simple yes (value=1)/no (value=0) option is presented for water uses. For the likelihood that water is impaired the percentage of past observed or modelled values can be examined. If for example 20 % of the past values were above the limit this station receives a value of 0.2. From this matrix a priority list of stations can be established by ranking the sums of the proposed stations. How many stations are actually chosen to be included in the monitoring program largely depends on the available budget.

Tab. 42 Decision matrix for prioritizing monitoring station locations

Indicator	Value	Range	Weight[1]	Station			
				1	2	3	n
Downstream water uses							
Drinking water supply	v_{drw}	yes=1 no =0	ω_{drw}	$v_{drw,1} * \omega_{drw}$	$v_{drw,2} * \omega_{drw}$	…	
Industrial water uses	v_{ind}	yes=1 no =0	ω_{ind}	$v_{ind,1} * \omega_{drw}$	…		
Agriculture	v_{irr}	yes=1 no =0	ω_{irr}	…			
Ecologically sensitive areas	v_{eco}	yes=1 no =0	ω_{eco}				
Likelihood of impairment							
Likelihood that threshold value is reached	v_{thr}	0…1	ω_{thr}				
Likelihood that trigger value is reached	v_{tri}	0…1	ω_{tri}				
Sum (normalized)		**0…1**		$\frac{\sum w_i \cdot v_{i,1}}{\sum w_i}$	$\frac{\sum w_i \cdot v_{i,2}}{\sum w_i}$		

1) Relative weights need to be determined based on a process of consultation of stakeholders

The system analysis of the Aconcagua Watershed allows making suggestions regarding the location of monitoring sites. Regarding locations of major water users which use surface water from Aconcagua main stem, there are many locations along the river where water is abstracted for irrigation. Industry usually uses groundwater, only in the lower Aconcagua watershed some industries (Oil Refinery RPC and BASF) abstract water from the river. Drinking water is abstracted from surface water in the upper part of the Aconcagua River upstream of San Felipe (Los Andes municipality) in the middle part (at Romeral, basin transfer for Valparaiso region) and in the lower part (Concón municipality; Compare Fig. 77). Obviously, information on nitrate concentration is most relevant for domestic water considering the potential impacts on human health and for sensitive ecosystems where eutrophication could lead to negative impacts. Thus high weights were attributed to downstream drinking water uses and lower weights to ecological and industrial water uses and to irrigation water use. The likelihood of reaching the threshold value was assigned with a higher weight than the likelihood of reaching the trigger value. The weights were chosen in such a way that the sum of all weights allocated to "downstream water users" equals the sum of weights for Likelihood of impairment". These weights were subjectively chosen by the author. For the final decision making process these weights need to be derived after expert and stakeholder consultations and negotiations.

Regarding the likelihood of water quality impairments the modelled nitrate values of the previous chapter serve to calculate the probability that nitrate is above certain defined values. The threshold value for nitrate contamination is 10 mg/l N. A trigger value is an initial alarm level when concentrations are still below an established threshold but are elevated. A trigger value for nitrate concentrations in surface waters is not defined in the Chilean legislation. For the present study a level of 5 mg l^{-1} was chosen, half of the actual threshold. If this level is reached in a sampling location it is a matter of concern for environmental managers. If other threshold values exist, they should be included in the decision matrix. In some countries values to protect waters from eutrophication or to protect aquatic life are recommended; these are usually between 1 and 5 mg NO3-N l^{-1}.

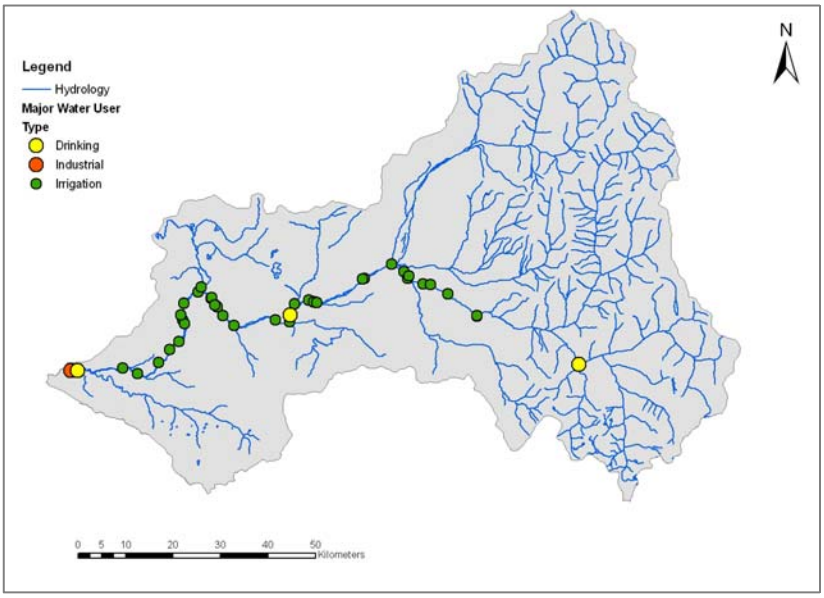


Fig. 77 Location of major water users of surface water of the Aconcagua River

The likelihood to reach threshold or trigger values is calculated on the basis of the modelled values between 1986 and 2006 as the number of days with values above the level, divided by the total number of values (7669).

