

The geochemistry of the Rhine and the Rhone. 5, Synthesis and conclusions

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Keywords : Rivers, geochemistry, acidification, mineral composition.

Every month 2 samples of the Rhine and 1 sample of the Rhone are analysed for about 20 chemical and physical variables at 7 stations by two monitoring agencies.

This paper presents some of our conclusions on the accuracy of these programmes and on the solubility of the calcium/carbonate/sulphate/phosphate system. In total we have analysed 916 data sets ; they were screened for imprecision before being used.

At all stations the water is saturated with CaCO_3 , but the « apparent » solubility product depends on the pH. The regression line can be described by $\text{IP}_{\text{Ca}} = 8.73 \times 10^{-15}$, pH^{15.667}.

In both the Rhine and the Rhone an acidification is seen and an increase of the sulphate concentration when going downstream. We have shown that the increase in sulphate concentration is due to the disposal of CaSO_4 . This addition of sulphate influences the quotient Ca/HCO_3 . The data fit very well the theoretical regression line $\text{Ca}/\text{HCO}_3 = 0.5(\text{SO}_4) + 0.5$.

The acidification originates from the mineralization of organic matter. For 6 stations downstream from the great lakes we found that the two rivers are saturated with hydroxy-apatite, the -log of the ionic product being 49.9 (Rhine ; $\sigma = 0.6$; $N = 259$) and 50.0 (Rhône ; $\sigma = 0.3$; $N = 479$). The o-phosphate concentration does not therefore depend on the phosphate loading of the rivers, but on the Ca concentration, the temperature and the pH. This has great influence on the transport of phosphate through the delta's of the two rivers. The disturbance of acidity and buffering capacity influences heavy metal behaviour as well.

Geochimie du Rhin et du Rhône. 5. Synthèse et conclusions

Mots clés : Fleuves, géochimie, acidification, équilibre minéral.

Une vingtaine de variables physiques et chimiques sont mesurées chaque mois par deux organismes de surveillance sur des échantillons d'eau prélevés dans 7 stations sur le Rhin et le Rhône.

Cet article présente quelques conclusions sur le degré de précision de ce programme de mesures et sur la solubilité du système Calcium/Carbonate/Sulfate/Phosphate. Un total de 916 séries de données a été analysé dont nous avons, au préalable, testé le niveau de précision.

Dans toutes les stations, l'eau est saturée en CaCO_3 mais le produit de solubilité « apparent » dépend du pH. La droite de régression s'écrit : $\text{IP}_{\text{Ca}} = 8.73 \times 10^{-15}$, pH^{15.667}.

Une acidification et une augmentation de la concentration en sulfates apparaît de l'amont vers l'aval à la fois dans le Rhin et dans le Rhône. Nous avons montré que l'augmentation des concentrations de sulfates est due à la destruction du CaSO_4 et qu'elle agit sur le rapport Ca/HCO_3 . Les données s'ajustent bien à la droite de régression théorique $\text{Ca}/\text{HCO}_3 = 0.5(\text{SO}_4) + 0.5$.

L'acidification provient de la minéralisation de la matière organique. Dans les deux rivières, les six stations à l'aval des grands lacs sont saturées en hydroxy-apatite, le log du produit ionique étant de 49,9 (Rhin ; $\sigma = 0.6$; $N = 259$) et 50 (Rhône ; $\sigma = 0.3$; $N = 479$). Par suite, la concentration en o. phosphate ne dépend pas de la charge de ces rivières mais des concentrations en Ca, de la température et du pH.

Ceci a une forte influence sur le transport de phosphates vers les deltas. La modification de l'acidité et du pouvoir tampon agit également sur le comportement des métaux lourds.

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Introduction

The chemical composition of the river Rhine is monitored by fortnightly samples from seven stations and that of the river Rhone by monthly samples from seven stations; for the Rhine full ionic balances are measured eight times a year. About 25 chemical and physical variables are measured and the results are published in the Commission Internationale pour la Protection du Rhin contre la Pollution and, for the Rhone, in the Annuaire de la Qualité des Eaux.

Quantitative conclusions are rarely drawn from the published data except general statements about increasing or decreasing pollution. Interactions between different variables are almost never studied.

In four articles we analysed some of these published data in more detail i.e. the data for flow rate; pH; concentrations of Ca, Mg, K, Na, Cl, SO₄, HCO₃, o-PO₄, Tot-P, O₂; temperature and electrical conductivity.

In this article I combine the conclusions of these four articles, compare them with the literature and describe possible consequences for water chemistry and management in the two deltas.

1. — Methods

Data on 15 physical and chemical variables in the Rhine were obtained from the Commission Internationale pour la Protection du Rhin contre la Pollution (1971-1979) and in the Rhone from l'Annuaire de la Qualité des Eaux (1975-1981). They are stored in our data bank RRque. On each river 7 stations were chosen, one above the Lake of Constance (Rhine) and one above the Lake of Geneva (Rhone), and 6 at increasing distances from these lakes towards the river mouths.

