Hydrological Process Investigation Using Water Quality Monitoring Data

R.M. Argent[1], A.W. Western[1], L.E. Neumann[1]

[1] Department of Civil and Environmental Engineering and eWater CRC, The University of Melbourne, Vic, 3010
email: R.Argent@unimelb.edu.au

Keywords: *Catchment modelling, Water quality, Monitoring data*

EXTENDED ABSTRACT

Various water quality parameters are measured routinely at sites across many countries, including Australia and New Zealand, largely as a part of institutional monitoring programs. With the current focus in hydrology on understanding processes from point to catchment scales, the potential exists for these data to provide information on dominant hydrological processes, albeit at coarser time and space scales than are often used in hydrological studies supported by specific and intense monitoring and use of specialist tracers. Methodological approaches to understanding hydrological processes across different scales include multi-scale and multi-site comparison, tracer and fingerprinting techniques, intense small scale hydrological studies, studies of seasonal influences, expansion of standard water quality monitoring parameter suites, catchment-based load differencing, and a range of statistical methods. Selection of a method or methods for use in a catchment should be based upon a staged approach, with preliminary investigation of seasonal and/or spatial patterns, followed by more intense (e.g. event sampling) investigation.

Data from a long term water quality monitoring station in Victoria, Australia (Nicholson River @ Deptford, #223204; Catchment area 287 km^2) was analysed to identify any potential relationships between flow and water quality parameters, both across the whole record and in seasonal periods. Seasons were defined by month start date rather than equinoxes and solstices, and the water quality parameters of interest (and number of data points) were dissolved oxygen (DO)(294), electrical conductivity (EC in-situ) (320), pH (328), suspended solids (SS) (156), Turbidity (304), filterable reactive phosphorus (FRP) (155), total phosphorus (TP) (157), nitrates and nitrites (NOx) (159), total Kjeldahl nitrogen (TKN) (159) and total nitrogen (TN) (159).

None of the variables were found to have strong concentration relationships with flow, although EC tended towards less variable values with increasing flow. This was not found, however, to be related to particular seasons. Similarly, there was no discernible seasonal influences on pH, FRP, TP and TN. All other parameters did, however, exhibit a seasonal influence of some kind. DO showed a generally higher concentration in winter (Jun.-Aug.) than other seasons, and was 40% higher on average in winter (11.6 mg/L) than summer (8.2 mg/L). Turbidity and SS had interesting seasonal responses (Figure 1), with average SS concentration being highest in spring, while turbidity showed a low average value in autumn, compared to other seasons.

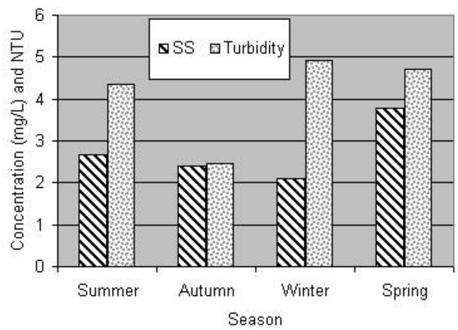

Figure 1. Average SS concentration (mg/L) and turbidity (NTU) for 223204

NOx had more than double the average concentration in winter (0.1 mg/L) than in other seasons (0.04 mg/L), while average summer TKN concentration (0.29 mg/L) was nearly double that of winter (0.16 mg/L). Autumn and spring concentrations fell between these, being 0.215 and 0.22, respectively.

These results suggest a potential range of processes affecting the concentration, from those driven by increasing flows (e.g. SS), metabolic activity (e.g. DO) or volatilisation (NOx), although it is also possible that different sources of flow and different pathways of flow may be discernible through more detailed investigation of these data.

1. INTRODUCTION

Stream water quality is influenced by many anthropogenic factors, including development, land clearing, fertiliser application, and forestry operations (Carpenter *et al.*, 1998). Management to improve water quality is therefore often focussed on these, and water quality data have a strong role in informing assessment of this.

