

Nature and Nurture: Environmental Isotope Story of the River Rhine

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The total dissolved load of the Rhine river increases downstream due to the combined impact of natural and pollution loads. The natural background, controlled by geology, is soon swamped by pollution, particularly from salt and coal mining activities in Alsace and the Ruhr area. The Rhine is also a net source of CO_2 from oxidation of excess organic productivity that is fuelled by nutrient pollution, a problem even more serious for some of its tributaries.

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From an anthropogenic perspective, the river Rhine represents one of the most important water-courses. It serves a highly industrialized population of approximately 41 million [16] and, together with Lake Constance, provides drinking water for about 20 million people [15,22]. Its drainage basin (Fig. 1) of some 224 500 km² yields an average annual water discharge of $\approx 72 \text{ km}^3$, which ranks it as the 40th largest river of the world [1,3]. Yet, in terms of the pollutant load the Rhine probably ranks among the top ten rivers [16]. Because of the long history of habitation and industrialization, the pollution load increased significantly over time as well as downriver. These trends have been clearly documented not only for major ions but also for some trace elements and for dissolved as well as particulate loads [9, 10, 13, 15, 18, 22, 31, 32, 35–37]. It is this long-term anthropogenic impact that causes some difficulty in establishing the “natural” background values, particularly taking into consideration that even the basin geology is changing downriver from mostly carbonate to mostly silicate rocks (Fig. 1). Zobrist and Stumm [42] estimated that for the Lower Rhine only H_4SiO_4 and HCO_3^- are present in almost natural concentrations, with other species being from $\approx 50\%$ (Mg^{2+} , Ca^{2+} , K^+) to $\geq 90\%$ (PO_4^{3-} , Na^+ , Cl^- , metals) of anthropogenic origin. In the last two decades, the temporal, but not the downriver, pollution trends have been stabilized and even reversed for some pollutants [2,14,15,22,27,31,37], such as metals, organics and phosphate, but not for nitrogen compounds which are only inefficiently removed by the present-day sewage plants. As a result, the Rhine is one of the most highly mineralized rivers of the world, with average suspended and dissolved load concentrations of 47.4 and 580 mg/l, respectively [16].

In addition, the river is a net source of CO_2 , with P_{CO_2} increasing downriver by a factor of 10–15 above the atmospheric value of 340 ppm (Fig. 2). Yet, the source of this CO_2 is enigmatic. Kempe [16,17] proposed that nutrient pollution causes high primary organic productivity by photosynthetic consumption of CO_2 in the upstream lakes. These organics, swept downriver and complemented by local anthropogenic input, are then microbially respired causing an increase in P_{CO_2} and a drop in pH. The problem with this scenario is that the diffusion of oxygen into the river would not suffice for the task, and an additional oxygen donor(s), such as nitrate, sulfate or phosphate, is called for. As stated by Kempe “cynically, one can say that the Rhine possibly would have turned anaerobic, were it not for its high pollution with nitrate”. An alternative explanation is that this CO_2 is delivered by highly polluted lowland tributaries. The advantage of isotopic tracing techniques over the purely chemical ones

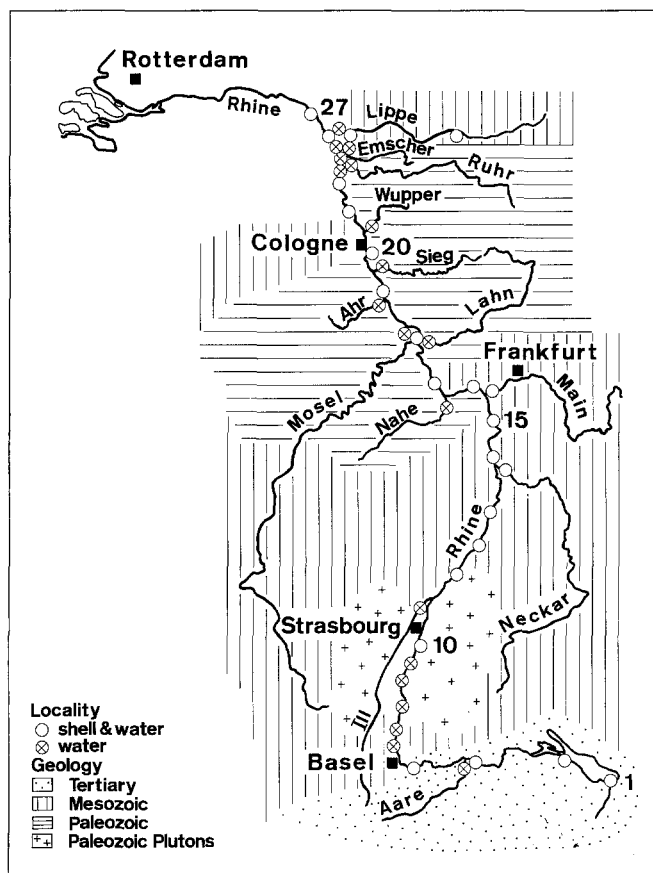


Fig. 1. Geographic map, sampling locations, and generalized geology of the Rhine river catchment area

is the potential ability to trace sources with differing isotopic signatures. In this contribution, we shall employ such isotopic techniques in an effort to elucidate the role basin geology may have played regarding the evolution of the background values for some cations in the dissolved load and for tracing the source of the enigmatic "excess" CO_2 .