Tab. 43 Decision matrix for prioritizing locations of stations in the Aconcagua

Indicator	**Weight[1]**	**Station**			
		Juncal	***San Felipe***	***Romeral***	***Puente Colmo***
Downstream water uses					
Drinking water supply	3	0	0	3	3
Industrial water uses	1	0	1	1	1
Agriculture	1	0	1	1	0
Ecologically sensitive areas	1	0	0	0	1
Likelihood of impairment					
Likelihood that threshold value is reached	4	0	0	0	0.04
Likelihood that trigger value is reached	2	0	0	0.01	0.44
Sum (normalized)		**0**	**0.17**	**0.42**	**0.46**

The weighted and normalized sums of the decision matrix identify *Puente Colmo* as the most relevant station. Considering the use of the lowest stretch of the Aconcagua River as source of drinking water combined with likely high levels of nitrate, Puente Colmo station should receive highest priority regarding monitoring location.

Modelling results presented in the previous chapter suggest that nitrate levels in the middle part of the Aconcagua did not reach elevated levels close to the threshold value (10 mg l^{-1}) at any given time in the past 20 years. In the lower part of the Aconcagua monitoring shows values at average of 1.5 mg l^{-1} with a maximum of 4.4 mg l^{-1}. Modelling results suggest that at certain times of the year (December 1997, December 1999, and January 2005) nitrate concentrations reached levels above the permissible limit. Even if the model is not validated for that part of the river it is likely that nitrate concentrations in years with low discharge show elevated values during the peak of irrigation demands associated with high nitrate inputs. So far nitrate is not measured at this crucial time (End of December, beginning of January). Current monitoring practice is to monitor in November and February.

7.1.3. Spatial correlation

If the time series of two stations are highly correlated, each of the stations´ time series can explain the results of the other. Monitoring at the two stations at the same time creates redundant information.

In the middle part of the Aconcagua, modelling results suggest that the nitrate concentrations time series of the stations "Romeral" and "San Felipe" are highly correlated. For monthly averages the Pearson correlation coefficient is 0.77 (Pearson probability 0.001). Here it can be suggested that one of the two monitoring stations can be dropped or one station can be monitored less intensively.

Since the station *Romeral* shows the higher average and maximum concentrations and is located directly upstream of drinking water abstraction plant, this station should be included in the monitoring by all means, whereas *San Felipe* would be the station with lower priority (see results of the decision matrix above) and could be dropped from monitoring activities.

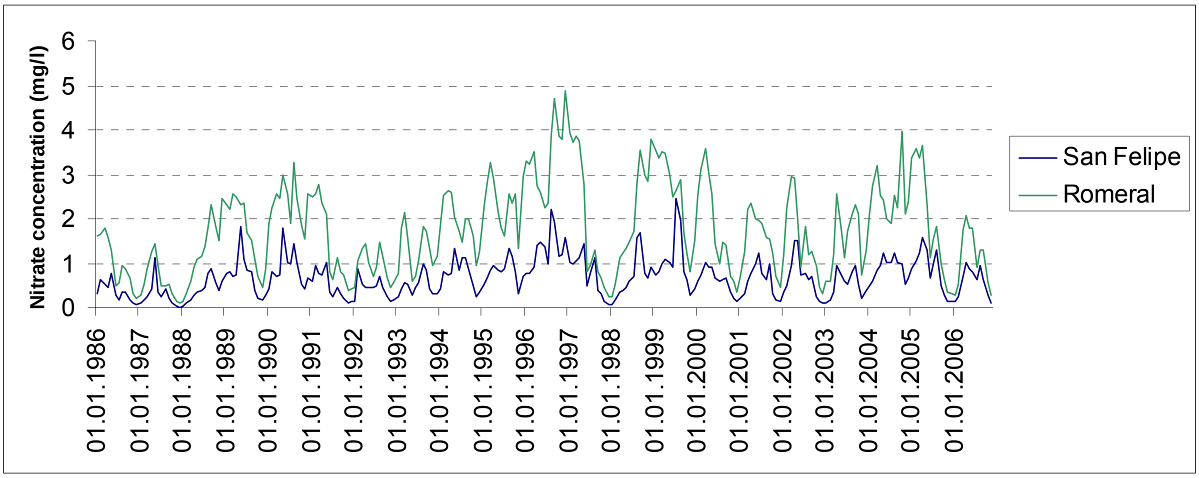


Fig. 78 Monthly time series for modelled nitrate concentration of Romeral and San Felipe stations