Thousands of streams across the world are monitored for water quality, with many variations in sampling frequency, periodicity and elements. Most sampling is regular, occurring monthly or seasonally, while discharge is often logged 'continuously' at automatic gauging stations, or daily via manual reading or remotely-accessed stations. Discharge records for a site can reveal significant information about the dominant hydrological processes at yearly, seasonal, or daily scales, or for events. However, *discharge* measured at a point carries no information on the pathways along which flow occurred, the distance travelled or the time since the water entered the system. These factors may, however, be elucidated from examination of water quality measures, such as chemical concentration, acidity or temperature.

Although the most extensive water quality data sets generally come from institutional monitoring, assessment and understanding of water quality characteristics and responses to management often comes from studies of specific sites, sources, pathways, forms or processes (Haygarth *et al.*, 2005). It is possible, therefore, that we are not utilising the information available from institutional sources to its fullest extent. This paper reviews aspects of the use of water quality data to inform understanding of catchment hydrology and responses to management, and examines the potential for use of data from one example site.

2. WATER QUALITY AND HYDROLOGICAL PROCESS STUDIES

The water quality monitoring and hydrological processes literature reveals a range of studies carried out at a broad range of scales from point and near-point studies considering hillslope or field flow pathways and timing, to catchment comparison based single or nested water quality stations. Many tracers or water quality parameters have also been used in these studies, ranging from those commonly monitored to specialist parameters for particular processes. The following explore some of the different study types.

2.1. Multi-Scale, Multi-Site Studies

The work of Heathwaite and Johnes (1996) provides an example investigation of the sources and pathways of nutrients across different scales. The study included particulate and soluble phosphorus (P), and organic, ammonium and nitrate forms of nitrogen (N). Methods included daily surface water samples from large catchments (eg ~350km^2), weekly subsurface water quality measurements for small catchments (~2km^2), and rainfall simulators for plots studies, over a period up to 2 years. The first of these are closest in kind to those commonly available from institutional sources, and these data were found to most clearly vary from year to year (e.g. dry year v wet) and season to season. Climate, primarily via discharge, was found to influence dominant N species, with, for example, ammonium showing summer peaks arising from riverine nitrite, and winter peaks possibly associated with N linked to increased sediment loads. Given this example, N and P species data from an institutional monitoring site may yield indications of the sources and dominant processes, but probably not the detailed pathways, contributing to nutrients at a monitoring point.

2.2. Tracking Water Quality Factor Sources Through Tracers and 'Fingerprinting'

In investigating flow paths in an example from Scotland, Soulsby *et al.* (2004) focussed on a similar scale to the previous example. In this, natural geochemical tracers (Gran alkalinity, silicate, pH, and conductivity) were measured across nested catchments, with sampling varying from a single day of 'snapshot' sampling across a wide area, to daily flow and fortnightly water quality samples. The selected tracers supported discrimination between surface soil flow sources, and flow arising from areas of deeper parent material. The results emphasised the importance of understanding the physical and chemical nature of runoff from contributing catchments, with, for example, baseflow being clearly identified by geological influences on chemistry.

Sediment source fingerprinting (e.g. Walling, 2005) has been used to identify both the travel times and pathways of flow and water quality components, via a variety of approaches that include cluster analysis/ ANOVA, correlation methods, discriminate function analysis, and mixing model analysis. Use of composite fingerprints of sediment source, using various chemical species, is increasing. These methods, however, often rely on specialist tracers, such as radionuclides, or on water quality parameters that are not commonly obtained, such as sedimentattached chemicals or sediment fractions. When considering analyses based on institutional monitoring, phosphorus may offer the best opportunity to distinguish between surface and sub-surface/channel sources, although this will depend upon the dominant pathways and local factors affecting all monitored chemical species.

