Assessing the representativity of catchments according to their size from hydrochemical observations

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Abstract This paper is concerned with the effect of catchment size on water quality observations. An example is provided from an agricultural area of central Brittany for catchments ranging from 0.17 to 12 km^2 in area. Three anions of contrasting hydrobiogeochemical properties (Cl, NO_3, and SO_4) were monitored in stream water. It is concluded that for operational determination of the main hydrological or hydrochemical features in a given region, the choice of the catchment for study must be directed by stable correlations between nitrate and chloride. Correspondingly, for process-oriented investigations and deterministic model testing, smaller catchments may be more relevant because observations will reflect specific characteristics of the site.

INTRODUCTION

The relevance of environmental studies at the catchment scale depends strongly on the selection of the study site. The choice of the size of the catchment is particularly important for the representativity of the results. The choice must be consistent with the aims of the investigation, process-oriented or operational. The aim of this paper is to discuss the interest of observations on stream quality variations in nested catchments for assessing this consistency. This aim is based on the assumption that if the same processes occur simultaneously in an area, each solute will follow the same trend in the different catchments. This will not be the case if a specific dominant process is responsible for the solute concentration variations in some catchments. Furthermore, as the catchment size increases, the integration of heterogeneous features of the landscape will result in homogeneous catchment response, similar to a buffer effect. The discussion is based on a catchment study in a farming area in western France.

MATERIALS AND METHODS

The study was conducted on the Coet Dan catchment, in an intensive farming zone in central Brittany (western France, UTM: 2° 50′W; 48°N). The catchment, described by Brun *et al.* (1990) and Loumagne *et al.* (1993), comprises the upper part of the Coet-Dan River, a tributary of the Evel River. The relief of the catchment area is gentle and the substratum consists of brioverian schists. These silty schists alternate locally with sandstone. Alluvial material covers the bottom of the valley. The soils consist of loamy material of weathered schists mixed with eolian loam, more abundant on the east-facing

hillslopes. The tops of the slopes are overlain with dystric or aquic eutrochrepts (sols bruns acides faiblement lessives). Glossaqualfs (sols degrades hydromorphes) and fluvents (sols alluviaux) cover the low ground. The mean annual rainfall is 711 mm. Saturated areas border the river. The land use of the basin is characterized by intensive farming of maize, wheat, temporary and permanent pasture for dairy and indoor stock farming and vegetables.

The catchment was divided into nine sub-catchments of various areas (Fig. 1, Table 1). A study of the variations in time and space of the concentration in stream water of NO_3^-, $SO_4^=$ and Cl^- was performed. The streams were sampled approximately fortnightly at the outlet of the catchments (sites 10 to 19, Fig. 1). Site 10 is a spring and site 18 is the outlet of the catchment. Sampling was undertaken between the rainfall-runoff events (except for the third sample) because the aim of this first approach was to analyze the trends in baseflow. The paper is based on measurements from November 1992 to June 1993. The concentrations were measured by ion chromatography (DIONEX).
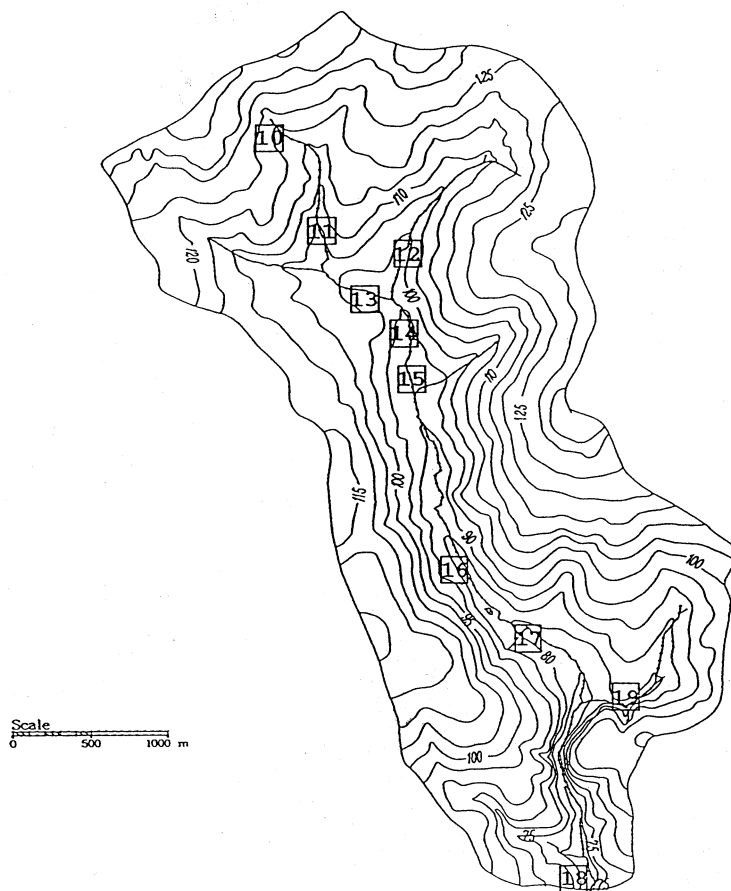