When regressions are calculated between two variables two procedures can be followed. Firstly all data for each river are grouped per year, and variations with time are studied. Secondly all data for a particular station are grouped and the variations between stations are studied. The first value (« river means ») is useful for comparison with other (whole) river data, the second (« station means ») may provide more information on the processes occurring, especially if conditions per station differ.

I use the following abbreviations: IP_{ca} for the ionic product of CaCO₃ and IP_{ap} for that of hydroxyapatite, i.e. [Ca²⁺]⁵[PO₄³⁻]³[OH].

2. — Hydrology

Both rivers have their origins on The Dammastock (Switzerland, at 3630m). The Rhone originates from the Rhone glacier, the Rhine starts as a confluence of small rivulets. They descend steeply and enter respectively the Lake of Geneva (Rhone) at 380 m and the Lake of Constance (Rhine) at 400 m; their flow rates are then 190 and 250 m³ sec⁻¹ respectively (see table 1). On leaving the lakes the rate is increased to 380 and 340 m³ sec⁻¹. The rivers rapidly lose more height (see figure 1) without much further increase in flow rate. The largest increases occur below 200 m for the Rhone and below 300 m for the Rhine. Flow rate at the river mouth is 1750 and 1400 m³ sec⁻¹ respectively.

3. — Results

In total we have used 916 data sets.

We have no absolute way of detecting the precision numerically. In the first place we have calculated the proportional imbalance (%) if the ionic balance was complete (in a few cases we ignored missing values for sulphate and nitrate):

$$\text{Proportional imbalance} = \frac{\text{sum cations} - \text{sum anions}}{(\text{sum cations} + \text{sum anions})/2} \times 100$$

We have shown on statistical arguments that data sets should be rejected if the imbalance is >4 % for the Rhine and >6 % for the Rhone. We also used a second screening procedure, which removed those data sets in which the IP_{ca} and the IP_{ap} are larger or smaller than the mean values plus or minus 3σ. In only 20 data sets, out of 916, did we find suspiciously high values for both IP_{ca} and IP_{ap}. We have thus concluded, that there is no reason to believe that calcium values are wrong even though the ionic imbalance was high. As high and low values occurred in about equal frequency this screening yielded no difference with the calculations made with the unscreened data.

In the article I apply a further test of the reliability of the data by calculating conductivity from the

Table 1. Water flow rate ($\text{m}^3 \text{sec}^{-1}$) at 7 stations in the Rhine (1971-1979) and at 7 stations in the Rhone (1975-1981).

	mean	range		mean	range
Schmitter	250	(240-260)	Port-du-Scex	190	(130-220)
Stein am Rhein	340	(250-390)	Collonges	380	(270-500)
Kembs	1000	(750-1150)	Bourget	450	(300-530)
Seltz	1150	(850-1300)	Villeurbanne	670	(480-780)
Koblenz/Br	1500	(850-1350)	Chasse	1100	(750-1400)
Bimmen/Lo	1900	(1300-2500)	St Vallier	1100	(800-1400)
Gorinchem	1400	(1000-1800)	Tarascon	1750	(1400-2300)

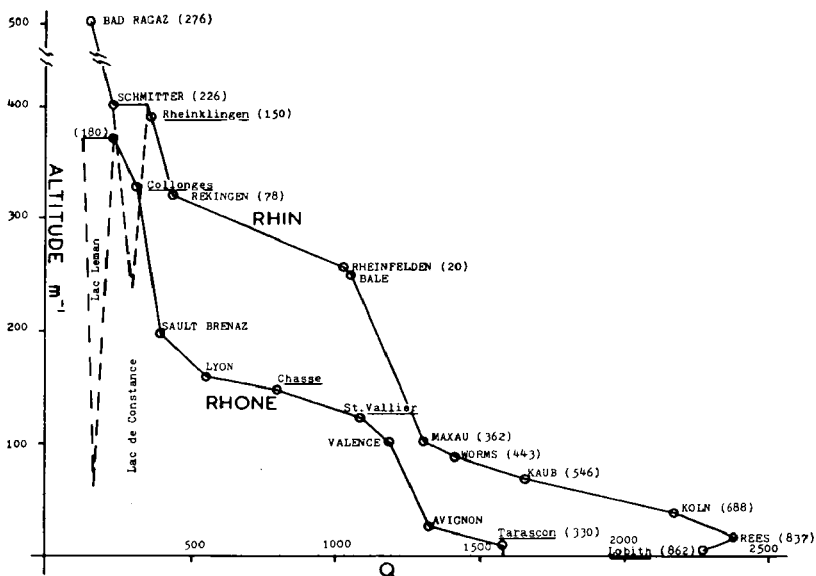


Fig. 1. Relation between flow rate ($\text{m}^3 \text{sec}^{-1}$) and altitude above sea level for the Rhine and the Rhone. Distances (km) from Basel (Rhine) or Lyon (Rhone) in parentheses.