2.3. Small Distance Hydrological Processes

There are many studies of point- and local-scale hydrological and water quality processes reported in the literature. Saunders *et al.* (2006), for example, examined surface and sub-surface pathways of organic carbon, N and P across a plot smaller than 20 m. Detailed assessment of the hydrological cycle and nutrient dynamics was done, revealing effects such as decreasing nitrate concentrations down a hillslope, due possibly to high organic matter influencing redox reactions, and also some effects of plant uptake. A study on a similar scale (McKergow *et al.*, 2006) measured infiltration and saturation excess overland flow, A-horizon and B-Horizon flows, for different riparian buffer systems. The findings identified various point scale differences in dominant pathways between seasons, events and buffer covers. These studies highlight the requirements for intense or continuous monitoring, along with specific instrumentation to monitor the processes of interest. Continuous monitoring was also noted as a requirement in a study of salt movement through surface and subsurface pathways in drained agricultural land (van den Eertwegh *et al.*, 2006). The monitoring used in these types of studies differs from that found in typical monitoring networks. It is possible, however, that long term monitoring data, when combined with short, intense studies, could contribute significantly to understanding of dynamics.

2.4. Seasonality Influences

The effects of land use and catchment size on N and P export rates in the Ardennes were investigated by Salvia-Castellvi *et al.* (2005) in a study running over 12 years. Dynamics of a number of small sub-catchments (up to 33.9 km^2), within two major rural catchments (306 and 424 km^2), were examined in detail. Sampling was initially undertaken fortnightly, but was found to be insufficient, and was replaced by a combination of autosamplers for events and weekly samples during hydrologically stable periods. Parameters included NO_3-N and NH_4-N, Total (TP) and soluble reactive P (SRP), and suspended sediment, all of which are part of common water quality monitoring in Australia. Load estimates were made using a variety of methods, dependent upon the sampling density. Climatic variations were found to have a dominant effect on annual and seasonal loads, via the obvious links between precipitation and runoff volume. Point sources had a large influence on total P load in dry periods, due to high SRP. Phosphorus seasonality was less obvious in areas with few or no point sources. In a typical storm a brief high increase was noted in TP concentrations, followed by a sharp decline. This occurred with increasing discharge, indicating dominance of subsurface and throughflow pathways (Salvia-Castellvi *et al.*, 2005).

In contrast to baseflow TP, it was found that storm TP tended to be associated with particles. Nitrate dominated the Nitrogen load, with high (low) concentrations in wet (dry) periods. In storms, a small decrease in Nitrate concentration was found on the rising limb, followed by an increase (often above pre-storm levels) to an event peak, due to nitrate leaching via subsurface flow pathways.

In comparison to the above study, institutional point monitoring offers no opportunity for examining event data, but may allow identification of wet and dry season concentration differences in addition to the dominant species. This may possibly indicate nutrient sources, and support identification of dominant flow paths and hydrological connection to such sources.

2.5. Inclusion of Extra Water Quality Parameters

In contrast to many studies that focus on inorganic sources of pollutants, Maie *et al.* (2006) investigated the dynamics of chromophoric dissolved organic matter (DOM) from diffuse sources inflowing to estuaries of the Florida Coastal Everglades. Seventy-three coastal and estuarine sites were sampled monthly over nearly 2 years. Salinity and TOC were included in sampling, along with parameters primarily related to fluorescence. Beyond typical water quality monitoring parameters, inclusion of fluorescence as an indicator of interest increased the ability to discriminate between sources and pathways, with seasonal variations in parameters being attributed to variations in primary productivity, water transport and exchange processes, and with sunlight identified as a dominant driver. The effects of primary productivity are of interest in terrestrial studies, where they may affect not only chemical processing, but also hydrological dynamics – something that may be identified in regular monitoring data through examination of inter- and intra-seasonal variations in parameters.