Fig. 1 Map of the catchment of Coet Dan, with the numbers of the sampling sites for the different sub-catchments (site 10 is a spring).

Table 1 Catchment area (in hectares), average concentration (in mmoles per litre) and standard deviation of concentrations of Cl^-, NO_3^- and $SO_4^=$ for each sample site, November 1992 to June 1993.

Number of site	Area	Cl^-	NO_3^-	$SO_4^=$
10	17	1.07 ± 0.11	1.00 ± 0.16	0.08 ± 0.02
19	42	1.32 ± 0.09	1.35 ± 0.14	0.11 ± 0.07
11	100	1.12 ± 0.13	0.98 ± 0.13	0.11 ± 0.03
12	195	0.96 ± 0.10	1.22 ± 0.17	0.08 ± 0.03
13	245	0.99 ± 0.10	0.95 ± 0.15	0.08 ± 0.03
14	472	0.95 ± 0.11	0.98 ± 0.17	0.08 ± 0.02
15	495	0.96 ± 0.11	1.00 ± 0.17	0.09 ± 0.03
16	672	0.93 ± 0.11	0.91 ± 0.22	0.10 ± 0.03
17	779	0.92 ± 0.07	0.84 ± 0.21	0.11 ± 0.04
18	1200	1.08 ± 0.08	0.99 ± 0.20	0.12 ± 0.04

RESULTS

Variation of Cl^-, NO_3^- and $SO_4^=$ in time and space

Each solute followed a specific trend during the year. The variation of Cl^- concentration with time was small at each site (Fig. 2(a)). The exception was the concentration in the third sampling date, taken during the peak flow of a large rainfall-runoff event. This event influenced the concentration at the uppermost site (spring, site 10) and had a major dilution effect on the amount of Cl^- in the different catchments. Except for the third sampling date, NO_3^- concentration (Fig. 2(b)) increased rapidly in autumn and winter, reached a maximum in February, and decreased slowly afterwards. Sulfate content decreased slowly (Fig. 2(c)) over the whole period, except for the last sampling date.

   The mean solute concentrations in the different catchments are similar (Table 1), except for the small ones (sites 11, 19 for Cl^-; sites 12, 19 for NO_3^-). In the largest sub-catchments (sites 16, 17, 18), the standard deviation of Cl^- concentration decreased and that of NO_3^- concentration increased. The cross-correlations between the time series of the sampling sites were calculated for each solute. For all ions, the cross-correlation coefficient was variable, and often was not significant between catchments smaller than 0.2 km^2. Small sites behave independently even if they are overlapping (e.g. for sites 10, 11, 13). Conversely, the correlation coefficients between the larger catchments were high, especially for the nitrate concentrations.