Samples and Analytical Techniques

The river was sampled at 27 localities from the inflow of the Alpine Rhine into Lake Constance to Emmerich at the German-Dutch border (Fig. 1). In addition, 13 major tributaries were sampled prior to their confluence with the Rhine. Sampling was carried out in the fall of 1988 and in the spring and fall of 1989. We sampled waters as well as shells of the recent freshwater mollusk *Dreissena polymorpha* Pall. These aragonitic shells are composed of three layers, with complex cross-lamellar (main type), homogeneous, and prismatic ultrastructures.

The temperature, pH, and conductivity of waters were measured and calculated in the field by standard techniques. Acidified and filtered, as well as nonacidified,

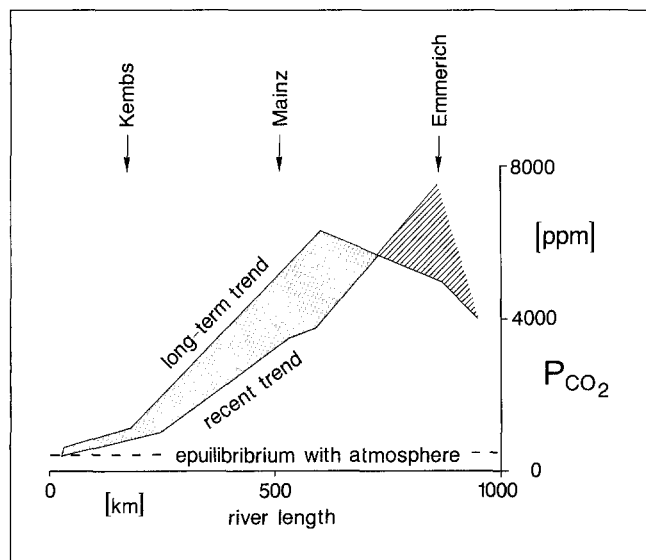


Fig. 2. Downriver evolution of P_{CO_2} for the river Rhine (after [16, 17])

aliquots of the samples were shipped to Bochum and stored in the cold. The acidified aliquots were utilized to determine Na^+ and K^+ by AES, Ca^{2+} , Mg^{2+} , Al^{3+} , Zn^{2+} , Fe_{Tot} and Mn^{2+} by AAS (Varian Techtron AA-6), and PO_4^{3-} by spectral photometry (Zeiss PMQ II), following the procedures listed in [34]. The Cl^- content was established by potentiometric titration, following the procedures listed in [7]. All these measurements were performed at the Institute for Geology, Ruhr University.

Total dissolved inorganic carbon species (CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-}) were precipitated in the field as BaCO_3 at pH 10. The CO_2 for the determination of oxygen and carbon isotopic composition from this precipitate as well as from the shells was liberated via phosphorylation at 50°C and measured on a Finnigan MAT-251 mass spectrometer in the new Isotope Laboratory of the Institute for Geology, Ruhr University. The oxygen isotopic composition of water was measured on a nonacidified aliquot at the University of Ottawa, Canada. Isotopic results are reported in the usual δ -notation as per mill difference from the PDB standard. Precision, as determined from replicate analyses, was usually better than 0.15‰ .

The preparation of shell and river-water samples for Sr isotopic measurements was done in 7- to 15-ml PFA vessels; 5 to 10 ml of river water was evaporated at 120°C , and the remaining salts were dissolved in cold 2.5 N supra pure HCl. The carbonate shells were ground in an agate mortar and 2 to 5 mg of powder dissolved in cold 2.5 N supra pure HCl. Sr was extracted via 4.5-ml quartz glass columns filled with Bio Rad AG50Wx8 ion-exchange resin, eluted with 2.5 N supra pure HCl. For mass spectrometry the Sr samples

were loaded on single Ta filaments using a loading liquid of Ta₂O₅, HNO₃, HF, H₃PO₄, and water [5]. The Sr isotope measurements were carried out on a five collector Finnigan MAT 262 solid source mass spectrometer at the Institute for Geology, Ruhr University. The ⁸⁵Rb signal was monitored but no Rb correction was performed, since a realistic Rb fractionation cannot be calculated. Samples with ⁸⁵Rb signals above 5 × 10⁻⁵ V were rejected. ⁸⁸Sr/⁸⁶Sr ratios were normalized to 8.375209. NBS 987 Sr carbonate, ocean water (France and Norway), and USGS EN-1 (*Tridachna* shell) standards yielded 0.710238 ± 8 (2δ_{mean} for 71 runs), 0.709149 ± 20 (11 runs), and 0.709134 ± 17 (10 runs), respectively. The total blank for Sr is below 1 ng, and loading blank below 5 pg. All these measurements are summarized in Tables 1 – 3.