7.1.4. Background stations

A monitoring strategy should include the definition of background monitoring stations in order to check if trends are just limited to those areas impacted by local human activities or if global trends are present. Consequently these background stations should be located upstream of any local human interventions at points which are related to watersheds are representative for the upstream areas. Another factor in selecting these sub-watersheds is accessibility via roads for sampling.

In order to detect possible sub-watersheds for background monitoring in the Aconcagua, a GIS- analysis was performed applying the following steps:

1. create a layer of sub-watershed of around 100 km² size,
2. select all those sub-watersheds where no water abstractions (hydropower, irrigation, industry, municipal) or other impacts (discharges, landfills, mining etc) are reported,
3. select sub-watersheds in proximity (100 m or less) of roads.

The selected sub-watersheds as well as water abstractions and contaminant sources are shown in Fig. 79. It would be adequate to select two background monitoring sites one in the northern and one in the southern part of the upper Aconcagua watershed. If one has to be chosen it would be the southern one (near Juncal) since this station is accessible by the international highway (connecting Chile with Argentina) throughout the year while the northern sub-watershed (Resguardo los Patos) is hardly accessible during the rainy season since the related road is not paved. In the middle and lower Aconcagua Basin there are no sub-watersheds without human impacts.

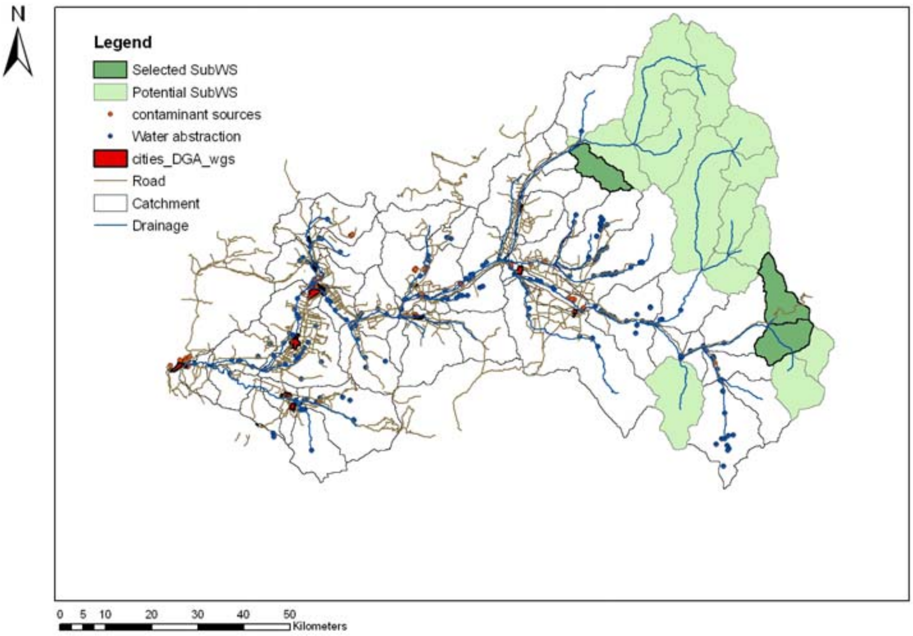


Fig. 79 Potential and selected sub-watersheds for background monitoring in the Aconcagua Watershed

Fig. 80 summarizes the monitoring locations and suggested priorities. The station San Felipe should be dropped from monitoring if budget is not sufficient or if stations should be closed in order to allow for higher frequent monitoring at other stations.