Comparison of variations in Cl^-, NO_3^- and $SO_4^=$

The relation between the solutes was first examined for each catchment for the whole sampling period. No clear trend was observed, because of the contrasting seasonal
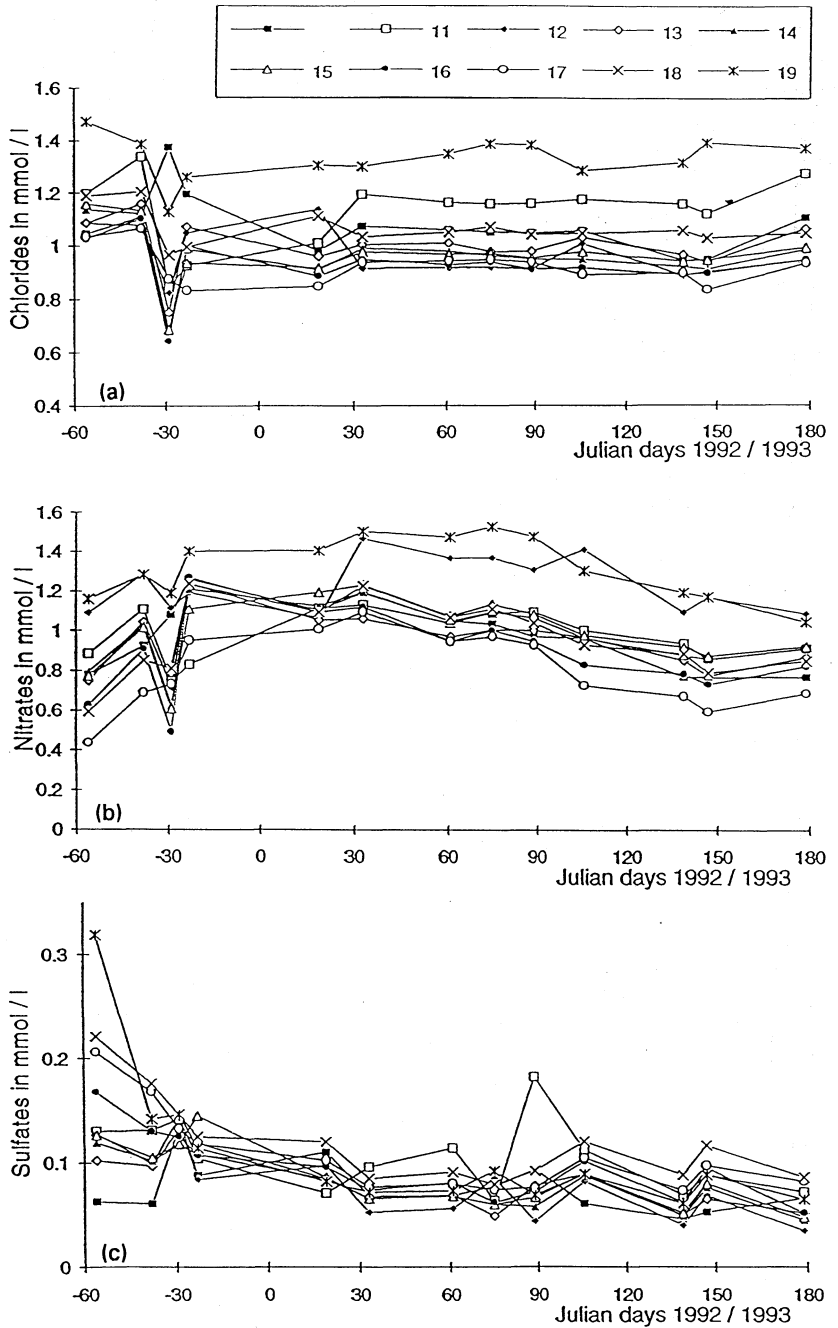
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Fig. 2 Variation in ionic concentration for the different catchments during the sampling period: (a) Cl^-; (b): NO_3^-; (c) $SO_4^=$.

variations of nitrate concentrations between autumn and spring. The data set was then split into two periods. The first period includes the samples collected between

5 November 1992 and 2 March 1993 (excluding the third sample date), and the second period runs from 16 March 1992 to 27 May 1993. To analyze the variability in the concentration at the different sites, normalized data (i.e. instantaneous concentration divided by the mean concentration of each catchment over the period considered) were calculated to minimize the influence of the mean level of concentration of each catchment.