Water Discharge and Its Sources

The principal sources of water and the total discharge vary seasonally by about a factor of 1.6, and such fluctuations are of prime importance for river chemistry. The dynamics of the river regime shows two peak periods, February – March due to lowland snowmelt,

and June – July caused by alpine snowmelt. The second peak tapers out below Cologne. The low-discharge period is August – November (cf. [8,18]). Our sampling, in 1988 and 1989, was carried out in late May and in early November. It should be noted that the mean water stand for the 1988 year was about one-third above [2,31], and for the 1989 year about 16 ‰ below [21], the long-term average.

The discharge of the Alpine Rhine at locality No. 1 is essentially alpine meltwater with a δ¹⁸O of about -12.5 ‰ SMOW, a value typical also for the Aare river (cf. [33]). In contrast, the oxygen isotopic composition of the lowland precipitation is about -8 ‰ [26,41], and this is reflected by the Rhine tributaries, particularly those north of the Main river (Fig. 3). Balance calculations based on the above values suggest therefore that in the Lower Rhine alpine meltwater accounts for ≈ 1/2 of the total in late May and ≈ 1/3 in late November. Since the Upper Rhine at Basel has δ¹⁸O_{water} of -11.5 ‰ SMOW, its water must account for ≈ 57 ‰ of the total Lower Rhine discharge in the spring and ≈ 43 ‰ in the fall. These estimates are in excellent agreement with hydrographic measurements [2]. The contribution of German tributaries to the to-

Table 1. Analytical results for spring sampling of the Rhine river. Chemistry was determined from the 1988 sampling program, while the isotopes were measured on samples collected in 1989. Temperature and pH were measured during both seasons

Locality	Temperature		Conductivity [μS/cm]	Na	Cl	K	Ca	Mg	PO ₄	Al	Fe	Mn	Zn	δ ¹⁸ O [‰ SMOW]
	[°C]	pH		[mg/l]					[μg/l]					
1 Rohrspitz	18.0	8.8	387	3	4	0.4	46	15	147	210	372	16	98	-11.9
2 Konstanz (seapark/harbor)	17.0	8.7	276	2	6	0.4	40	15	20	150	177	14	2	-12.1
3 Between Reinheim and Lienheim, near Reckingen	17.0	8.6	302	3	8	0.9	41	12	97	25	102	8	6	-11.9
4 Between Rheinfelden and Kaiseraugst (km 149)	17.0	8.3	322	7	8	1.2	48	11	136	150	295	26	13	-11.6
5 500 m NW Istein, parking Steinplatz (km 180)														
6 Steinstadt ferry (km 193.5)														
7 Niederimsigen, gravel pit Flüchiger														
8 NW of Burkheim (km 233)														
9 Weisweil (km 249)														
10 Wittenweiler (km 264.8)	21.5	8.6	773	85	155	6.4	44	11	198	190	118	11	13	-11.4
11 Hügelheim (km 331)	19.5	8.8	693	80	128	5.1	46	11	222	373	95	12	13	-11.3
12 Neuburgweier (km 354)	19.5	8.1	688	77	122	4.6	52	12	283	25	73	18	34	-11.1
13 Rheinhausen (km 394)	20.0	8.3	670	76	114	3.7	46	15	309	132	410	42	44	-10.8
14 Petersau (km 439.5)	19.5	8.1	941	86	161	7.3	42	12	359	113	312	68	58	-10.8
15 Guntersblum (km 472.5)	21.5	8.2	696	73	115	4.9	38	10	285	190	533	39	38	-10.9
16 Elteville (km 513)	22.0	8.5	669	60	77	4.3	36	17	703	133	220	47	52	-9.8
17 Loreley (km 553)	22.0	8.6	622	63	79	4.0	34	15	488	95	137	31	38	-10.2
18 Koblenz-Pfaffendorf (km 591)	21.0	8.6	714	75	112	4.7	34	12	427	390	245	45	58	-10.2
19 Erpel (km 634)	21.0	8.9	753	79	123	4.9	24	10	584	355	430	69	66	-10.2
20 Köln-Westhofen (km 683.2)	21.0	8.8	753	81	120	5.5	28	12	430	170	227	49	44	-10.0
21 Neuss-Üdesheim (km 727.3)	18.0	8.4	733	95	111	5.0	24	10	493	263	288	73	65	-9.9
22 Uerdingen bridge (km 765)	18.0	8.5	744	73	108	5.2	23	22	442	285	374	70	53	-9.5
23 Duisburg-Homberg bridge (km 779)														
24 Baer (km 786)														
25 Spellen (km 808)														
26 Wesel bridge (km 813.5)	20.0	8.3	1025	77	164	5.9	22	11	312	303	240	68	47	-9.9
27 Emmerich bridge (km 854)	19.5	8.6	961	82	148	5.3	23	12	487	373	545	96	90	-9.9