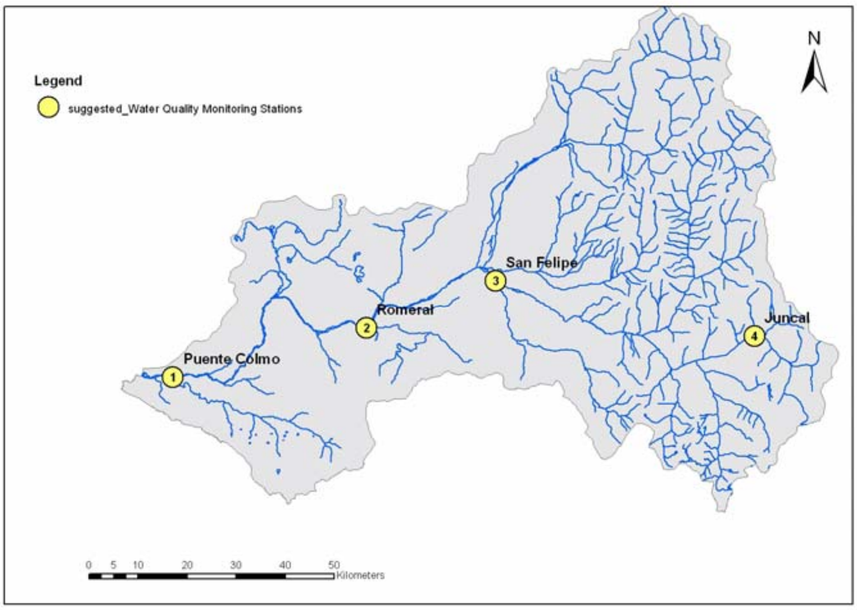


Fig. 80 Suggested monitoring sites and their priorities

1= highest priority

4 = background station

7.2. Monitoring Frequencies

Next to the location of monitoring stations, water quality monitoring design needs to determine optimum monitoring frequencies. In many cases the objective of monitoring is to estimate the true mean of a sampled population (compare chapter 2). This could be, for example the monthly or annual mean of nitrate concentrations in order to calculate pollutant loads, to determine long-term trends or to check for compliance with standards.

In the following, for the site of Romeral an analysis on optimum sampling frequency is performed. San Felipe station can be excluded from the further monitoring design since its information can be represented by station Romeral as was shown by the correlation analysis. The lower Rio Aconcagua (at or near Puente Colmo) was not included in the analysis since here validation of the model was not satisfactory, as was reported in the previous chapter.

The crucial question regarding monitoring design which is followed here is "*how many samples need to be taken per year in order to estimate the true mean?".*

The modelled data of nitrate concentration for 1986 - 2006 permits us to calculate the variance of nitrate concentration and derive suggestions for an adequate monitoring frequency in order to estimate the mean. For this purpose the approach presented in chapter 2.2.2.1 is followed and the formula which was used to calculate the number of samples is repeated here:

$$n = s^2 \frac{t_{(\frac{\alpha}{2})}^{2}}{d^2} \qquad \textbf{(23)}$$

Where:
n = minimum number of measurements
d = maximum permitted error ($\bar{x}$ - μ)
t = value t-Student for the selected significance level (α)
*s*² = variance

The use of the percentiles of the normal distribution is correct if we can assume that the sampling distribution of $\bar{x}$ is normal. Looking at the sample distributions for the different hydrological years we see that these are far from normal (see Fig. 81). A method for assessing the $\bar{x}$ distribution is needed. The Bootstraping method (EFRON and TIBSHIRANI, 1993) was used to create $\bar{x}$ sampling distributions testing for normality. The original sample (one hydrological year) represents the population from which it was drawn. The Bootstrap method consists of resampling from this sample many times to mimic what we would get if we took many samples from the population. The bootstrap distribution of a statistic, based on many resamples, represents the sampling distribution of the statistic, based on many samples.