Table 2. — Total number of cases for each of the stations in the Rhine and the Rhone for which conductivity data and ionic balances are available. The number of cases where the calculated conductivity is larger or smaller than 7 % or 8 % of the measured conductivity is given, while finally also is indicated whether the imbalance in the ionic composition is larger or smaller than 6 % or 7 %.

The mean errors in the ionic balance are indicated between parentheses.

COND : calc/meas. % (ION. BAL.)	OK		>1.07		<0.93		TOT	OK		> 1.08		<0.92	
	<6	>6	>6	<6	>6	<6		<7	>7	>7	<7	>7	<7
SCHMITTER	32	1	0	0	0	3	36	34	0	0	0	0	2
	(7)	-	-	-	-	(3%)		-	-	-	-	-	(4%)
STEIN	21	12	3	4	10	4	54	24	12	3	4	9	2
	(21)	(26)	(13)	(23)	(5)	(22)	(26)	(11)	(24)	(2)	(24)	(2)	
KEMBS	21	10	2	4	11	6	54	26	10	2	4	9	3
	(17)	(10)	(2%)	(21)	(3)	(2)	(18)	(11)	(2)	(24)	(4)		
SELTZ	13	1	0	15	0	24	53	18	0	0	14	0	21
	(6%)	-	(2)	-	(2)	(2)	-	-	(2)	-	(2)		
KOBLENZ	17	0	0	10	1	43	71	23	0	0	10	1	37
	-	-	(1)	(19)	(2)	(2)	-	-	(2)	(19)	(2)		
BIMMEN	30	1	0	4	1	36	72	35	1	0	4	1	31
	(8)	-	(3)	(7)	(1%)	(1%)	(8)	-	(3)	(7)	(1%)		
GORINCHEM	18	4	3	6	15	24	70	21	7	3	6	10	23
	(9)	(8)	(4)	(17)	(2)	(2)	(9)	(4)	(9%)	(24)	(2)		
PORT-DU-SCEX	36	11	10	11	8	8	84	43	13	8	8	7	5
	(10)	(13)	(2)	(17)	(3)	(3)	(10)	(14)	(2)	(19)	(3)		
COLLONGES	38	7	0	1	10	16	72	55	6	0	1	3	7
	(7)	-	(5)	(8)	(3)	(8)	(8)	-	(4)	(9%)	(2%)		
BOURGET	40	7	0	1	4	20	72	55	8	0	1	2	6
	(12)	-	(1)	(8)	(3)	(3)	(11)	-	(1)	(8)	(3)		
VILLEURBANNE	32	10	0	0	5	25	72	49	6	0	0	4	13
	(9)	-	-	(8)	(2)	(2)	(11)	-	-	(8)	(2)		
CHASSE	38	1	1	0	2	30	72	52	3	0	0	0	17
	(8)	(19)	-	(8)	(3)	(3)	(12)	-	-	-	-	(3)	
ST. VALLIER	25	5	1	0	10	31	72	41	7	0	0	5	19
	(9)	(14)	-	(8)	(2)	(2)	(11)	-	-	(9)	(3)		
TARASCON	22	3	0	0	15	30	70	28	5	0	0	9	28
	(9)	-	-	(9)	(3)	(3)	-	(5)	-	(10)	(3%)		
	383	73	20	56	92	300	924	504	78	16	52	60	214

measured concentrations of the major ions and comparing the so-called « calculated conductivity » with the measured one. Table 2 gives the number of cases in which the calculated conductivity is more than 7 % and secondly more than 8 % different from the measured one. It also indicates whether the ionic imbalance is larger or smaller than 6 % and secondly more than 7 %. The table shows that it makes little difference whether 7 % & 6 % or 8 % & 7 % is taken as criterion for satisfaction. With the « hard » criteria few more cases are placed in a non-satisfactory group than with the « soft » criteria. E.g. the table shows that at Schmitter 32 cases fall

in the satisfactory group if the « hard » criteria are taken and 34 if the « soft » criteria are taken. In several stations, however, fewer than half the cases fall in this group; it makes again little difference whether « hard » or « soft » criteria are taken for satisfaction. The second largest group is the group where the ionic composition is balanced, but the calculated conductivity is too small. As the conductivity measurement is in principle relatively simple, this suggests important errors in the ionic balance, e.g. replacement of a divalent ion by another one. We have no further ways of testing these results but suggest that the methodology is carefully reexamined.

Table 3a. — Coefficients of the regression line between ionic strength factor [$F = \sqrt{IS}/(1 + \sqrt{IS})$] and conductivity (Co) : $F = A + B \times Co$ in 7 stations in the Rhine. Regression coefficients and standard error of the estimate are shown. The last column gives the total number of cases. For all stations except Schmitter a second line shows the results when points have been rejected because they were larger than the mean on the x-axis plus 2 times the standard deviation. In the case of Stein (and of Tarascon in Table 3b) two further subsets are shown. These are :
 2) after rejecting with 2.5 times the standard deviation on the y-axis
 3) after removing cases with error larger than 6 % in the ionic balance.