Table 2. Analytical results for fall sampling of the Rhine river. Samples for chemical (Na to Zn) and conductivity measurements were collected and measured in the fall of 1988. Water for isotopic measurements ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$) was sampled in the fall of 1989. Temperature and pH were measured in both years

Locality	Temperature		pH		Conductivity [$\mu\text{S}/\text{cm}$]	Na [mg/l]	K	Ca	Mg	PO ₄			Al	Fe	Mn	Zn	$\delta^{18}\text{O}$ [$^{\circ}/\text{‰}$ SMOW]	$\delta^{13}\text{C}$ [$^{\circ}/\text{‰}$ PDB]	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{18}\text{O}^*$ [$^{\circ}/\text{‰}$ PDB]	$\delta^{13}\text{C}^*$ [$^{\circ}/\text{‰}$ PDB]
	1988	1989	1988	1989																	
1	12.0	9.4	9.1	8.7	322	5	1.6	46	9	131	218	1325	81	22	-13.4	-4.4	0.708504*	-10.6	-7.6		
2	13.0	13.7	8.0	8.9	272	4	1.4	45	22	306	303	691	88	66	-12.2	-6.1	0.708466*	-9.6	-7.1		
3	11.0	12.0	8.5	8.1	305	6	1.5	35	9	114	166	72	0	5	-11.7	-8.0	0.708560*	-10.3	-8.6		
4	13.0	14.0	8.0	8.0	320	7	2.0	38	6	214	294	242	14	9	-11.6	-8.6	0.708459*	-11.5	-8.0		
5		13.6		7.8											-11.2	-9.2	0.708444				
6		13.5		7.9											-11.0	-9.4	0.708484				
7		13.8		8.0											-11.1	-8.7	0.708477				
8		14.6		8.2											-11.0	-8.0	0.708734				
9		14.4		7.9											-11.1	-8.6	0.708667				
10	14.5	14.6	8.3	8.3	649	73	5.5	39	7	257	264	170	14	10	-11.1	-8.9	0.708744*	-10.2	-9.2		
11	14.5	14.4	8.1	8.3	387	20	4.0	38	7	266	239	187	2	33	-11.3	-8.1	0.708719*	-9.4	-8.4		
12	9.5	14.5	8.5	7.8	642	66	5.3	47	8	52	586	56	88	5	-11.0	-8.4	0.708671*	-8.8	-10.5		
13	13.0	17.7	8.4	8.7	811	89	6.5	41	7	430	186	295	43	13	-11.0	-8.4	0.708741*	-10.5	-8.8		
14	13.0	16.6	8.1	7.7	1024	105	10.2	55	8	596	169	280	69	28	-10.6	-9.8	0.708808*	-10.6	-9.8		
15	13.0	15.7	8.2	7.6	846	90	8.5	48	8	511	197	266	22	15	-10.8	-8.5	0.708721*	-10.4	-8.9		
16	13.5	13.6	8.6	7.3	830	71	7.2	59	16	1437	135	228	43	33	-8.9	-10.7	0.708870*	-8.9	-10.5		
17	12.5	15.0	7.9	7.9	803	79	6.7	58	12	1083	378	578	69	35	-10.2	-9.2	0.708784*	-10.0	-9.7		
18	12.5	13.7	8.6	7.9	779	78	6.5	48	11	1011	324	374	65	44	-9.5	-8.9	0.708803*	-10.3	-9.6		
19	12.0	13.0	8.7	7.7	692	70	6.0	46	10	897	301	529	69	37	-9.3	-8.3	0.708805*	-9.8	-8.9		
20	11.5	13.6	8.5	7.7	664	53	5.7	49	10	866	265	369	54	28	-9.4	-9.4	0.708817*	-9.2	-9.5		
21	15.5	13.8	7.8	7.7	834	75	6.1	52	10	990	274	501	75	27	-9.5	-9.8	0.708843*	-9.4	-9.2		
22	15.0	12.6	8.0	7.6	732	65	5.9	49	10	840	308	398	67	31	-9.2	-9.0	0.708830*	-9.4	-9.5		
23		12.0		7.5											-9.3	-8.8	0.708871				
24		11.8		7.5											-9.3	-8.7	0.708874				
25		13.6		7.4											-9.3	-8.2	0.709108				
26	9.5	13.6	7.9	7.6	1161	109	7.5	64	12	970	353	487	85	49	-9.1	-9.6	0.709076*	-9.2	-9.5		
27	9.0	13.0	7.9	7.9	986	96	6.7	64	11	1164	378	918	106	56	-9.6	-8.2	0.708923*	-9.1	-9.0		

