

## **Improving the Reliability of Catchment Mass Input: Output Estimations from Sub-Optimal Data in Areas of Urban Growth**

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A new mass input:output formula is presented which makes full use of available data which are commonly sub-optimal for mass input:output analysis. Results indicate that some useful information on wet and dry fallout may be obtained from bulk precipitation data only, and that the new formula provides generally more reliable results for catchment chemical mass export under various conditions than other simpler formulae. Care is taken not to assume rates of natural denudation from the results in the light of an inability clearly to separate non-denudational from denudational components of mass export, and natural from man-induced components of denudation.

### **Introduction**

Catchment mass-balance (input:output) analysis has become increasingly popular over the past thirty years as a technique for determining chemical denudation rates (e.g. Eriksson 1955, Douglas, 1968, Cleaves et al. 1970, Goudie 1970, Saunders and Young 1983) and investigating various chemical fluxes, especially of nutrients (e.g. Bormann and Likens 1967, Swank 1984, Feller and Kimmins 1984). The rise in popularity is both a function of an increased awareness of the importance of hydro-chemical processes in catchments, and of significant improvements in the theoretical and empirical foundations of input and output estimations.

With few exceptions (e.g. Hembree and Rainwater 1961) the chemical denudation formulae used prior to the late 1960's made no provision for mass inputs to catchments (e.g. Livingstone 1963, Williams 1965) and it has been determined that under certain conditions these formulae greatly overestimate chemical denudation rates (Goudie 1970). Nevertheless, such simple formulae appear to have remained very popular; Saunders and Young (1983) found only one of the thirty-one articles they reviewed (published from 1959 to 1981) accounted for mass inputs to catchments and Rodda and Jones (1983) ignore mass inputs in their study of mean annual loads of some British rivers. The popularity of such simple formulae has even endured considerable technical advances, such as the development of wet and dry fallout collectors (Fisher et al. 1968, Terstriep et al. 1982, Chan et al. 1984), and theoretical advances (e.g. Winkler 1970) which have provided significant improvements in our understanding of mass input:output dynamics. This is primarily because, apart from specific experimental catchments (e.g. Lewis and Grant 1978), the detailed precipitation and stream quantity and quality data necessary to obtain such improved understanding are not available, either because such data have not already been collected or because their collection is too expensive and labour intensive to be warranted. More typically, mass input:output analyses use only minimal bulk precipitation data (Henrickson and Wright 1977, Christopherson et al. 1982, Feller and Kimmins 1984, Heaton 1984, Tate and Bates 1984) from which broad assumptions are often made (e.g. regarding dry fallout rates; Skartveit 1981), and may employ highly aggregated streamflow data (e.g. Goudie 1970) which do not account for rapid changes in streamflow quality and quantity. Such data sets are sub-optimal for catchment mass input:output analysis.

These issues of insufficient data are incorporated into some recommended methods for the calculation of long-term solute loads (Goudie 1981, pp 194-195), the most elaborate of which employs equations which require weekly stream water quality values, continuous streamflow data and bulk precipitation estimates. However, even this "elaborate" method is affected by "... 'time-dominating' low-flow periods..." (Goudie 1981) resulting in significant overestimations of load, and does not provide any information on the relative importance of wet precipitation and dry fallout.

These shortcomings are addressed in this paper which specifically tests the effectiveness of using a new formula on a sub-optimal data set like that described above. The formula is explained below and comparisons are made to a simple load estimate formula and a popular aggregated input:output formula (Goudie 1970, Goudie 1981 pp 140). Two basic questions are therefore addressed.

- 1) Is there an acceptable way to estimate wet and dry fallout rates from simple bulk precipitation data?
- 2) Can more accurate and reliable estimates of chemical denudation rates be made from sub-optimal data using more efficient formulae?