	A	B X 10 ⁻⁴	r ²	Std. Error X 10 ⁻³	N
Schmitter	0.03	1.3	.92	1.4	36
Stein	0.05	0.46	.15	2.9	54
	0.05	0.68	.23	2.7	53
2)	0.05	0.62	.23	2.5	52
3)	0.05	0.65	.42	1.8	29
Kembs	0.05	0.56	.49	2.7	54
	0.05	0.76	.61	2.4	53
Seltz	0.06	0.44	.74	5.4	53
	0.06	0.45	.72	5.4	52
Koblentz	0.06	0.40	.69	4.6	71
	0.06	0.48	.76	4.1	70
Bimmen	0.07	0.36	.56	6.3	72
	0.07	0.35	.46	6.4	68
Gorinchem	0.07	0.38	.66	5.5	70
	0.06	0.42	.71	4.9	67

For the calculations of the solubility products of $CaCO_3$ and $Ca_5(PO_4)_3OH$ the ionic activity coefficients are needed. This calculation has not often been done before, partly because activity coefficients in dilute solutions, which it has been assumed that fresh waters are, are near 0, and because they cannot be calculated unless the concentration of the major ions has been measured. Golterman & Meyer (1985 b) have shown that the first assumption is not true ; they found activity coefficients between 0.61 and 0.75 in the two typical hard waters of the Rhine and the Rhone. The second restriction, though very often true, is fortunately not true for the Rhine and the Rhone data. We have therefore tried to calculate the ionic strength « IS » from the conductivity. In the calculation of the ion activity coefficients not « IS » but the factor $\sqrt{IS}/(1 + \sqrt{IS})$ is applied, so we calculated the relation between this factor and the (measured) conductivity. Table 3 gives the linear regression lines and the standard errors of the estimate. In some stations the relation is close, in others it is less so. This was partly due to the fact that often a single, far outlying point occurred. After rejection of these points (rejecting all points further away than 3 σ from the mean on the x-axis), sometimes

the correlation improved much (Collonges, Bourget, Villeurbanne). In the stations Stein am Rhein and Tarascon a large variance remained ; this is probably due to the variation in the chemical composition at these stations and to imprecise measurements. The regressions here did not become much better after rejecting the points further away than 2.5 times the standard deviation from the mean on the y-axis as well. In Stein am Rhein some improvement was found after rejecting the points with an imbalance larger than 6 % in the ionic balance.

It is clear from table 3 that when the coefficient of correlation is high, the slope approaches 0.81 - 1.1 (Rhone) and 0.5 - 0.6 (Rhine) ; Schmitter shows a value nearer to the Rhone value ; the difference between the Rhine and the Rhone values reflects the higher sodium chloride concentration in the Rhine.

4. — Variations in time and space

In the stations above the lakes (Schmitter and Port-du-Scex) the calcium concentration varies in a distinct seasonal pattern between 1.5 and 2.5 mmol l⁻¹. If the $Ca/HCO_3/CO_3$ system is in equilibrium

Table 3b. — Idem for 7 stations of the Rhone.

	A	B X 10 ⁻⁴	r ²	Std.Error X 10 ⁻³	N
Port-du-Scex	0.04	1.2	.81	2.6	84
	0.04	1.2	.81	2.5	83
Collonges	0.05	0.63	.36	2.5	72
	0.04	1.1	.79	1.5	71
Bourget	0.06	0.38	.31	2.7	72
	0.04	1.0	.85	1.3	70
Villeurbanne	0.06	0.33	.27	2.7	72
	0.04	0.96	.83	1.3	71
Chasse	0.05	0.72	.85	1.4	72
	0.05	0.76	.79	1.4	69
St Vallier	0.05	0.77	.88	1.5	72
	0.05	0.81	.83	1.5	68
Tarascon	0.07	0.10	.10	4.2	70
	0.06	0.35	.27	3.8	69
	2) 0.06	0.33	.26	3.6	68
	3) 0.06	0.38	.31	3.8	57

with the partial CO₂ pressure in the air, these changes can for the larger part be explained by the influence of the temperature on this system, with the sulphate concentration as a second influence. The temperature has an influence on the K_w, the K₁, the K₂ and the solubility of CO₂, as in saturated solutions.

$$Ca = K_s \cdot (H^+)^2 / CO_2 \cdot K_1 \cdot K_2,$$

in which K_s = solubility product of CaCO₃; K₁ and K₂ the dissociation constants of H₂CO₃; CO₂ = concentration of carbon dioxide in equilibrium with the gas phase. CO₂, K₁ and K₂ are temperature dependent; the dependence is given in annex I. Table 4 gives the results of the calculations made with sulphate, CO₂ pressure and temperature as independent variables. The results show that the solubility increases by 40 % when the temperature decreases from 20° C to 0° C, and that sulphate concentration increases the calcium solubility without changing the temperature effect.