* Isotope measurement on *Dreissena* (fall 1988)

Table 3. Analytical results for sampling of tributaries (sampled in May 1989 and November 1988; waters from the vicinity of Fessenheim atomic power station – Grand Canal and brine culvert – sampled in September 1990)

Tributary	Temperature [$^{\circ}\text{C}$]		pH		$\delta^{18}\text{O}$ [$^{\circ}/\text{‰}$ SMOW]		$\delta^{13}\text{C}$ [$^{\circ}/\text{‰}$ PDB]	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{18}\text{O}^*$ [$^{\circ}/\text{‰}$ PDB]	$\delta^{13}\text{C}^*$ [$^{\circ}/\text{‰}$ PDB]
	May	Nov.	May	Nov.	May	Nov.				
Aare		16.4		7.9	-11.6	-11.7	-8.5	0.708299		
Ill		13.1		7.5	-9.7	-9.6	-10.1	0.708742		
Neckar		15.2		8.0	-8.7	-8.7	-9.8	0.708588	-5.9	-9.8
								0.708582*		
Main		13.2		7.1	-8.5	-8.8	-14.4	0.708766	-5.6	-14.4
								0.708821*		
Nahe		11.6		8.0	-8.2	-7.8	-11.9	0.711129		
Lahn		11.5		8.0	-6.7	-8.3	-11.6	0.709271		
Mosel		12.5		7.6	-7.6	-7.3	-9.7	0.708886		
Ahr		8.7		7.5	-8.1	-8.3	-7.3	0.710926		
Sieg		10.4		7.8	-7.6	-8.0	-12.1	0.710700		
Wupper		12.0		7.3	-7.6	-8.3	-12.1	0.711061		
Ruhr		10.4		7.6	-7.9	-8.3	-10.3	0.708874		
Emscher		14.5		7.6		-7.2	-12.3	0.709638		
Wesel-Datteln										
Canal at	20.0	8.5	8.2	8.8	-7.5	-6.9	-9.1	0.708595*	-6.9	-10.7
Voerde										
Datteln-Hamm										
Canal at	21.0	8.5	8.2	8.3	-5.1	-3.7	-5.6	0.707719*	-4.6	-6.7
Hamm-										
Uentrop										
harbor										
Lippe		15.2		8.1	-9.9	-9.6	-10.2	0.709307		
Grand Canal at Rumersheim-le-Haut								0.708410		
								0.708412		
Brine culvert between Rumersheim-le-Haut and Blodelsheim								0.709462		
								0.709481		
Grand Canal at Nabsheim								0.708819		
								0.708818		

* Isotope measurement on *Dreissena polymorpha* (November 1988)

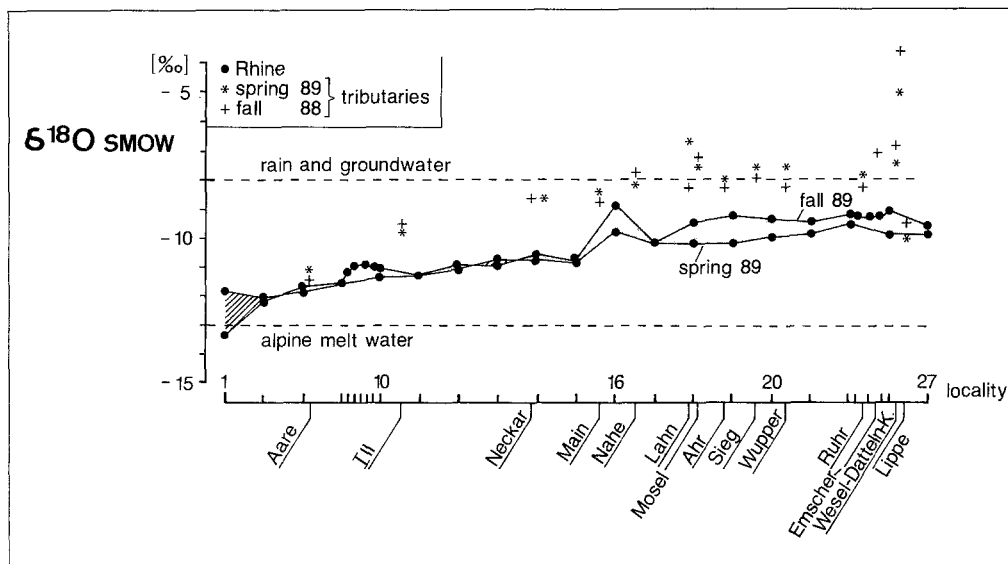


Fig. 3. Oxygen isotopic composition of water for the Rhine river and its tributaries

tal water budget of the Rhine is thus about equal to that of the Swiss sources.