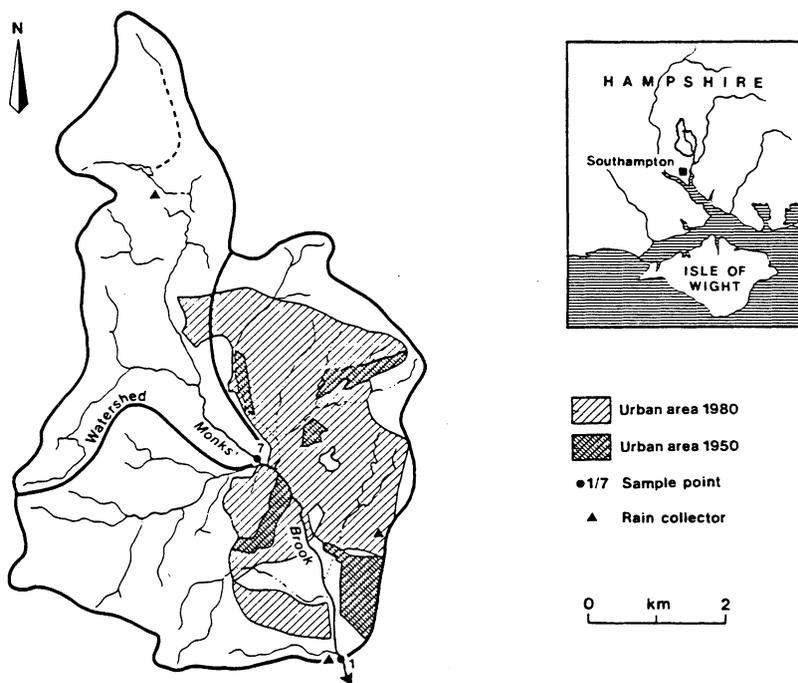


Fig. 1. The Monks' Brook catchment showing urbanisation and sampling locations.

### Raw Data Collection

The data used in this investigation were collected for the Monks' Brook (33.03 km<sup>2</sup>), Hampshire, England for the whole of 1979. Two sample sites, one at the catchment outlet (affected by the urban area) and one draining the upper third of the catchment (rural) (Fig. 1), were monitored continuously for discharge using stage recorders (Ott and Munro types) and rating curves (supplied by Southern Water and the author). These sites were monitored weekly for chemical water quality (Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>-N, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup> and total dissolved solids-TDS). In addition, a series of 8 storms were monitored for these same constituents at both sample sites.

Bulk precipitation data were collected from three rain collectors throughout the catchment. The collectors were very similar to those described by Reynolds (1984) consisting of polypropylene funnels and collection vessels partly encased in opaque plastic to omit sunlight. Collections were made after every precipitation event.

Precipitation quantity data were obtained from Southern Water for an autographic gauge in the centre of the catchment. Although, as reported elsewhere (e.g. Feller 1975; Reynolds 1984) spatial variation in input was minimal, average (mean) values for the three collectors were used for the whole catchment. Sample analysis included titration ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ), select-ion electrode ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ -N) and atomic absorption spectrophotometry (for all cations).

### Methodology

Estimates of catchment chemical mass export (total chemical load) for each determinand were made using three formula described in turn here.

It is important to remember a basic assumption that applies to all the equations, which is that the vegetation of the region in question has to be in chemical equilibrium for the mass export rate estimates to be meaningful (Likens et al. 1967).

#### Method A- Simple load calculation

$$D_j = O_j = Q \bar{C}_{qj} \quad (1)$$

where:

- $D_j$  – chemical mass export rate for constituent  $j$  in tonnes  $\text{yr}^{-1}$
- $O_j$  – output or load of constituent  $j$  in tonnes  $\text{yr}^{-1}$
- $Q$  – annual basin discharge in  $\text{m}^3$
- $\bar{C}_{qj}$  – mean concentration of constituent  $j$  per unit  $Q$ , and it is assumed first that input to the catchment is negligible and second that  $\bar{C}_{qj}$  is representative of all discharge rates through the year that make up  $Q$ .

#### Method B – Simple input:output formula (Goudie 1970)

$$D_j = O_j - I_j \quad (2)$$

where:

- $D_j$  – chemical mass export rate for constituent  $j$  in tonnes  $\text{yr}^{-1}$
- $O_j$  – output or load of constituent  $j$  in tonnes  $\text{yr}^{-1}$

$$I_j = P \bar{C}_{pj} \quad (3)$$

and:

- $P$  – annual basin precipitation in  $\text{m}^3$

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$\bar{C}_{pj}$  = mean concentration of constituent  $j$  per unit  $P$ , and it is additionally assumed that  $\bar{C}_{pj}$  is representative of all the precipitation through the year that makes up  $P$ .

**Method C** – The general formula proposed here is:

$$D_j \equiv (O_{sj} + O_{bj}) = (I_{wj} + I_{dj}) \quad (4)$$

where:

- $D_j$  – chemical mass export rate for constituent  $j$  in tonnes  $\text{yr}^{-1}$
- $O_{sj}$  – output or load during stormflow in tonnes  $\text{yr}^{-1}$
- $O_{bj}$  – output or load during baseflow in tonnes  $\text{yr}^{-1}$
- $I_{wj}$  – input in the form of wet precipitation in tonnes  $\text{yr}^{-1}$
- $I_{dj}$  – input in the form of dry fallout in tonnes  $\text{yr}^{-1}$

and:

$$O_{sj} = \sum_{i=1}^n (\bar{C}_{ij}) (\bar{Q}_i T_i) \quad (5)$$

where:

- $\bar{C}_{ij}$  – mean concentration of constituent  $j$  for storm hydrograph  $i$  in tonnes  $\text{m}^{-3}$
- $\bar{Q}_i$  – mean discharge rate for storm hydrograph  $i$  in  $\text{m}^3 \text{sec}^{-1}$
- $T_i$  – duration of storm hydrograph  $i$  in seconds
- $n$  – number of storms in period (e.g. year)

and:

$$O_{bj} = \bar{C}_{bj} T_b \bar{Q}_b \quad (6)$$

where:

- $\bar{C}_{bj}$  – mean baseflow concentration of constituent  $j$  for the year in tonnes  $\text{m}^{-3}$
- $T_b$  – duration of baseflow conditions for the year in seconds
- $\bar{Q}_b$  – mean baseflow discharge in  $\text{m}^3 \text{sec}^{-1}$

and:

$$I_{wj} = \bar{C}_j R_v \quad (7)$$

where:

- $\bar{C}_j$  – mean wet precipitation concentration for constituent  $j$  in tonnes  $\text{m}^{-3}$
- $R_v$  – annual rainfall volume in  $\text{m}^3$

and:

$$I_{dj} = T F_j A \quad (8)$$

where:

- $T$  – duration of year when dry fallout occurred in seconds (approximately  $3 \times 10^7$ )  
 $F_j$  – dry fallout rate in tonnes  $\text{sec}^{-1} \text{m}^{-2}$   
 $A$  – catchment area in  $\text{m}^2$  ( $3.3 \times 10^7$ )

Because only bulk precipitation data were available Eq. (4) is amended to:

$$D_j = (O_{sj} + O_{bj}) - I_j \quad (9)$$

where it is assumed that

$$I_j = I_{wj} + I_{dj} \quad (10)$$

This assumption has been challenged (Skartveit 1981) although data have been published which show “Reasonable correspondence...” (Terstriep et al. 1982). Eq. (9) was tested as the new formula (method C) against Eq. (1) (method A) and Eq. (2) (method B).

It is clear that the main aim of using Eq. (9) is to ensure that different discharge rates and associated constituent concentrations are realistically represented. Although, with respect to chemical mass export, the importance of measuring wet and dry fallout separately cannot be tested, estimates of their relative importance can be obtained from Eqs. (7) and (8).

Most of the components of Eqs. (5) through (8) are self-explanatory. However, the derivation of  $\bar{C}_{ij}$  (Eq. (5)) and  $\bar{C}_j$  and  $F_j$  (Eqs. (7) and (8) respectively) require further explanation.

#### Mean Concentration of Constituent j for Storm Hydrograph i ( $C_{ij}$ )

Of the 29 storm hydrographs that occurred during 1979, only 8 were monitored closely enough to provide actual measured values for  $\bar{C}_{ij}$ . Values of  $\bar{C}_{ij}$  for unmonitored storms were estimated from known values by regressing  $\bar{C}_{ij}$  against average storm discharge  $Q_i$  (the mean value of the fifteen minute ordinates for the duration of the storm). However, with the small data set the results were not acceptable so the inferior method of simply employing a mean value was used. Thus, the values for  $\bar{C}_{ij}$  are not totally representative of the storm hydrograph concentrations that actually occurred. The monitored storms were generally slightly less than average intensity which suggests some degree of overestimation.

#### Mean Wet Precipitation Concentration ( $C_j$ ) and Dry Fall out Rate ( $F_j$ )

Because rainfall-only measurements for wet precipitation were not made,  $C_j$  cannot be directly determined. Dry fallout measurements were not made either but

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Table 1 - Dry fall-out analysis regression results

Constituent	<i>r</i>	<i>A</i>	<i>B</i>	<i>F<sub>j</sub></i>	<i>n</i>
Cl <sup>-</sup>	-0.179	6.56	negative	N/A	35
HCO <sub>3</sub> <sup>-</sup>	0.1688	13.98	1.86×10 <sup>-6</sup>	4.09×10 <sup>-14</sup>	34
SO <sub>4</sub> <sup>2-</sup>	-0.1467	6.27	negative	N/A	21
NO <sub>3</sub> <sup>-</sup> -N	0.5983**	1.61	6.02×10 <sup>-7</sup>	1.32×10 <sup>-14</sup>	30
Ca <sup>2+</sup>	0.5028**	1.49	1.09×10 <sup>-6</sup>	2.39×10 <sup>-14</sup>	38
Mg <sup>2+</sup>	0.0897	0.41	1.28×10 <sup>-8</sup>	2.82×10 <sup>-16</sup>	38
K <sup>+</sup>	0.0509	0.66	2.53×10 <sup>-8</sup>	5.56×10 <sup>-16</sup>	37
Na <sup>+</sup>	-0.2494	2.55	negative	N/A	37
Fe <sup>2+</sup>	0.3772**	0.07	2.46×10 <sup>-8</sup>	5.41×10 <sup>-16</sup>	37
Zn <sup>2+</sup>	0.1665	0.07	1.10×10 <sup>-8</sup>	2.41×10 <sup>-16</sup>	29

note: \*\* = significant at  $\alpha = 0.01$

$A$  in mg  
 $B$  in mg sec<sup>-1</sup> } i.e. corrected for volume of rainfall in collector