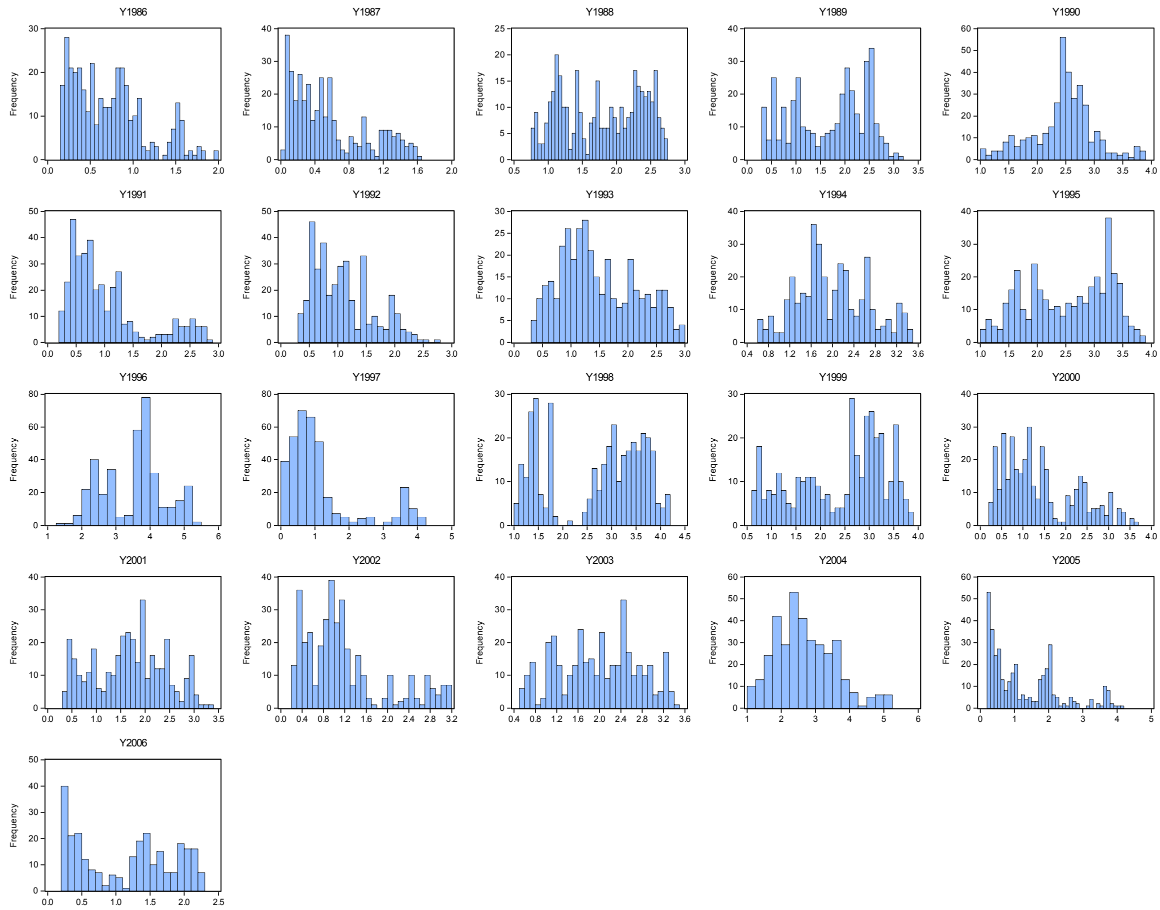


Fig. 81 Histograms of nitrate concentration of the hydrological years

If a histogram of the bootstrap estimates is approximately normal in shape, we may use normal theory to find confidence intervals for the unknown parameter as shown above. If the shape is not normal, the sampling distribution is not normal and more advanced techniques are needed to find a confidence interval, i.e. the confidence interval can be set up with the percentiles of the created bootstrap distribution.