An interesting anomaly, with exceptionally heavy $\delta^{18}\text{O}_{\text{water}}$, was identified in the Wesel-Datteln-Hamm Canal, particularly in the Hamm-Uentrop harbor. We have no logical explanation for this ^{18}O enrichment, unless the Canal contains an admixture of seawater or perhaps of deep mine waters. Neither seems to be the case. Interestingly, the Uentrop locality is in the vicinity of the only German high-temperature reactor, but we are not aware of any causal relationship. One possibility is that the Canal water may have been utilized to cool the reactor block, although today the discharge of cooling water appears to be channeled into the Lippe. If it is indeed utilized for cooling, this may have caused the oxygen isotopic fractionation. Recently, the reactor was closed down.

Chemical Evolution of the River

Based on its dissolved load of 580 mg/l [16] and considering that the river catchment area is dominated by carbonate rocks, the Rhine would be expected to plot among the rock-dominated calcium-bicarbonate rivers of Gibbs [11], with $\text{Na}/(\text{Na} + \text{Ca})$ ratios of about 0.1. The excessively high Na concentrations, leading to downriver $\text{Na}/(\text{Na} + \text{Ca})$ ratios of ≈ 0.6 (Tables 1, 2), are a clear measure of anthropogenic pollution (cf. Chap. 5 in [4]) and reflects a high load of salts [25,36]. Although the molar Na to Cl ratios remain about 1 along the entire river length, the total load of both ions jumps by one order of magnitude between localities 4 and 10 and increases less rapidly afterwards (Tables 1, 2; Fig. 4). It is this downstream evolution toward the

polluted state, particularly in terms of isotopes, that is of major interest to this study.

Factor analysis of the 1988 measurements from Table 2 – not reproduced here – identifies four major factors that control the *downriver evolution* of chemistry. Factor 1 has high positive loadings for conductivity (a measure of the Total Dissolved Load), Na, K, Ca, PO_4 , $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$, whereas $\delta^{13}\text{C}$ loads negatively. Cl also loads positively on this factor, as documented by the spring data (Table 1). Factor 1 is interpreted as *anthropogenic pollution*, although a proportion of the downriver evolution is undoubtedly of natural origin. This is particularly the case for oxygen isotopes that reflect a progressive mixing of alpine and lowland waters as discussed in the previous section. Furthermore, most of the lowland tributaries, from Nahe to Emscher, drain Paleozoic terranes (Fig. 1) that are dominated by silicate rocks, including a high proportion of mineralogically immature sandstones. These rivers may therefore contribute high proportions of ions such as Na, Cl, and K. In contrast, the tributaries in the upper reaches of the Rhine river drain predominantly carbonate terranes. The Mosel, and to a degree the Lippe, are special cases to be discussed later. Factor 2, with loadings of Ca, Mg, PO_4 , Fe, Mn, and Zn can be interpreted as a *geogene* factor. In contrast to the previous case, the catchment area geology plays the dominant role, while the anthropogenic component is of second-order importance only. As a result, the downriver trends are considerably less pronounced than those dominated by the anthropogenic factor. It should be noted, however, that some species – particularly the PO_4 – are controlled in the first instance by anthropogenic factors and only the residual reflects the geogene tendencies. Even this residual may only mimic the geogene distribution and may in fact origi-