$F_j$  in tonnes sec<sup>-1</sup> m<sup>-2</sup> (corrected for collector orifice of 0.045 m<sup>2</sup>;  $F_j \equiv B \times 22 \times 10^{-9}$ )

estimates of the dry fallout rate,  $F_j$ , which allows subsequent calculation of  $I_{dj}$  (and therefore estimation of  $I_{wj}$  from Eq. (10), were made in the following manner.

Based upon the broad assumption that the longer a bulk precipitation collector is left in the field, the more dry fallout it will collect, concentrations of a constituent in samples were regressed against the time the collector was in the field (Table 1). This assumption is not very robust bearing in mind the likelihood of systematic variation in chemical composition with the length of dry spells preceding storms and the probable non-linear relationship between circulatory and noncirculatory dry fallout components over time. Nevertheless, the gradient of the regression line,  $B$ , is the first estimate for  $F_j$  in mg sec<sup>-1</sup>,  $F_j$  being expressed in tonnes sec<sup>-1</sup> m<sup>-2</sup>. Only Ca<sup>2+</sup>, Fe<sup>2+</sup> and NO<sub>3</sub><sup>-</sup>-N data resulted in statistically significant  $F_j$  values but in the absence of any other technique all  $F_j$  values that were positive were used to estimate  $I_{dj}$  and  $I_{wj}$ . Values for  $I_{dj}$  were not possible at all for Cl<sup>-</sup>, Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> which displayed slightly negative regression lines. These three constituents are generally very closely associated with wet precipitation only.  $F_j$  and  $I_{dj}$  were therefore assumed to be zero for these constituents.

Although not all of the results were statistically significant, the approach at least makes use of available data in an objective fashion which is considered by the author to be superior to making broad assumptions regarding wet and dry fallout rates (Henrickson and Wright 1977; Skartveit and Gjessing 1979). However, the problem of unknown amounts of circulatory input remains, and it is in no way suggested that generally reliable dry fallout data can be derived by simple regression analysis.

## Results

1) *Mass Input* – Table 2 gives the results of analysing the bulk precipitation data in terms of wet and dry fallout. Although the dry fallout ( $I_d$ ) data are crude estimates, and statistical confidence can only be expressed for  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{NO}_3^-$ -N values, a clear pattern emerges. Those ions primarily derived from the sea,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Na}^+$ , are not evident in dry fallout. Those ions derived primarily from the land surface,  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ , are evident dry fallout.

$\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$  and  $\text{Fe}^{2+}$  appear particularly important in dry fallout; these ions feature in the geochemical make up of the catchment which is dominated by Chalk and Bracklesham Bed ( $\text{Fe}^{2+}$  rich) outcrops.  $\text{NO}_3^-$ -N and  $\text{Zn}^{2+}$  are special cases, having no natural sources in the catchment but being closely associated with nitrogenous fertilizer application and an iron galvanizing metal works respectively – both situated in the catchment. These results indicate that the dry fallout proportion of chemical precipitation into the catchment is predominantly circulatory and should therefore be discounted in mass export or denudation calculations. This also suggests that bulk precipitation samplers overestimate inputs rather than underestimate as indicated by Feller and Kimmins (1984).

This does not solve the problem of how much of the bulk precipitation is circulatory however, because the proportions of wet precipitation which are circulatory and non-circulatory remain unknown. In the case of  $\text{Zn}^{2+}$  for example, it is very likely that the vast majority for the wet precipitation is circulatory given the existence of the galvanizing works. Similarly, a good proportion of the  $\text{NO}_3^-$ -N wet precipitation may be derived from farmland and washed out during storms. In addition, nitrogen may enter the catchment as  $\text{NH}_4^+$  and leave as  $\text{NO}_3^-$ -N (Martin 1979) which places doubt upon the significance of  $\text{NO}_3^-$ -N input values.

Short of guess work, a best estimate of effective chemical precipitation input ( $I_x$  – Table 2) can be made taking these considerations into account. These estimates are used to produce adjusted chemical mass export rates according to Eq. (11) (this is called method C').

$$D_j = (O_{sj} + O_{bj}) = I_{xj} \quad (11)$$

2) *Mass output* – Table 3 presents the raw mass output data for both the rural and urban catchments. There are two major points to be made from this table.