K_s is theoretically 0.45 × 10⁻⁸ at 0° C and 0.41 × 10⁻⁸ at 20° C (Stumm and Morgan, 1981). At Schmitter we have found 0.6 × 10⁻⁸ (range 0.3 - 0.9) and at Port-du-Scex 0.3 × 10⁻⁸ (range 0.2 - 0.6), but no seasonal variation can be detected (see table I and II in Golterman & Meyer, 1985b). High values, however, occur in April and May. The small differences in the calcium concentration are probably

more related to the higher pH values in Schmitter compared to those in Port-du-Scex than to an essential difference in the apparent solubility product.

Sulphate concentrations show seasonal variations at these two stations clearly related to water flow (see fig. 2a). This variation is therefore probably an erosion effect¹. Through the sulphate concentration the flow rate may influence the Ca/HCO₃/CO₃ system. In the stations downstream, this natural pattern is no longer visible. Both Ca and SO₄ concentration fluctuate at high levels and the variations seem to be related more to human impact; the high calcium concentration depends on increased acidity (see below), the sulphate concentration on the disposal of gypsum. Sulphate still shows some relation with the water flow, but this relation is not always clear (e.g. see Tarascon & Gorinchem, fig. 2b).

In both the Rhine and the Rhone we see an acidification and increase of sulphate concentration when going downstream. Often these are assumed to be chemically related. However, Golterman & Meyer (1985c) have shown that there is only a weak regression between Ca/HCO₃ and pH, but a very strong

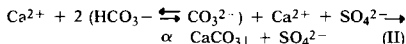
1. Rough estimates show that less than 10 % (probably less than 5 %) of the sulphate in the Rhine (about 1 mmol l⁻¹) may be derived from acid rain.

Table 4. — Solubilities of Ca^{2+} (in mM Ca^{2+}) at 20°C and at 0°C and their ratio $R_{20/0}^{20}$ and concomitant pH (in parentheses) as a function of the concentrations of sulphate (mM) and carbon dioxide (atm).
Third and fourth line the same, but now with K_s calculated as a function of pH: $K_s = 8.73 \text{ pH}^{15.667} \times 10^{-23}$ (but with the theoretical K_s as minimum value).

Temp	$\text{CO}_2 = 10^{-3.5}$		$\text{CO}_2 = 10^{-2}$		$R_{20/0}^{20}$					
	20°C	0°C	20°C	0°C	20°C	0°C				
0 mM SO_4	0.57	(8.36)	0.80	(8.41)	1.39	1.79	(7.36)	2.53	(7.41)	1.39
1 mM SO_4	0.91	(8.26)	1.28	(8.3)	1.39	2.85	(7.26)	4.00	(7.31)	1.39
0 mM SO_4	3.60		4.92		1.37	1.79		2.53		1.41
1 mM SO_4	4.73		6.42		1.36	2.85		4.00		1.40

one between Ca/HCO_3 and sulphate. This indicates that the increase in sulphate is caused by an input of sulphate in the form of CaSO_4 rather than as H_2SO_4 , the acidification originating from the mineralization of organic matter.

Golterman & Meyer (1985c) have shown that the addition of CaSO_4 influences the quotient Ca/HCO_3 and therefore the $\text{Ca}/\text{HCO}_3/\text{CO}_2$ system, according to the relation.



α is the mol fraction of carbonate that will precipitate).

In a saturated situation, when doubling the Ca concentration, the carbonate concentration needs only to be halved in order to re-establish equilibrium, so α is very small compared with the molarity of the calcium bicarbonate present.

Theoretically the regression line should be $\text{Ca}/\text{HCO}_3 = 0.5(\text{SO}_4) + 0.5$ when the concentrations are expressed in mmol l^{-1} and $\text{Ca}/\text{HCO}_3 = 0.5(\text{SO}_4) + 1$ when the concentrations are expressed in meq. l^{-1} with the bicarbonate originally present being 2 meq l^{-1} .

If all data are taken together per river per year, the value of r^2 is high, and the slopes approach the theoretical value 0.5, while if the data are taken together per station the values of r^2 are less high, probably because of a lower variation per station than for all stations together. For Schmitter and Port-du-Scex the r^2 values are smaller ($r^2 = 0.31$ and 0.28 respectively), while the slopes are less steep (0.1 and 0.3, see Golterman & Meyer, 1985 c). I therefore believe that in these stations the seasonal variations of the calcium and bicarbonate concentrations are

for the larger part controlled by the temperature and the CO_2 -partial pressure, with sulphate as a small modifying factor.