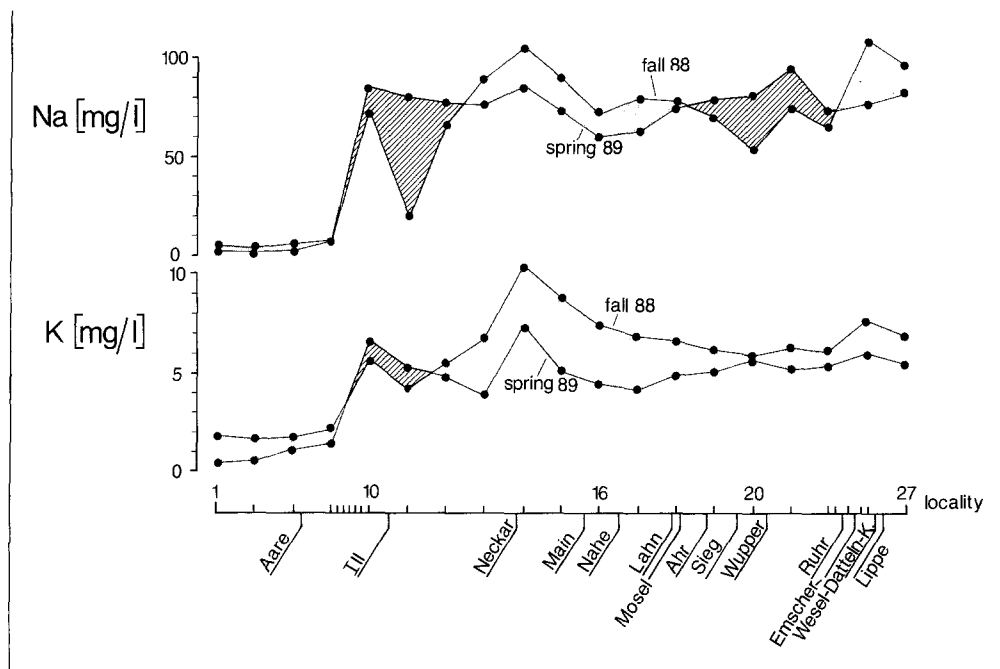


Fig. 4. Sodium and potassium contents of the Rhine river water

nate from diffuse agricultural runoff, as opposed to point sources that dominate PO_4 loading on factor 1. Factor 3 is somewhat enigmatic and reflects mostly the unusually low temperature and high Al and Mn concentrations at locality 12 (Table 2). All these are probably anomalous local data. Substituting the pH and T measurements from the 1989 fall sampling, temperature loads on its own factor. Similarly, in the 1988 spring set (Table 1), temperature loads positively on factor 1, that is, water becomes warmer downriver; a feature clearly expected from the declining proportion of the alpine meltwater in the total spring discharge. Were it not for the anomalous data at locality 12, alumina would also follow the above geogene trend. We therefore consider the fall 1988 measurements at locality 12 to be anomalous and disregard Factor 3 in the subsequent discussion.

Finally, Factor 4 reflects variations in pH, which in the spring of 1989 followed their own specific pattern. In contrast, in the fall pH declined downriver (Tables 1, 2). An analysis of the 1989 spring data (Table 1) yields factors that are only marginally different from the fall set. The above identified factors will be discussed in detail below.

Anthropogenic Pollution

The downriver evolution for the bulk of the dissolved load is well illustrated by Na and K trends (Fig. 4), with conductivity and Cl having analogous distributions (see also [2,31]). The large concentration jump

between localities 7 and 8 is caused by discharge of wastewaters from the Alsatian salt mines (KCl, NaCl) into the Grand Canal near Fessenheim [15,23] and subsequently into the Rhine at Breisach. This salt injection controls the background chemistry of the Rhine river along its entire subsequent flow path. A persistent pollution throughout the Mannheim – Ludwigshafen industrial area and from the Neckar basin contributes additional salts. Subsequently, the river starts to heal itself, a trend particularly visible at low water level stands in the fall. A diffuse industrial pollution, however, soon reverses this healing trend. In the fall, the setback begins at about Cologne (locality 20), while in the spring the deterioration becomes evident already from the confluence with the Nahe (locality 16). This is probably because the anthropogenic input is visible earlier if discharged into the cleaner spring waters. Superimposed on this diffuse industrial background pollution is a large spike from the coal mines of the Ruhr area, pumped into the Rhine via the Emscher [15,19,20,31].

Dissolved phosphorus, one of the main nutrients, has a distribution transitional to that of the geogene ions. Nevertheless, the largest spike in the Rhine – undoubtedly of anthropogenic origin – appears after its confluence with the Main river (Fig. 5). This point may have repercussions for the later discussed CO_2 budget. The Sr isotopic evolution of the Rhine river mimics that of sodium and other anthropogenic ions (Fig. 6). The largest ^{87}Sr spikes appear again at Breisach and at Emscher, with only a marginal gain between these two localities. The Sr isotopic composition of the rivers is

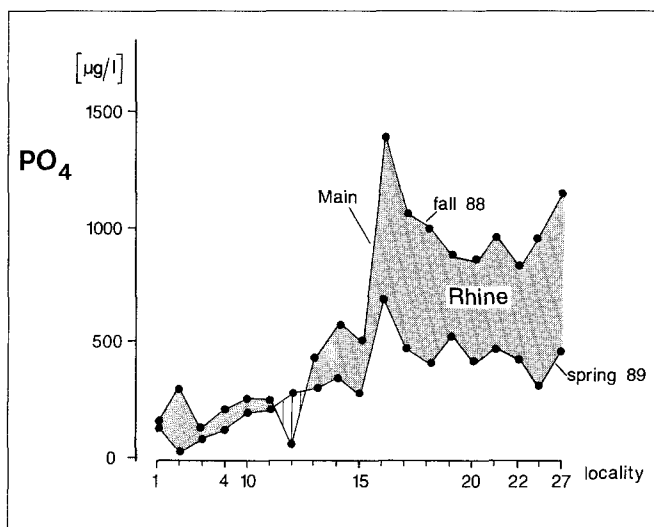


Fig. 5. PO_4 content of the Rhine river water

controlled in the first instance by the geology of their catchment area [12,28,38,40]. The older the rocks and the higher the proportion of Rb-rich silicate lithologies, the higher the $^{87}Sr/^{86}Sr$ ratios of the waters. This is clearly reflected in the $^{87}Sr/^{86}Sr$ of the tributaries (Table 3, Fig. 6). The tributaries draining predomi-