First, it is clear that although stormflow periods are associated with chemical dilution, the increased discharges mean that a significant proportion of mass output occurs during storms. This result is in direct contrast to data presented by Cleaves et al. (1970-pp. 3025) for eastern United States which indicated that only 10% of the dissolved load was associated with storms. It is also clear that stormflows are comparatively more important in terms of mass output in rural areas than in urban areas.

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Table 2 – Wet and dry fallout Input data for Monks' Brook for 1979

	Bulk ( $I$ )		Dry ( $I_d$ )		Wet ( $I_w$ )		% Dry	Best Estimate $I_x$	
	Urban	Rural	Urban	Rural	Urban	Rural		Whole	
							Catchment	Urban	Rural
Cl <sup>-</sup>	129	46	0	0	129	46	0	129	46
HCO <sub>3</sub> <sup>-</sup>	454	162	40.5	14.5	413.5	147.5	9	413	147
SO <sub>4</sub> <sup>2-</sup>	101	36	0	0	101	36	0	101	36
NO <sub>3</sub> -N	76.0	27	13.1	4.7	62.9	22.3	17	63	22
Ca <sup>2+</sup>	88.0	31	23.7	8.5	64.3	22.5	27	64	22
Mg <sup>2+</sup>	11.5	4.1	0.3	0.1	11.2	4.0	3	11.2	4.1
K <sup>+</sup>	18.9	6.7	0.5	0.2	18.4	6.5	3	18.4	6.5
Na <sup>+</sup>	58.0	20.7	0	0	58	20.7	0	58	20.7
Fe <sup>2+</sup>	3.0	1.0	0.5	0.2	2.5	0.8	16	2.5	0.8
Zn <sup>2+</sup>	2.2	0.8	0.2	0.1	2.0	0.8	3	0	0

all values in tonnes yr<sup>-1</sup> except where indicated

Bulk =  $I$  (used in both Eq. (2) Method B and Eq. (9) Method C)

Dry =  $I_{dj}$  (Eq. (8))

Wet =  $I_{wj} = I_j - I_{dj}$  (Eq. (10))

$I_x$  = used in Eq. (11) method C: see text

Table 3 – Stormflow and baseflow Output data for the Monks' Brook, 1979

Constituent	Aggregate <sup>1</sup>		Total <sup>2</sup>		Baseflow <sup>3</sup>		Stormflow <sup>3</sup>		Stormflow %	
	Urban	Rural	Urban	Rural	Urban	Rural	Urban	Rural	Urban	Rural
Cl <sup>-</sup>	319	49	396	50.4	168	18.0	228	32.4	58	64
HCO <sub>3</sub> <sup>-</sup>	980	218	1181	214.9	471	65.3	710	149.6	60	70
SO <sub>4</sub> <sup>2-</sup>	383	73	465	74.8	195	26.3	270	48.5	58	65
NO <sub>3</sub> -N	134	36	147	34.87	46	9.87	101	25.0	69	72
Ca <sup>2+</sup>	341	68.4	424	68.0	182	21.57	242	46.4	57	68
Mg <sup>2+</sup>	46.9	11.9	65.9	12.6	34.0	4.79	31.9	7.79	48	62
K <sup>+</sup>	34.3	7.3	40.3	6.95	15.3	1.76	25.2	5.19	62	75
Na <sup>+</sup>	129.3	21.3	162	21.8	70	7.71	92.2	14.4	57	64
Fe <sup>2+</sup>	19.8	5.6	18.7	4.87	2.93	0.50	15.78	4.37	84	90
Zn <sup>2+</sup>	1.05	0.09	0.91	0.076	0.06	0.006	0.85	0.07	93	92

Values in tonnes yr<sup>-1</sup> except where indicated

1 – Using yearly mean discharge and concentration data; Eq. (2) Method B

2 – Used in Eq. (9) Method C

3 – See general formula (Eq. (4))

Second, it is apparent that the use of a broad aggregate average (Table 3) leads to underestimation of mass output in urban areas but not in rural areas. (Aggregate in this sense means all data for the year, i.e. not separated by flow rate.) This is because of the wide ranges in concentration that occur in urban areas due to extensive dilution – a direct result of a high runoff-rainfall ratio. This is perhaps most apparent for  $K^+$  which, in contrast to all other cations, is known to exhibit a generally positive relationship to stream discharge (Walling and Foster 1975).