For the autumn and winter periods, there was no general trend in the NO_3^- *vs* Cl^- relation (Fig. 3(a)). The correlation coefficient calculated for the autumn/winter period for each site indicated a variable correlation between NO_3^- and Cl^-, either positive (e.g. site 11) or negative (e.g. site 18). When values of the correlation coefficients are plotted *vs* catchment areas (Fig. 4(a)), a scale effect appears in the variation of the correlation coefficient; the correlations are randomly distributed for the small catchments and become more significant and negative with increasing area. The relation between concentrations of NO_3^- and $SO_4^=$ was examined in the same way, with similar results (Fig. 4(b)). The correlation coefficient between NO_3^- and $SO_4^=$ was close to -1 for the largest catchments. For the spring period, all catchments exhibited the same trend. The correlation ($r = 0.74$) between the concentrations of NO_3^- and $SO_4^=$ was positive and independent of catchments (Fig. 4(b)).
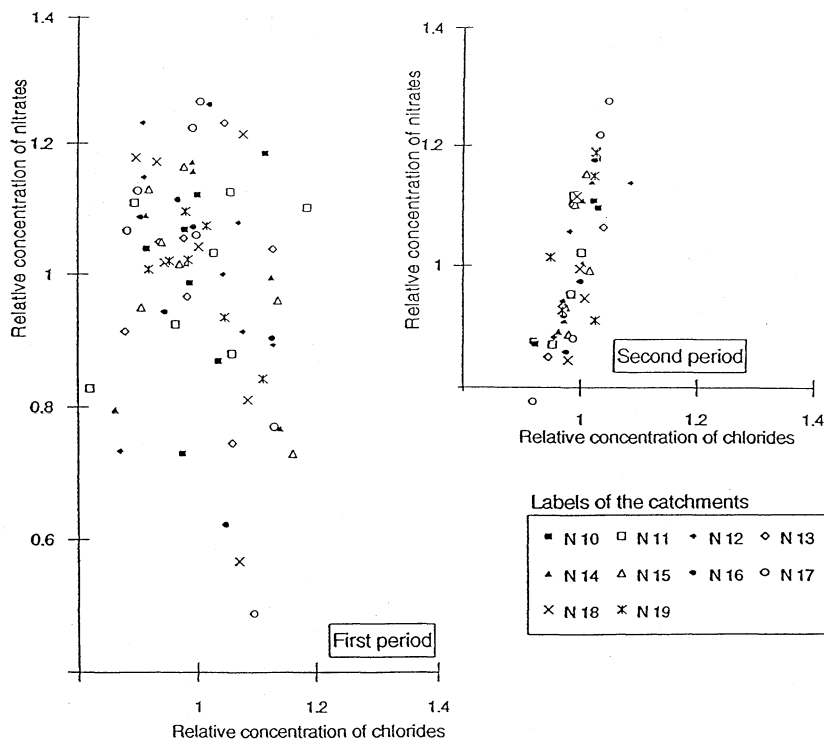

Fig. 3 Variation of normalized NO_3^- versus Cl^- concentrations: (a) for the first period (autumn and winter); (b) for the second period (spring).
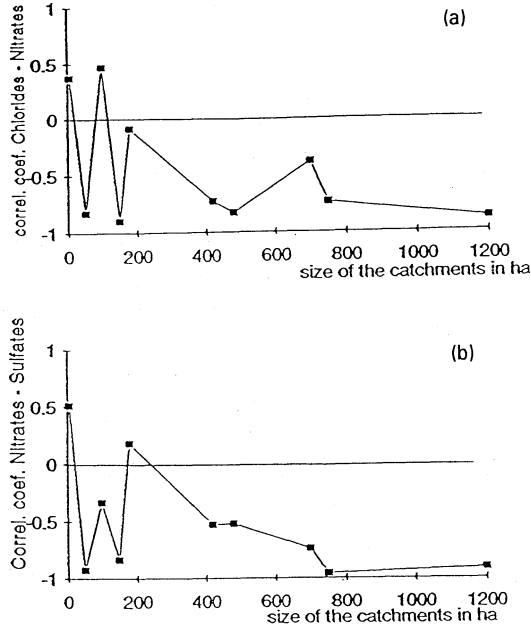
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Fig. 4 Correlation coefficients between (a) Cl$^-$ and (b) NO$_3^-$ *vs* the size of catchments at the Coet Dan site.

DISCUSSION

The three solutes studied have different cycles in the catchment system. Chloride is usually considered a conservative tracer of the water cycle because it is not significantly involved in biological and adsorption processes (Ambroise, 1992; Pinder & Jones, 1969). In the Coet Dan catchment, Cl$^-$ concentration decreases slowly with depth so that shallow groundwater has the highest concentration, close to the mean concentration of the river. The Cl$^-$ concentration in rainwater is low, and close to the deep groundwater concentration. This suggests an anthropogenic origin, related to mineral and organic fertilization. Therefore, Cl$^-$ variations in the river are caused by the mixing in varying proportion of shallow and deep groundwater, the shallow groundwater concentrations being affected by rainfall and evaporation.

Nitrate comes almost exclusively from mineral and organic fertilizers. It is strongly taken up by the crops, but it is barely adsorbed in the soils. The other sinks of nitrate are the "surface" denitrification in waterlogged areas and the "deep" denitrification in the groundwater due to the oxidation of iron and sulphur. As for Cl$^-$, the nitrate concentrations decrease slowly with depth in the groundwater, and the concentration in precipitation is low. The difference is that, in summer, some surface waters exhibit a low concentration of nitrate due to "surface" denitrification, but a rather high concentration of chloride due to evaporation. During autumn, the concentration of chloride in streams decreases due to dilution by rainwater, whereas the concentration of nitrate increases due to the decrease of biological activity; a significant contribution of water from waterlogged areas to streams may lead to a negative correlation between NO$_3^-$ and Cl$^-$ contents. Conversely, if mixing between non-denitrified surface water and deep ground-

water is dominant, a positive correlation is observed.