2.6. Estimation of the Contribution of Various Parts of the Catchment to Total Load

Phosphorus dynamics across scales was investigated by Haygarth *et al.* (2005), in a study of P movement from plot to hillslope to sub-catchment to catchment (~1000 km^2). The investigation covered P process coherence and dominant processes of P dynamics at different scales of observation. Processes included point source flows, particulate and colloidal transport, catchment storage, connectivity, and storm flows and recharge. It was found that different processes dominate at different scales, with the dominant process determined to a degree by hydrological energy. This has implications for studies based on monitoring station data, where energy is generally high, that produce management recommendations related to on-ground actions, where energy may be low at times. Determination of where and when various processes dominate is a key factor to consider here.

Comparison of monitoring data from stations positioned in series offers some potential for identifying sources of contaminant loads. Albek (2003), for example, found that an urban and industrial area positioned between monitoring stations significantly impacted water quality. In this study application of the non-parametric Kendall-Theil Robust Line regression method allowed clear separation of point and diffuse loads. This supported ongoing monitoring of management effects focussed on reducing both these loads, albeit with little regard to positioning of management activities in relation to dominant contaminant pathways.

The SPARROW (spatially referenced regression on watershed attributes) approach (Smith *et al.*, 1997) is a method built upon the analysis of data from multiple water quality monitoring stations. SPARROW includes not only spatially referenced sources of pollutants, but also attributes related to transport of contaminants, so can provide predictions of both spatial nutrient yields and in-stream changes to constituent loads during transport. An advantage of this approach is the focus on data available from a network of water quality monitoring stations, without the need for specialist tracers or studies.

A spatial analysis approach was also used by Elshorbagy *et al.* (2005), although in this case the investigation focussed upon faecal pollutant sources rather than nutrients. A two-stage approach was used, with regression relationships first established between flow and coliform concentration. Artificial Neural Networks were then used to assess distribution of faecal loads amongst spatially-distributed sources. Methods of this nature are appealing in the ability to extend point monitoring data to include spatial relationships, but lack information on dominant processes.

Another potential method for analysing water quality samples from multiple sites is 4-R-Mode multi-component statistical analysis. This was used (Lambrakis *et al.*, 2004) to examine the behaviour of nitrate. As with the fingerprinting approach mentioned earlier, this study used water quality parameters (eg Ca^{2+}, Mg^{2+}) to identify source factor influences, such as nearby agricultural activities, buildings, and aquifer characteristics, on observed nutrient concentrations.

The above examples show the role of statistical methods in hydrological and spatial characteristic analysis related to water quality data. The term 'chemometrics' has been adopted for this by some authors (e.g. Singh *et al.*, 2005), referring to application of statistical techniques, such as cluster analysis, to analysis of water quality variations with regards to spatial and temporal effects. An example (Singh *et al.*, 2005) of this used water quality sampling from 10 sites with over 20 parameters per site. Correlation analysis associated water quality parameters with:

- season, and
- site, although site relations were predominantly geological rather than anthropogenic.

This indicates potential for periodic monitoring data to support identification of contributing areas and possibly also periods during which particular areas are actively contributing to catchment load. Similarly, Vega et al (1998) found seasonal and spatial indicator correlations with data taken from three-monthly water quality monitoring from 3 sites over 2.5 years.

One issue with studies such as these is that the parameters are to some degree lumped, with statistics used as an *indicator* of influences, such as high variability in parameters used to indicate seasonal or other climatic variations. Limited or no attempt is made to examine contributing temporal or spatial influences, such as events occurring some time (eg hour, day or week) before the measurement time, and which may be identifiable from examination of flow and climatic data.

The above sections review some of the methods that are used to elucidate hydrological process information from examination of water quality data, and highlight the opportunities that may exist to extract more information from readily available long term water quality records. Method selection in a given problem situation should use a staged approach, starting with investigation of seasonal and/or spatial patterns, followed by more intense (e.g. event sampling) investigation.