When the stormflow dilution effect is low,  $K^+$  concentrations increase and the aggregate average concentration for  $K^+$  will be higher than the average baseflow concentration leading to a larger aggregate mass output estimate (Table 3). Conversely, when stormflow dilution is excessive, such as from an urban area, even  $K^+$  values may be reduced during storms (Prowse 1981) leading to a lower estimate using aggregate data (Table 3).

Ions which displayed significant and recurrent stormflow flushes,  $Fe^{2+}$  and  $Zn^{2+}$ , for both the rural and urban catchment have higher aggregate estimates (Table 3). All other ions displayed stormflow dilution; where the dilution is minimal (rural areas) aggregate estimates are close to  $O_t$  estimates; where dilution is excessive (urban areas), aggregate estimates are considerably lower than  $O_t$  estimates (Table 3).

3) *Chemical Mass Export Estimates* – Tables 4a and 4b show estimates of catchment chemical mass export, or total chemical load rates using the four different methods described above (Eqs. (1), (2), (9) and (11); respectively methods A, B, C and C'). The term catchment chemical mass export is used because chemical denudation connotes natural processes and part of the results are for an urbanized catchment. This paper concerns only the measurement of mass export and not the identification of strictly denudational and non-denudation components of the mass export. Table 4a refers to the rural subcatchment of the Monks' Brook and Table 4b to the whole catchment as affected by urban areas (Fig. 1).

For the rural subcatchment it is clear that method A (Table 4a) is totally inappropriate because it ignores precipitation inputs. The more important precipitation input is to the mass-balance of a constituent, the more in error the method becomes as witnessed by the high  $\Delta 1$  and  $\Delta 2$  values for  $Cl^-$  and  $Na^+$  which are almost entirely derived from the atmosphere in the rural subcatchment. Also, note that method A performs best for constituents primarily derived from rocks within the basin such as  $Fe^{2+}$  (Tables 4a and 4b).

By contrast, method A has a much improved performance for the urban catchment (Table 4b) where it overestimates by between 60% and 25% on chemical load estimates from methods B and C respectively. This is simply because urban areas export considerably more dissolved material per unit input (precipitation from the atmosphere). Nevertheless, method A intuitively should lead to overestimation

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**Table 4a – Comparison of Catchment Chemical Mass Export Estimations – Rural Catchment for 1979**

row	constituent	Chemical Mass Export Estimate $D_i$				Ratio Difference in $D_i$ ( $\Delta D_i$ )			
		A	B	C	C'	$\Delta 1$ A:B	$\Delta 2$ A:C	$\Delta 3$ B:C	$\Delta 4$ C:C'
1	Cl <sup>-</sup>	4.15	0.25	0.37	0.37	16.6	11.2	0.67	1.00
2	HCO <sub>3</sub> <sup>-</sup>	18.48	4.75	4.48	5.76	3.9	4.1	1.06	0.77
3	SO <sub>4</sub> <sup>2-</sup>	6.12	3.14	3.29	3.29	1.9	1.9	0.95	1.00
4	NO <sub>3</sub> <sup>-</sup> -N	3.05	0.76	0.67	1.09	4.0	4.6	1.13	0.61
5	Ca <sup>2+</sup>	5.80	3.17	3.14	3.89	1.8	1.8	1.01	0.80
6	Mg <sup>2+</sup>	1.01	0.66	0.72	0.72	1.5	1.4	0.92	1.00
7	K <sup>+</sup>	0.62	0.05	0.02	0.04	12.4	31.0	2.52	0.5
8	Na <sup>+</sup>	1.80	0.05	0.09	0.09	36.0	20.0	0.56	1.00
9	Fe <sup>2+</sup>	0.47	0.39	0.33	0.35	1.2	1.4	1.18	1.00
10	Zn <sup>2+</sup>	0.007	+0.06	+0.06	0.007	$\alpha$	$\alpha$	1.00	$\alpha$
11	$\Sigma$ I-10	41.59	13.10	12.97	15.61	3.2	3.2	1.01	0.83
12	TDS	41.79	12.81	12.63	-	3.3	3.3	1.02	-
13	Average % discrepancy in estimates				=	680%	663%	25.5%	14.9%