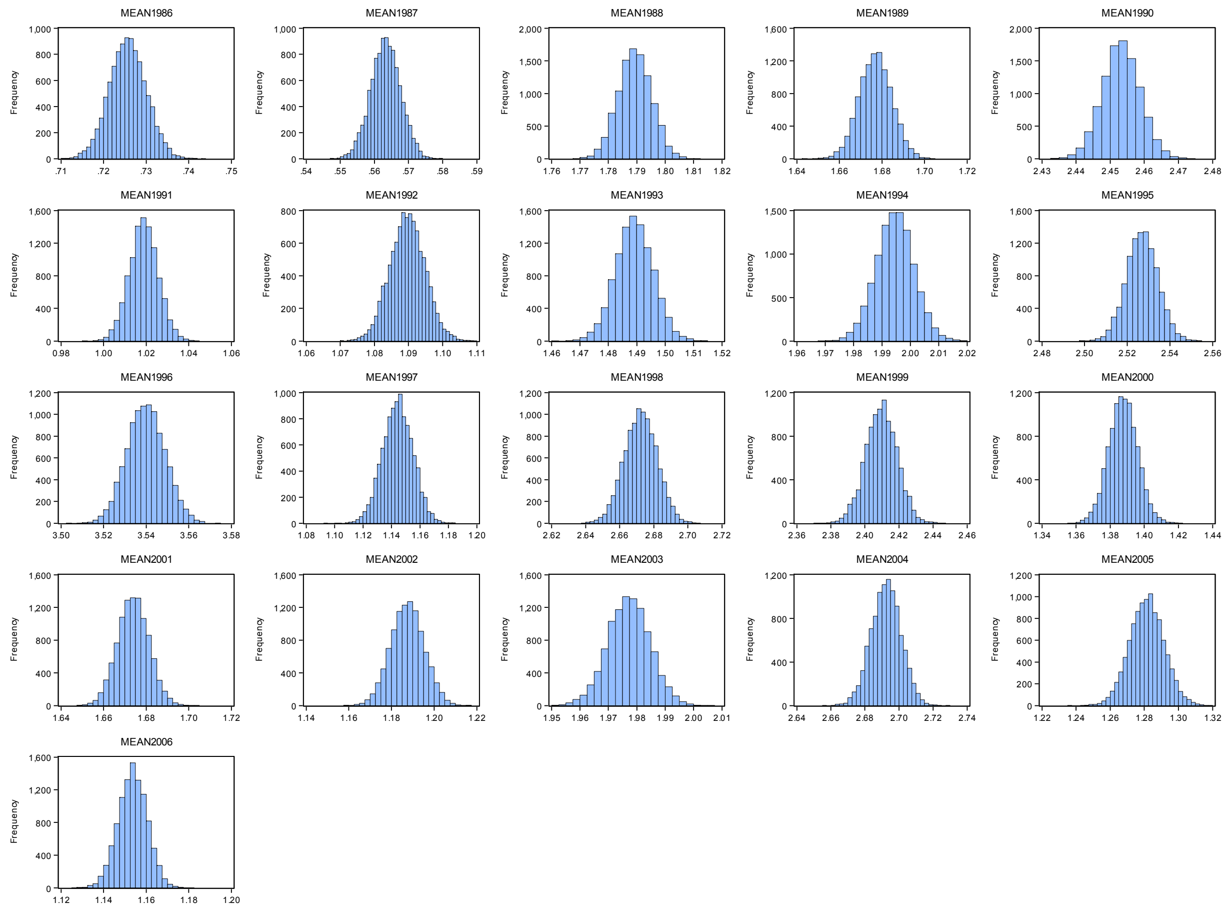


Fig. 82 Bootstrap distribution histograms for the 21 hydrological years

In Fig. 82 we can see the bootstrap distribution histograms (10,000 replications) for the mean of the 21 hydrological years. They are all normally distributed according to the Jarque-Bera statistic. So we come to the conclusion, that the use of the normal standard distribution is correct when estimating the sample size and equation 23 may be applied to calculate sampling frequencies.

The results of the calculation of minimum required sample numbers are shown in Tab. 44 (compare also Fig. 83). It shows the variance of nitrate concentrations for the different hydrological years and the related minimum sampling frequencies according to different statistical levels (confidence levels, 1 - α) calculated for different permitted errors (d) when estimating the sample mean (0.3 mg l^{-1} and 0.5 mgl^{-1}). While average annual discharge and nitrate concentration are clearly correlated, high variance of nitrate may occur in low flow / high nitrate (hydrological years 1997/1998 or 2005/2006) as well as in high flow / low nitrate (hydrological years 1996/1997, 1998/1999) years. Thus, there is no direct relationship between the average hydrological condition in a hydrological year and the variance of nitrate concentration.

If we opt for a high statistical confidence level (0.95) and would like to estimate the true mean with a permissible error of +/- 0.3 mg l^{-1} than – depending on the hydrological year – between 10 (1986/1987) and 51 (1997/98) samples per year are necessary. This means that with weekly sampling, even in a year with high variance of nitrate concentrations like in (1997/98) the mean could be estimated +/- 0.3 mg l^{-1} with a confidence level of 95 %. If biweekly sampling is chosen this statistical security would only be obtained in 50 % of the years, but in that case in all years an estimate of +/- 0.5mg l^{-1} at a 95% confidence level could be guaranteed. In any case, the current monitoring practice of taking four samples per year is far from being sufficient and in order to obtain reliable results from a nitrate monitoring program at least biweekly sampling should be aimed at.

Tab. 44 Minimum annual sampling frequencies calculated on basis of modelled variance (Romeral Station)

Hydrological year	Average NO3 conc.	Average Q	Variance	Minimum number of samples per year			
	mg l-1	m³ s-1		CL 90 d= 0,5	CL= 90, d=0,3	CL= 95, d= 0,5	CL= 95, d= 0,3
1986/1987	0.73	52	0.18	5	8	5	10
1987/1988	0.56	90	0.19	5	8	5	11
1988/1989	1.79	15	0.33	5	12	8	17
1989/1990	1.68	23	0.59	8	20	12	28
1990/1991	2.45	11	0.30	5	11	7	15
1991/1992	1.02	40	0.44	7	15	9	21
1992/1993	1.09	36	0.27	5	10	5	14
1993/1994	1.49	28	0.45	7	16	10	22
1994/1995	1.99	19	0.45	7	16	10	22
1995/1996	2.53	15	0.53	8	18	11	25
1996/1997	3.54	11	0.79	11	26	15	36
1997/1998	1.14	69	1.14	14	36	20	51
1998/1999	2.67	15	0.93	12	30	17	42
1999/2000	2.41	20	0.85	11	27	16	39
2000/2001	1.39	44	0.71	10	23	14	33
2001/2002	1.67	35	0.54	8	18	11	26
2002/2003	1.19	66	0.60	8	20	12	28
2003/2004	1.98	25	0.56	8	19	11	26
2004/2005	2.69	17	0.76	10	25	14	35
2005/2006	1.28	68	1.03	13	33	18	46

Hydrological year: April – March; CL= confidence level (%), d= maximum allowable error (mgl^{-1})