3. AN EXAMPLE STREAM

To examine this further, a water quality data record from the Nicholson River @ Deptford (Number 223204, Position E147.697, S37.593; Catchment Area 287 km^2) was examined. This station, in eastern Victoria, has daily discharge available for most of the period from May 1961 to present, and water quality at various intervals (commonly monthly) from August 1975 to present (table 1). This station was selected from amongst those being used in an on-going study as it is typical of many stations in Australia for which data are available, in addition to having more frequent TN and TP data for 2004-2006. The catchment land use is dominated by forest and forest product operations.

Parameter	**Start Date**	**End Date**	**Samples**
Air temperature	Apr-2005	Present	23
Ammonia	Dec-2002	Jul-2003	8
Average daily flow (historic)	May-1961	Mar-1973	3751
Colour (filt.)	Nov-1993	Present	156
Discharge	Aug-1975	Present	342
Dissolved oxygen (DO)	Aug-1975	Mar-2005	294
DO client supplied	Jan-2005	Present	25
Electrical conductivity (EC) (25°C)	Jan-2005	Present	23
EC (at stream temperature)	Jan-2005	Present	25
EC (in-situ)	Aug-1975	Mar-2005	320
Nitrates and nitrites (NOx)	Nov-1993	Present	159
pH (in-situ)	Aug-1975	Present	328
pH (lab)	Dec-2003	Dec-2003	1
React. Phosphorus (filt) (FRP)	Nov-1993	Present	155
Suspended solids (SS)	Nov-1993	Present	156
Temperature (in-situ)	Aug-1975	Present	335
Total dissolved solids	Mar-2005	Present	22
Total Kjeldahl nitrogen (TKN)	Nov-1993	Present	159
Total nitrogen (TN)	Nov-1993	Present	159
Total phosphorus (TP)	Nov-1993	Present	157
Turbidity (in-situ)	Aug-1975	Present	304
Turbidity (lab)	Jan-2003	Present	26

Table 1. Water Quality Data Availability (in April 2007) for Nicholson River @ Deptford

Table 1 provides a summary of the water quality data for 223024. The number of samples for each parameter gives an idea of the frequency and period of measurements, with high numbers of points (eg >300) indicating monthly data for most of the full period (1975-2006), medium numbers of samples (eg ~150) indicating monthly data for a much lesser period, and small numbers (eg 8) indicating periods of sampling related to opportunistic activities or special studies.

Consideration is first given to any monthly or seasonal effects on flow, as these may influence dominant pathways. Figure 2 shows clearly the dominance of flow towards the winter and spring months.

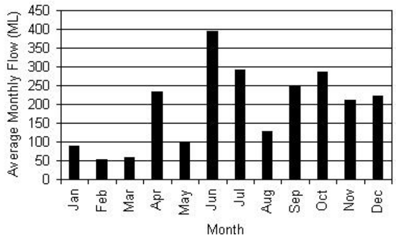

Figure 2. Average Monthly Flow for 223204

A limited number of the available parameters have both a reasonable number of samples and the potential to be linked to hydrological processes, such as differentiation between surface and sub-surface sources. These are DO, EC (in-situ), pH, SS, Turbidity, FRP, TP, NOx, TKN and TN. Comparison of these against flow will be undertaken, either for the full record or seasons of interest. The time of concentration for the catchment was estimated to be less than 24 hours, so flow on the day of measurement will be used.

Dissolved oxygen has no discernible correlation with flow (Figure 3; NB 7 points with flow>500 have been omitted), so seasonal median values were compared.