However, IP_{Ca} and thus K_s (from formula I) seems not to be a constant. When calculating the ionic product IP_{Ca} , we have found a strong relationship between the calculated IP_{Ca} and pH, which are described by the following (numerical) regression equations:

$$\begin{aligned} \text{RHONE: } \text{IP}_{\text{Ca}} &= 2.17 \times 10^{-14} \cdot \text{pH}^{15.2} \text{ (river mean)} \\ &= 2.01 \times 10^{-17} \cdot \text{pH}^{18.6} \text{ (stations mean)} \\ \text{RHINE: } \text{IP}_{\text{Ca}} &= 8.16 \times 10^{-16} \cdot \text{pH}^{16.8} \text{ (stations mean)} \\ &= 4.97 \times 10^{-12} \cdot \text{pH}^{12.6} \text{ (river mean)}. \end{aligned}$$

The overall mean equation for this set is

$$\text{IP}_{\text{Ca}} = 8.73 \times 10^{-15} \cdot \text{pH}^{15.667}$$

Between pH 7.0 and 8.2 the 4 lines do not differ substantially from the overall mean (see fig. 3). I have now recalculated the influence of the temperature on the solubility of CaCO_3 , taking into account the influence of the pH on the K_s . The results are given in table 4 and show that, although the concentration of Ca is considerably higher, the ratio of $(\text{Ca}^{2+})_{0^\circ\text{C}}/(\text{Ca}^{2+})_{20^\circ\text{C}}$ remains constant.

In the next article Golterman & Meyer (1985 d) have calculated the ionic product of hydroxy-apatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, in order to test whether the solubility product is an applicable concept for natural water. If the concept holds true, then in a lot of cases the value of the ionic product will be close to that of the (still unknown) solubility product. In many cases where the ionic product is not close to the solubility product the explanation is undersaturation. This seems to be the case for the stations above the two lakes, i.e. Schmitter and Port-du-Scex, and they were

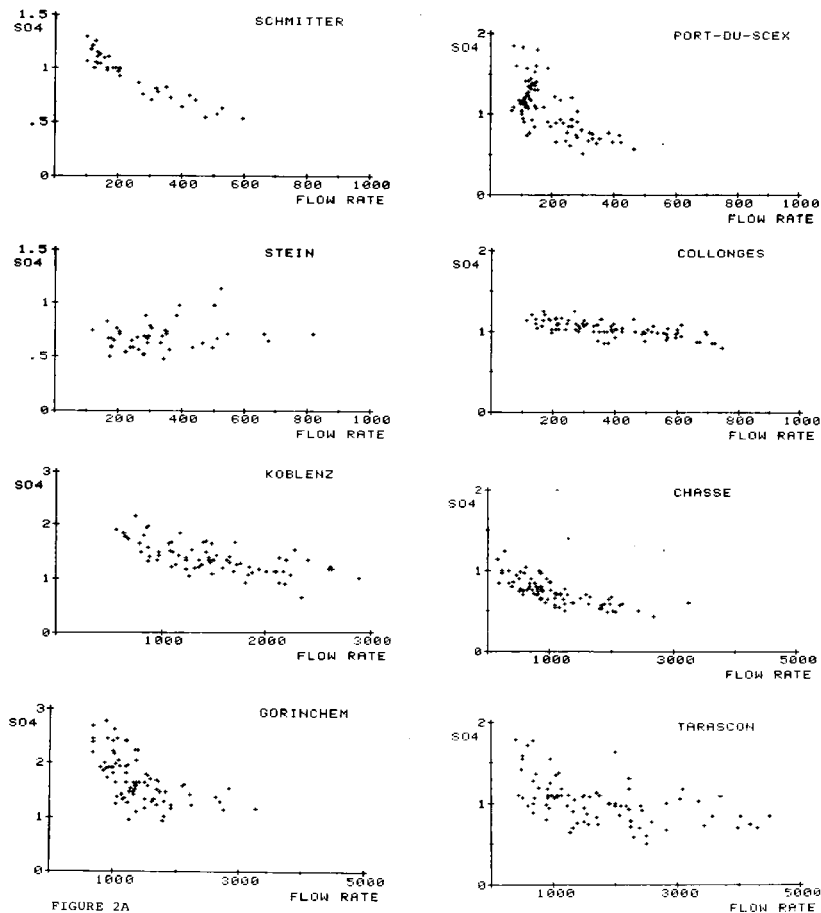


Fig. 2. Sulphate (mmol l^{-1} ; y-axis) against flow rate ($\text{m}^3 \text{sec}^{-1}$; x-axis) in 1 station upstream and 3 stations downstream of the Lakes of Constance and Geneva.

2A. River Rhine — 2B. River Rhone.

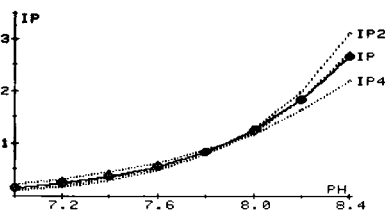


Fig. 3. 4 regression lines between IP_{Ca} ($\text{mol}^2 \text{l}^{-1} \times 10^8$) and pH. The lines IP1 and IP3 fall together with the « mean » line.

therefore omitted. For the other stations we found a mean value for $-\log IP_{ap} = 49.9$ (Rhine : $\sigma = 0.6$; $N = 259$) and 50.0 (Rhone : $\sigma = 0.3$; $N = 479$). This means that the two rivers are saturated with respect to hydroxy-apatite and that the concept holds true.