**Table 4b – Comparison of Catchment Chemical Mass Export Estimations – Urban Catchment for 1979**

row	constituent	Chemical Mass Export Estimate $D_i$				Ratio Difference in $D_i$ ( $\Delta D_i$ )			
		A	B	C	C'	$\Delta 1$ A:B	$\Delta 2$ A:C	$\Delta 3$ B:C	$\Delta 4$ C:C'
1	Cl <sup>-</sup>	9.66	5.75	8.16	8.16	1.7	1.2	0.70	1.0
2	HCO <sub>3</sub> <sup>-</sup>	29.67	15.92	22.01	23.25	1.9	1.3	0.72	0.95
3	SO <sub>4</sub> <sup>2-</sup>	11.59	8.54	11.02	11.02	1.4	1.1	0.78	1.0
4	NO <sub>3</sub> <sup>-</sup> -N	4.06	1.76	2.15	2.54	2.3	1.9	0.82	0.85
5	Ca <sup>2+</sup>	10.32	7.66	10.17	10.89	1.3	1.0	0.75	0.93
6	Mg <sup>2+</sup>	1.42	1.07	1.65	1.66	1.3	0.8	0.65	0.99
7	K <sup>+</sup>	1.04	0.47	0.65	0.66	2.2	1.6	0.72	0.99
8	Na <sup>+</sup>	3.91	2.16	3.15	3.15	1.8	1.2	0.69	1.0
9	Fe <sup>2+</sup>	0.59	0.51	0.47	0.49	1.2	1.3	1.08	0.96
10	Zn <sup>2+</sup>	0.03	+0.04	+0.04	0.03	$\alpha$	$\alpha$	1.00	$\alpha$
11	$\Sigma$ I-10	72.36	44.08	59.35	61.82	1.6	1.2	0.74	0.96
12	TDS	76.51	47.50	61.48	-	1.6	1.2	0.77	-
13	Average % discrepancy in estimates				=	66%	29%	24%	3.7%

notes: A = Method A; simple output data only (Eq. (1))  $D_i$  values in tonnes km<sup>-2</sup>

B = Method B; simple input:output data (Eq. (2))

C = Method C; Eq. (9) C' = Eq. (11)

Conversions: tonnes km<sup>-2</sup> × 0.4254 = tons mile<sup>-2</sup>

tonnes km<sup>-2</sup> × 10.0 = kg ha<sup>-1</sup>

tonnes km<sup>-2</sup> × 0.735 = m<sup>3</sup> km<sup>-2</sup> (assuming a bulk density of 1.36 g cm<sup>-3</sup>)

tonnes km<sup>-2</sup> × 0.735 = Bubnoff units

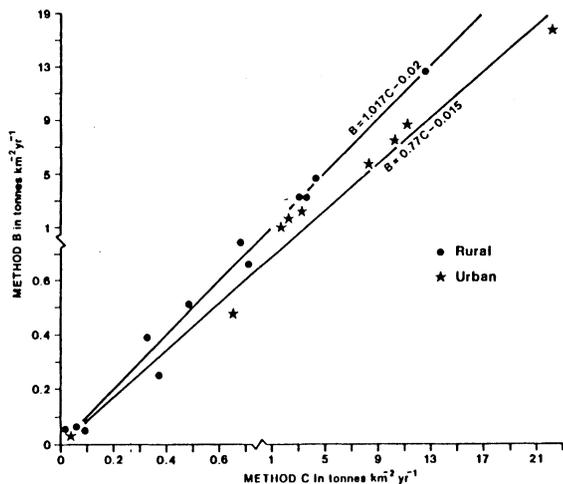


Fig. 2.  
Comparing mass export estimations  
by different methods and upon ur-  
banisation.

and the results of this analysis indicate that the levels of the overestimation would be generally unacceptable.

Method B, which utilizes bulk precipitation data and aggregated discharge data, produces very similar estimates for  $D_j$  for the rural catchment to those from method C, which uses bulk precipitation data and discharge data separated into stormflow and baseflow components (Table 4a). The average percentage discrepancy of 25.5% is not a true reflection of the similarity of the estimates. More indicative is the  $\Delta 3$  value of 1.01 for  $\Sigma$  and 1.02 for TDS. The  $\Delta 3$  outliers for  $\text{Cl}^-$  and  $\text{Na}^+$  (0.67 and 0.56) indicate that these ions are extraordinarily significant during stormflows and are therefore underrepresented by method B. This is most probably because of road salt wash-off which affected part of the rural subcatchment during the winter months. Road salt wash-off is most noticeable during storms.

The degree of agreement between the two methods for the rural subcatchment is best illustrated in Fig. 2. In terms of total chemical mass export method B provides estimates within 2% of those for method C for the rural catchment although, assuming method C to be inherently more accurate, less confidence may be expressed in estimates by method B for a individual ions.