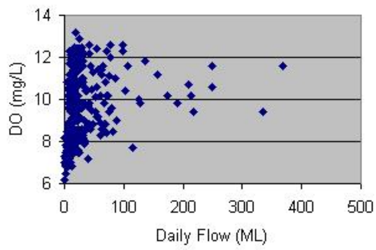

Figure 3. DO v Flow for 223204

Medians for summer (Su, Dec-Feb), autumn (A), winter (W) and spring (Sp) were 8.2, 9.8, 11.6 and 9.8, respectively, indicating the potential for further investigation of seasonal flow effects, particularly summer and winter, on DO. Electrical Conductivity (Figure 4) showed a similar disinclination to correlate with flow, although the trend with high flows to an EC value at or below 100 suggests a seasonal effect. However, both winter and summer were found to have a median value of 100 µS/cm.

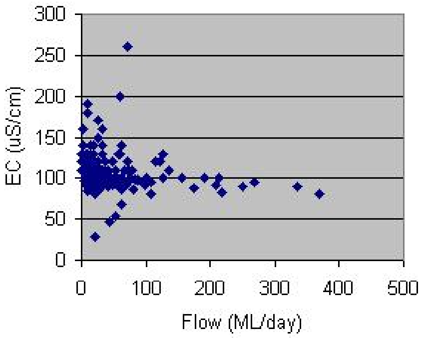

Figure 4. EC v Flow for 223204

pH values ranged between 5.7 and 8.0, with no correlation with flow, nor any seasonal distinctions. Somewhat surprisingly, SS and Turbidity also exhibited no clear correlation with flow, although each did have a stand-out season, with spring average SS being 1.4 or more times larger than other seasons (although median values were similar, suggesting skewed data), and average autumn turbidity being approximately half of the other seasons. These suggest the occurrence of high spring flows raising SS concentrations and low autumn flows maintaining generally low turbidity, although further investigation would be required to determine if further effects, such as surface flows sources, could be identified in the record.

FRP was found to provide evidence only of a steady generation process and low analysis discrimination, with over 80% of samples returning the same concentration, 0.003 mg/L. Total Phosphorus showed a similar, but slightly broader, cluster of values with, again no clear overall or seasonal relationship with flow.

Nitrogen parameters (NOx, TKN and TN) exhibited some interesting behaviour, although none had a clear response with flow across the full record. Average TN concentration was found to be similar across seasons (average 0.36, 0.29, 0.27 0.29 for Su, A, W, Sp) while NOx had more than double the average concentration in winter (0.1 mg/L) than in other seasons (0.04 mg/L) (Figure 5). Conversely, average summer TKN concentration (0.29 mg/L) was nearly double that of winter (0.16 mg/L), with autumn and spring being 0.215 and 0.22, respectively.

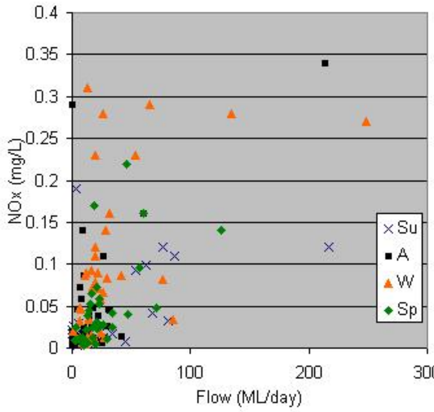

Figure 5. NOx v Flow for 223204

These results for nitrogen suggest a combination of factors influencing concentration, possibly arising from different contributing sources or from different processes (e.g. denitrification) dominating in different seasons.

4. CONCLUSIONS

There is a considerable range of approaches that can be used to explore water quality data, and to determine from these any information relevant to source areas, hydrological pathways and dominant processes. The detail that can be extracted is largely dependent on nature of the data – data collected with high frequency from a small catchment, or one with a small mix of influencing factors, can generally reveal more than those from larger catchments with a higher mix of influences.

Despite the simplicity of the preliminary analysis performed on the data from station 223204, a number of interesting factors have emerged, suggesting that further investigation may yield information relevant to the assessment of source areas for various water quality parameters, or possibly the interaction of surface and groundwater at different times.

Flow, TN and TP have been gathered at a higher frequency (eg weekly and event) for this site over the period October 2004 to November 2006, which may provide greater discrimination of flow-concentration relationships, although the analysis here suggests that analysis of N species may have been more informative.