There are many measurements of IP_{ap} in the literature and the data range between 10^{-50} and 10^{-58} . Our analysis confirms the highest value. Most often, however, a wrong value for the K_3 of H_3PO_4 has been used, without influence of the temperature on the system constants (see discussion in Golterman & Meyer, 1985d)². The agreement with the value presented in this article is therefore probably accidental.

Kramer (1964) used values between $10^{-55.8}$ (0°C) and $10^{-57.2}$ (30°C). Jahnke (1981) reported values ranging between $10^{-54.6}$ and $10^{-58.8}$ (values are reported on a half unit cell basis). Neither Kramer nor Jahnke indicate, however, which value for K_3 was used. They pointed out, that the ionic products give no information on the composition of the solid phase due to incongruent dissolution of the hydroxy-apatite. The ionic products enable us to calculate only what concentrations of o-phosphate and calcium can co-exist at a given temperature and pH. If pure hydroxy-apatite were to be brought into solution, the ratio of Ca : P would, of course, be different (although the solubility product would remain the same). As we are dealing with hard waters - often carrying still undissolved $CaCO_3$ - to which phosphate is being added, the composition of the solid

phase is mainly $CaCO_3$ with coprecipitated apatite. The calcium concentrations in these waters are usually controlled by the solubility of the $CaCO_3$ system and range therefore between 2 (equilibrium situation) and 4-5 mmol l^{-1} (acidified waters). Thus the acidification of hard waters by decomposition of organic matter influences not only o-phosphate concentrations and its transport through delta areas, but also other processes depending on the pH, such as speciation and transport of heavy metals.

The difference between Kramer's and Jahnke's values and ours is also due to the fact that we did not calculate the influence of the ionic activity coefficients. For the Rhine and Rhone this is possible, but the ionic composition is usually not recorded in the limnological literature, and comparison with our value would become more difficult. Because the ionic activity coefficients influence the dissociation constants as well, the influence of the activity coefficient is pH dependent. I estimate that for hard water rivers or lakes, at pH between 7 and 8 the activity coefficient is about 0.1 and the solubility product decreases to about 10^{-51} .

5. — Problems and conclusions

5.1. — The problems

The ionic product and the solubility product should be calculated taking into account the influence of the ion activity coefficients. However, in many studies on the solubility of phosphate in relation to calcium concentration and pH, the concentrations of other ions are not sufficiently or not at all known. Therefore, we give the ionic product of apatite without a correction for the ion activity coefficients assuming that - as we are dealing here only with calcium rich waters - in this type of water the main components are the calcium and bicarbonate ions, and that therefore these corrections will usually be of the same magnitude. For further precise understanding in studies of the solubility of apatite, the total ionic composition should be measured.

The second problem is that in calculation of the ionic product we use the third dissociation constant of phosphoric acid, K_3 (Clymo & Golterman 1985). The value of this constant and especially its dependence on temperature, is not very well known. We know of only one series of measurements in the

2. In Golterman & Meyer (1985d) a wrong formula for the third dissociation constant of H_3PO_4 (K_3) was printed; the correct one $p K_3 = 2397.4 / (273 + T) + 4.2364 - (2.6061 \times 10^{-3})(T + 273) + 6.3834 \times 10^{-5}(273 + T)^2$ (Temp. in $^\circ \text{C}$) was used.

temperature range of natural waters (Ghosh *et al.* 1980). There are many measurements at 20° C and the agreement is not good. The range of values published in the literature is $2 \cdot 20 \times 10^{-13}$ (Gosh *et al.* 1980). A fairly small change of K_3 would cause a great difference in the IP_{ap} (and thus in the K_s), but not in its standard deviation. The ionic product is furthermore extremely dependent on the pH. The observed variation around the mean value could easily be attributed to errors in the measurement of the pH. For a more precise measurement the pH should be measured to an accuracy of 0.02 units (Clymo & Golterman 1985).

5.2. — Conclusions

The value for the solubility product does not give any information on the chemical composition of the precipitate, only on which concentrations of calcium and phosphate can co-exist at a given pH and temperature. A solution of these ions will have a completely different composition if the solution is in equilibrium with a pure apatite or with a solution with a fixed calcium carbonate concentration, e.g. such as exists in natural fresh waters, where phosphate is being added to existing solutions of calcium bicarbonate, the calcium concentration being controlled by the solubility of calcium carbonate at a given pH and temperature.