Three sources of $SO_4^=$, of similar importance, are identified: atmospheric input, agriculture and weathering of sulphur minerals in bedrock. The mean concentrations in rain water, groundwater and stream water are close to 0.1 mmol l^{-1}, but large variations are observed. Deep denitrification results in an increase of $SO_4^=$ concentration as the NO_3^- content decreases.

The temporal variations of Cl^- suggest that the different catchments, excluding the spring (site 10), follow similar hydrological processes. The variations of $SO_4^=$ also show similarity of behavior of the catchments. The variations of NO_3^- concentrations are not as homogenous. The differences are related to site-specific features. For example, in catchment 17, the concentration of nitrate is low and decreases strongly in spring. In this area, bottom lands are often waterlogged and covered with permanent pastures or wood lots and a pond is present. All of these factors suggest a high denitrification and uptake potential.

The cross-correlation results show a clear scale effect with a threshold between 0.2 and 0.4 km^2, dividing the catchments into two groups. Smallest catchments behave independently whereas larger catchments behave similarly.

During the first sampling period, from November to March, a scale effect was also observed in the nitrate/chloride and nitrate/sulphate relations; in the larger catchments, the nitrate concentration was strongly and negatively correlated with the two other solutes, which fits well with the interpretation given above. In small catchments, the relations were looser because a specific local pattern can be dominant.

During the spring sampling period, a large decrease of NO_3^- concentrations was observed, along with a less significant decrease of Cl^- concentrations, independent of the size of the catchment. This period was dry and these variations were due to two major processes. First, the slow decrease in chloride reflects the increasing contribution of the deep groundwater. Second, the decrease in nitrates was partly due to the contribution of deep groundwater, but mainly was the result of an increase in biological activity.

CONCLUSION

Although these results must be confirmed by more detailed investigations, they offer guidance on characterizing catchments within a region, taking into account both catchment size and hydrochemical behavior. The variability of processes within different catchments depends on the season. In the present case, at the beginning of spring, after the period of heavy rainfall, each sub-catchment reacted in the same way as did the entire catchment. Therefore, all the catchments are representative, because the dominant processes are not scale-dependent. In autumn and early winter, the hydrological and hydrochemical processes exhibit increased variability. The smaller catchments behave differently, depending on the local specificity. As the size of the catchment increases, an average behavior emerges due to the balancing of different processes.

Therefore, a general survey of major ions in different sub-catchments can facilitate the choice of a study catchment, depending on the objective of the study. When that objective is the assessment of the mean hydrological or hydrochemical features in a given region, the choice is directed by a stable correlation between NO_3^- and Cl^-, allowing use of empirical relations and simple, global models. When the objective is a

process study or the testing of deterministic models, the choice of smaller catchments may be more relevant, because observations at the outlet of the catchment reflect more closely the specific characteristics of the site.

These results agree with those of Wood *et al.* (1988, 1990), who defined a Representative Elementary Area from a hydrological perspective. This concept of representative elementary area was introduced using only topography and rainfall data. The use of hydrochemical observations is a promising tool to make this concept more precise, especially in the context of increasing water quality concern.

REFERENCES

Ambroise, B. (1992) Hydrologie des petits bassins versants ruraux en milieu tempère − processus et modèles. In: *Les Flux dans les Volumes Pedologiques et à Leur Limites: Approches Spatiales à l'Echelle du Bassin Versant* INRA, coll. "le point sur" (sous presse).

Merot, Ph. & Bruneau, P. (1993) Sensitivity of bocage landscapes to surface runoff: application of the KIRKBY index. *Hydrol. Proc.* **7**, 167-176.

Merot, Ph. & Bruneau, P. (1992) Echelle spatiale représentative d'un bassin versant sur le plan géochimique, note présentée par G. Pedro. *C. R. Acad. Sci.* **315**(II), 1097-1103.

Pinder, G. F. & Jones, J.F. (1969) Determination of the water component of peak discharge from the chemistry of total runoff. *Wat. Resour. Res.* **5**, 438-445.

Wood, E., Sipavalan, M. & Beven, K. (1990) Similarity and scale in catchment storm response. *Rev. Geophys.* **28**, 1-18.

Wood E., Sipavalan, M., Beven, K. & Band, L. (1988) Effect of spatial variability and scale with implication to hydrological modeling. *J. Hydrol.* **102**, 29-47.