$\Delta 3$  values greater than 1 indicate ions which are not significant during storm flows, i.e. they are generally diluted to a degree that the increased discharge rate cannot compensate for. Chemical loads for such ions are thus overestimated by method B. Conversely  $\Delta 3$  values less than one indicate that stormflow dilution is minimal (there may even be increases in concentration) and loads are increased by the greater discharges. Chemical loads for such ions are thus underestimated by method B. All but one of the  $\Delta 3$  values for the urban catchment are less than 1.0 indicating very clearly the importance of the increased runoff-rainfall ratio and stormflow magnitudes associated with urban runoff. Thus, for the urban catchment not only are the estimates for individual ions from method B significantly in error

but the general relationship between B and C values is substantially different from the line of equivalence (Fig. 2). The overestimation of  $\text{Fe}^{2+}$  by method B is a direct result of the effect of rare high concentration levels (chemograph flushes) which disproportionately affect the aggregate mean concentration level used in method B. Such rare high concentrations are restricted to stormflow occurrences in method C.

In an effort to account for circulatory precipitation "input" the values from method C were adjusted using  $I_x$  data from Table 2, and Eq. (11). The results (C') are slightly different to C for ions which are partly deposited as dry fallout assuming that dry fallout is predominantly circulatory. The more important dry fallout becomes the greater the difference in estimates. The majority of these discrepancies lie within 10%, most within 4% which is probably well within the precision limits of the methods.

However, for the rural subcatchment, where precipitation inputs are comparatively more important, chemical mass export estimates for ions such as  $\text{NO}_3^-$ -N may be up to 40% higher than those made by method C. If the  $I_x$  values are assumed to be more representative than  $I$  (i.e. C' is our best estimate), then it is somewhat ironic that estimates using the simpler method B may be more realistic than those from the more complex method C for certain ions that enter significantly as dry fall-out (Table 4a). However, this "success" of method B is fortuitous and it remains intuitively less realistic and reliable than method C. The degree to which method C underestimates actual mass export is controlled primarily by the relative importance of circulatory and non-circulatory components of mass input to a catchment, and partly controlled by the relative importance of input and output which is a function of the runoff-rainfall ratio.

## **Conclusion**

Three main conclusions can be drawn from this study. First, mass input:output calculation methods which retain as much information as possible from sub-optimal data sets are intuitively more accurate and suitable for mass input:output studies (Table 5). Certainly by ignoring precipitation inputs to a catchment method A is universally unacceptable. By the same token, by ignoring changes in stream chemistry related to stream discharge, method B is acceptable only where runoff-rainfall ratios are small, and even then not for individual ions. Method C attempts to account for chemical differences in baseflow and stormflow and appears to be applicable to all situations without undue error.

There is some evidence to show that if circulatory dry fallout is significant, as it may be in continental areas (Swank and Henderson 1976), estimates of chemical loads for specific ions may be unreliable using method C. This conclusion is tentative because there appears to be no generally acceptable way to estimate wet and dry fallout ratios from simple bulk precipitation data (question 1 on page 222).

Table 5 – Suitability of methods given certain conditions

Condition	A	B	C	C'
low runoff-rainfall ratio (e.g. rural)	x	✓	✓	✓
high runoff-rainfall ratio (e.g. urban)	x	x	✓	✓
high dry fall-out ratio	–	–	?	✓

Further research into the relationships between bulk, wet and dry precipitation are required and such analyses as discussed here require considerably more testing.

Second, the results highlight the importance of urban areas in terms of solute loads regardless of source, and reinforce the need to consider the impact on chemical mass export rate estimates of high runoff-rainfall ratios. However, it must be remembered that mass output from urban areas does not represent natural chemical denudation (Meade 1969) and a significant proportion of urban solute streamloads may be anthropogenic (e.g.  $\text{Na}^+$  and  $\text{Cl}^-$  from road salt) or the result of man-induced accelerated chemical denudation (Janda 1971).

Third, and perhaps most important, it appears that meaningful and accurate estimates of chemical mass export and denudation rates will only be feasible when estimates of the proportion of chemical precipitation which is circulatory can be made. Until then it can only be assumed, based upon intuition more than fact, that more sophisticated methods such as C are actually more accurate than methods such as B.

It has been demonstrated that measurable 'error' in C estimates could result if the circulatory proportion is even as low as 10%. Furthermore, with respect to urban areas, there is no indication of how much of the output is truly denudational given the probable importation of materials such as mineral fertilizers (Meade 1969) into the catchment, i.e. anthropogenic sources. Nevertheless, Method C does appear to provide more reliable mass input:output estimations and until circulatory information is available, it seems reasonable to make the most of those data that are available and use methods similar to that proposed here (Method C) for more accurate and reliable chemical mass export estimates and generally more informative mass input:output analyses (question 2, page 222).

### Acknowledgements

This study was substantially completed whilst the author was in receipt of a grant from the Natural Environment Research Council of the United Kingdom. I am indebted to Dr. G.M. Aubertin, Tinka Hyde, Judy Haschenburger and an anonymous reviewer for constructive criticism of earlier drafts.

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First received: 2 January, 1985

Revised version received: 14 June, 1985

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