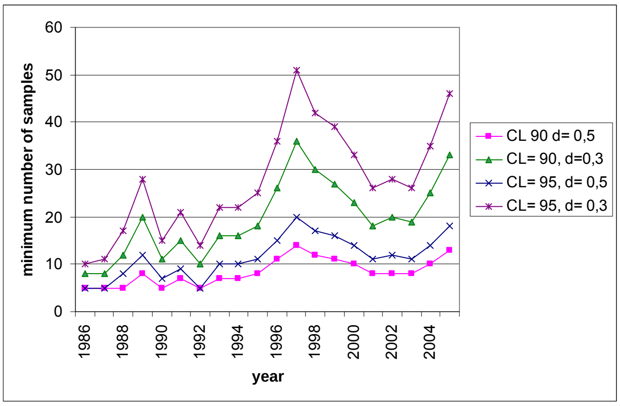


Fig. 83 Minimum number of samples needed to estimate the mean for different statistical criteria

CL= confidence level, d = maximum allowable error to estimate the mean

The analysis of this section leads to the recommendation to significantly increase monitoring frequency in at least one of the monitoring stations at Aconcagua main river. On the other hand the number of stations may be reduced by at least one (San Felipe). It could be shown that the significant difference of variance of nitrate concentration between hydrological years in the Aconcagua leads to a wide range of recommended sampling frequencies and that the analysis of spatial correlation of nitrate concentrations can lead to relevant conclusions regarding the location of monitoring stations. Another conclusion is that the analysis of variance of nitrate concentration over space and time proofs to be a useful tool in order to derive recommendations on sampling frequency and location.

8. Discussion and Conclusions

The presented work proves that it is possible to reconstruct time series of nitrate and to determine spatial correlations of variables at different stations for the Aconcagua River based on input data of discharge, land use and pollution sources. This allows determining the water quality for several points in the river stem at any given day of the modelled time span (here 1986 – 2006). These data can be used to develop suggestions for an improved monitoring system. Furthermore, they can be used to make estimates on the nitrate concentration of places and times actually not monitored.

The employed **export coefficient model** to determine the impact of irrigated agriculture, by far the largest source for nitrate contamination in the river, is well suited for the task of predicting nitrate concentrations. It is adequate for a situation like in Chile with no pronounced history in environmental monitoring and consequently low data availability.

On the other hand there are some **critical points** related to the chosen approach as well. First of all, the fact that export coefficients are being determined empirically is a strong simplification of highly complex processes which occur on the irrigation field and at the sub-watershed level regarding water and nitrogen dynamics. The model does not allow analysing further the cause-effect relationships. We do not know if the nitrate is exported due to certain irrigation management practices or if it is related to soil or other environmental conditions. It just provides an empirical value regarding the amount of nitrate export combining base and overland flow and assumes the same behaviour for all irrigation perimeters.

The validation of modelling results was acceptable, at least for the upper-middle part of the watershed. However, another critical point in the study was that limited validation data were available. With just four measurements per year, in some years even less, it is difficult to finally judge on the utility of the proposed model.

If we accept that the model does represent the spatio-temporal behaviour of nitrate concentration, it is very well suited to **derive recommendations for monitoring**. In fact, sound estimates of the variance of a constituent is a prerequisite to apply more sophisticated, statistic-based techniques of monitoring design as described in scientific literature. Some of these methods applied to the case study result in clear recommendations: Among several alternatives for water quality monitoring locations, priorities could be identified, giving the decision maker a basis for including or excluding a monitoring station, depending on available resources. Furthermore, the number of monitoring stations in the main Aconcagua River could be reduced due to high correlation of time series of two stations located in the upper-middle and lower-middle part of the Aconcagua (Romeral and San Felipe stations). Measurement frequency should be increased to at least 27 (biweekly) measurements per year in order to derive any reliable estimate for the mean annual nitrate concentration.

Even though the approach was applied to the case of the Aconcagua River, it can be easily **transferred to other regions**. The crucial prerequisites for applying the method are

- the presence of measured or reliably modelled data of daily discharge data and
- a realistic estimate of the major nitrate emitting water uses.

For the latter, data on land and fertilizer use dynamics and data on point sources are necessary. The analysis of their spatial and temporal distribution can be supported by interpretation of satellite imagery and/or agricultural or population censuses as shown in this work.

The other watersheds of Central and Northern Chile are characterised through similar conditions as the Aconcagua in terms of major soil characteristics, hydrological pattern, irrigation systems, and cultivated crops. Thus, it is likely that with the use of the same nitrate export coefficients as determined in this work, reliable results can be expected related to the simulation of the spatio-temporal behaviour of nitrate. In other areas it would be necessary to verify nitrate export coefficients through specially designed empirical studies.