5. REFERENCES

Albek, E., (2003), Estimation of point and diffuse contaminant loads to streams by non-parametric regression analysis of monitoring data. *Water, Air, and Soil Pollution*, 147, 229-243.

Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., Smith, V. H., (1998), Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications*, 8 (3), 559-568.

Elshorbagy, A., Teegavarapu, R. S. V., Ormsbee, L., (2005), Framework for assessment of relative pollutant loads in streams with limited data. *Water International*, 30 (4), 477-486.

Haygarth, P. M., Condron, L. M., Heathwaite, A. L., Turner, B. L., Harris, G. P., (2005), The phosphorus transfer continuum: Linking source to impact with an interdisciplinary and multi-scaled approach. *Science Of The Total Environment*, 344 (1-3), 5-14.

Haygarth, P. M., Wood, F. L., Heathwaite, A. L., Butler, P. J., (2005), Phosphorus dynamics observed through increasing scales in a nested headwater-to-river channel study. *Science Of The Total Environment*, 344 (1-3), 83-106.

Heathwaite, A. L., Johnes, P. J., (1996), Contribution of nitrogen species and phosphorus fractions to stream water quality in agricultural catchments. *Hydrological Processes*, 10 (7), 971-983.

Lambrakis, N., Antonakos, A., Panagopoulos, G., (2004), The use of multicomponent statistical analysis in hydrogeological environmental research. *Water Research*, 38 (7), 1862-1872.

Maie, N., Boyer, J. N., Yang, C. Y., Jaffe, R., (2006), Spatial, geomorphological, and seasonal variability of CDOM in estuaries of the Florida Coastal Everglades. *Hydrobiologia*, 569, 135-150.

McKergow, L. A., Prosser, I. P., Weaver, D. M., Grayson, R. B., Reed, A. E., (2006), Performance of grass and eucalyptus riparian buffers in a pasture catchment, Western Australia, part 1: riparian hydrology. *Hydrological Processes*, 20 (11), 2309-2326.

Salvia-Castellvi, M., Iffly, J. F., Borght, P. V., Hoffmann, L., (2005), Dissolved and particulate nutrient export from rural catchments: A case study from Luxembourg. *Science of the Total Environment*, 344 (1-3), 51-65.

Saunders, T. J., McClain, M. E., Llerena, C. A., (2006), The biogeochemistry of dissolved nitrogen, phosphorus, and organic carbon along terrestrial-aquatic flowpaths of a montane headwater catchment in the Peruvian Amazon. *Hydrological Processes*, 20, 2549-2562.

Singh, K. P., Malik, A., Singh, V. K., (2005), Chemometric analysis of hydro-chemical data of an alluvial river - a case study. *Water, Air, and Soil Pollution*, 170, 383-404.

Smith, R. A., Schwarz, G. E., Alexander, R. B., (1997), Regional interpretation of water-quality monitoring data. *Water Resources Research*, 33 (12), 2781-2798.

Soulsby, C., Rodgers, P. J., Petry, J., Hannah, D. M., Malcolm, I. A., Dunn, S. M., (2004), Using tracers to upscale flow path understanding in mesoscale mountainous catchments: two examples from Scotland. *Journal Of Hydrology*, 291 (3-4), 174-196.

van den Eertwegh, G., Nieber, J. L., de Louw, P. G. B., van Hardeveld, H. A., Bakkum, R., (2006), Impacts of drainage activities for clay soils on hydrology and solute loads to surface water. *Irrigation And Drainage*, 55 (3), 235-245.

Vega, M., Pardo, R., Barrado, E., Deban, L., (1998), Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Research*, 32 (12), 3581-3592.

Walling, D. E., (2005), Tracing suspended sediment sources in catchments and river systems. *Science of the Total Environment*, 344 (1-3), 159-184.