The solubility of o-phosphate and its dependence on calcium concentration and pH can be shown (calculated) as :

$$o\text{-PO}_4 = \left(1 + \frac{H^+}{K_3} + \frac{(H^+)^2}{K_2 K_3}\right) \sqrt{\frac{10^{-50} (H^+)}{(Ca^{2+})^5 K_w}} \text{ mol l}^{-1}.$$

Thus, if water of one of the rivers arrives at the delta, slightly acidified (e.g. pH = 7.5) with Ca = 60 mg l⁻¹, the o-phosphate concentration in the saturated situation will be 0.2 mg l⁻¹. Then, after re-establishing equilibrium with the air, the pH will increase to 8.3, the calcium will precipitate to about 40 mg l⁻¹ and the o-phosphate concentration will decrease to about 0.04 mg l⁻¹. Thus 0.16 mg l⁻¹ (=g m³) will precipitate. For the Rhone delta this means a precipitation of $400 \cdot 10^6 \times 0.16 \text{ g m}^3 = 64 \text{ ton y}^{-1}$. Besides this amount all phosphate adsorbed on the sedimenting material will enter the bottom sediments. Finally, photosynthesis may further increase the pH, causing a second precipitation (although this quantity is smaller than that rendered insoluble as a result of the first pH increase,

because the remaining dissolved fraction after re-equilibrating is already very small). In the Rhine delta similar processes occur on an even larger scale, both in the Haringvliet, where some 70 % of the Rhine water re-equilibrates with the atmosphere and in Lake IJsselmeer, through which about 10 % of the Rhine water ($7 \cdot 10^9 \text{ m}^3 \text{ y}^{-1}$) passes.

The second conclusion is that the o-phosphate concentration does not depend on the phosphate loading of the river, but on the calcium concentration together with temperature and pH. Decreasing the loading may not reduce the dissolved phosphate and increasing the loading will cause only the suspended phosphate to increase. The measurement of the suspended phosphate annual transport is more difficult than that of the dissolved and the frequency of sampling should be determined by the flow rate and should not be at fixed intervals e.g. fortnightly. The consequences for monitoring programmes are considerable.

Two remarks on the practical usefulness of the monitoring programmes must be made :

1. Since 1979 bicarbonate concentration in the Rhine is no longer being published. This means that checking the precision of the data is no longer possible. Secondly bicarbonate is a key-element in the understanding of the relationship between calcium, sulphate and phosphate concentrations. It seems highly desirable that bicarbonate be once more included in the published reports. In the Rhone the Tot-P concentration is not being measured. As the o-phosphate concentration depends on the calcium concentration, the pH and the temperature AND NOT ON THE LOADING, it would be useful to include the Tot-P determination in order to be able to calculate the total phosphate loading of the river.
2. In several stations a much better accuracy can be obtained. The station SCHMITTER should be compared with obtained data to see whether improvements are possible.

Annex

The temperature dependence of the pK_1 , pK_2 and the solubility of CO_2 is calculated as :

$$\begin{aligned} pK_1 &= 6.57886876 - 0.01321 \times TE + 1.801022 \times 10^{-4} \times TE^2 - 6.33015138 \times 10^{-7} \times TE^3 \\ pK_2 &= 10.6259395 - 0.0147603436 \times TE + 1.18529764 \times 10^{-4} \times TE^2 - 8.08342353 \times 10^{-8} \times TE^3 \\ CO_2 &= (130.83 - 0.82506 \times TE + 1.3116 \times 10^{-3} \times TE^2) \times 10^{-3.5/44}. \end{aligned}$$

References

- Annuaire de la Qualité des Eaux. Rivières et Canaux 1976 - 1981, vol. VI, Bassin Rhône - Méditerranée - Corse.
- Clvmo (R.S.) & Golterman (H.L.). 1985. — Precision and accuracy of the determination of the ionic product of hydroxy-apatite. *Hydrobiologia*.
- Commission internationale pour la protection du Rhin contre la pollution. Tableaux numériques 1971-1979.
- Golterman (H.L.) & Meyer (M.L.). 1985. — The geochemistry of two hard water rivers, the Rhine and the Rhone. Part 1 : Presentation and screening of data. *Hydrobiologia*, 126, 3-10.
- Golterman (H.L.) & Meyer (M.L.). 1985b. — The geochemistry of two hard water rivers, the Rhine and the Rhone. Part 2 : The apparent solubility product of calcium carbonate. *Hydrobiologia*, 126, 11-19.
- Golterman (H.L.) & Meyer (M.L.). 1985 c. — The geochemistry of two water rivers, the Rhine and the Rhone. Part 3 : The relations between calcium, bicarbonate sulphate and pH. *Hydrobiologia*, 126, 21-24.
- Golterman (H.L.) & Meyer (M.L.) 1985 d. — The geochemistry of two hard water rivers, the Rhine and the Rhone. Part 4 : The apparent solubility product of hydroxy-apatite. *Hydrobiologia*, 126, 25-29.
- Ghosh (A.K.), Ghosh (J.C.) & Prasad (B.). 1980. — Third dissociation constant of phosphoric acid from 283.15 K to 323.15 K. *J. Indian Chem. Soc.*, vol. LVII, 1194-1199.
- Jahnke (R.A.), 1981. — Current phosphorite formation and the solubility of synthetic carbonate fluor apatite. Thesis University of Washington.
- Kramer (J.R.). 1964. — Sea Water : Saturation with apatites and carbonates. *Science* : 146, 637-8.
- Stumm (W.) & Morgan (J.J.). 1981. — *Aquatic Chemistry. An introduction emphasizing chemical equilibria in natural waters.* 780 pp. John Wiley & Sons, Inc. New York etc.