Another question is the **transferability of the approach to other parameters** than nitrate. The most important prerequisite in order to model concentrations and the resultant variability of any water quality parameter is the presence of a good representation of the hydrological components of the watershed since the spatio-temporal dynamics of water quantity determine water quality to a large extent. The next question is the availability of data on contaminant sources and finally data on the chemical and physical processes which take place within the river system.

While nitrate is highly soluble and the relevance of transport processes via particulate matter is relatively low, in the case of other constituents like phosphates or heavy metals this is different and adds complexity to the system. If we take the example of heavy metals, a contaminant class of major relevance in many parts of Chile due to the highly intensive mining activities, it is evident that in this case contaminant source data are not easy to quantify. Heavy metals are not released from mines on a continuous base but are rather related to sporadic, often illegal discharges. In addition, heavy metals also have a different environmental behaviour than nitrate. While in the case of nitrate denitrification is the most important factor determining nitrate transformation to other substances, in the case of heavy metals more complex processes occur regarding sedimentation and re-suspension. Here an interesting field for future research opens up to test if the variability of other constituents in surface water can be sufficiently described with an export coefficient approach combined with high frequent runoff data.

The developed model is very appropriate to be **integrated into the national Chilean monitoring system**. It is not only adequate in order to aid monitoring design, but also to support the analysis of monitoring results. With the help of the model, judgements on nitrate concentrations can be made even for times and places where no measurements took place. Over time, with more monitoring results being generated, the quality of the model could be improved and revalidated. If the reliability of the model increases, it can even serve to reduce monitoring frequencies in the future, since the model will be able to reliably predict nitrate concentrations which could substitute direct measurements. Furthermore, the model can determine if at a given point it is likely that critical concentrations of nitrate may be reached during the year. In the case of the Aconcagua, in the middle part of the watershed, for example, which serves to supply over half a million of people with drinking water, modelling results show that nitrate-N concentrations are not likely to surpass even 5 mg l^{-1}, which is clearly below critical concentration regarding its use for human consumption (10 mg l^{-1}).

With the procedure described in this thesis a powerful **tool** is at hand in order **to optimize water quality monitoring systems** regarding the selection of sampling locations and sampling frequencies, even in areas where overall data availability is low. It can help to take rapid decisions on monitoring system design without having to establish water quality time series over many years with high temporal resolution. Thus, it can contribute to allocate budgets for water quality management more efficiently.

The suggested approach to determine water quality constituent variability is in principle applicable to any watershed. The export coefficients which are apt to describe the export of nitrate from a certain land use are often available in literature but in other cases have to be determined empirically for each case study.

Further research is recommended to test the validity of the approach described here for other constituents. In fact, water quality monitoring design needs to consider cases with multiple objectives and multiple constituents. Thus, the research presented here is a contribution to a wider field of science with a significant research demand and a high application potential.

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Curriculum Vitae

Name	Lars Wolfgang Ribbe
Geburtsdatum / -ort	28.06.1968 / Bremen
Nationalität	deutsch

Zeitraum	
1974-87	Grundschule, Sekundarstufe I und II, Leeste, KGS Weyhe
10/1987 – 02/1994	Studium Chemie an der Universität Bremen
09/1990 – 06/1991	Studium der Chemie und Umweltwissenschaften an der University of Maryland, College Park, USA
07/1991 – 09/1991	Institute of Fundamental Studies (IFS), Kandy , Sri Lanka: "Pestizidanalytik (Parathion) mittels GC-MS"
01/1993 – 07/1993	School of Environmental Sciences (SES), University of Poona, Indien: "Phys./Chem. Wasseruntersuchungen der Flüsse Mula und Pavana zur Bestimmung anthropogener Einflüsse auf die Wasserqualität"
09/1994 – 07/1997	Masterstudiengang „Technologie in den Tropen" an der Fachhochschule Köln
05/1996 – 09/1996	Forschungsaufenthalt am Arab Centre for Studies of Arid Zones and Dry Lands (ACSAD), Damaskus, Syrien: "Nitratbelastung von Grundwasser im Damaskus Becken".
10/1996 – 12/1996	Jerusalem Water Undertaking (JWU), Ramallah, West Bank: "Der Wassersektor in der West Bank: Ressourcen und Akteure"
seit 08/97	Wissenschaftlicher Mitarbeiter am Institut für Tropentechnologie, Fachhochschule Köln
seit 12/2004	Geschäftsführer ITTrms e.V Köln (Wissenschaftliche Weiterbildung)

Köln, 04.01.2008 **Lars Ribbe**

Selbständigkeitserklärung

Ich erkläre, dass ich die vorliegende Arbeit selbständig und unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe

Köln, **Lars Ribbe**