nantly the Tertiary and Mesozoic carbonate terranes of the Upper Rhine (Aare to Main) have relatively nonradiogenic Sr isotope ratios, while those draining the predominantly silicate (graywackes, shales) terranes of the Middle Rhine (Nahe to Ruhr) carry strontium enriched in its 87 isotope. The Mosel is a partial exception to this pattern. This river drains in its upper reaches a Tertiary and Mesozoic carbonate terrane. It also receives the already discussed pollution from the Alsatian salt mines [23,24]. As a consequence, the Mosel acquires its entire dissolved load, and the Sr isotopic composition, in advance of the river entry into the Paleozoic Eifel/Hunsrück area. Similarly, the Lippe and the Wesel-Datteln-Hamm Canal acquire their relatively nonradiogenic Sr from the Cretaceous carbonates of the Münster basin, these carbonates inheriting such Sr from Jurassic and Cretaceous seawater that had one of the lowest $^{87}Sr/^{86}Sr$ ratios of the entire Phanerozoic [6,29,39].

The above discussion shows that the geology of the catchment area is clearly reflected in the Sr isotopic composition of the Rhine tributaries. This signal may therefore be utilized to evaluate the magnitude of natural background trends. The Sr isotopic compositions of the Aare and the Upper Rhine (0.7083–0.7085)

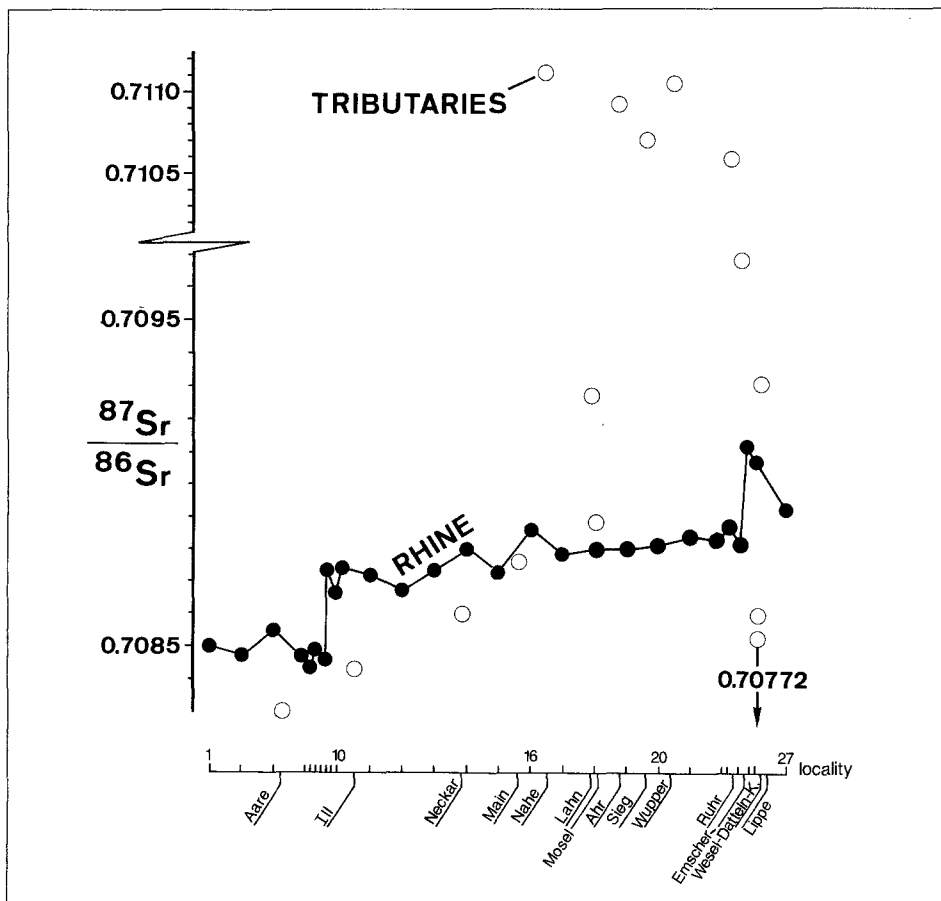


Fig. 6. Sr isotopic composition for water (shells) of the Rhine river and its tributaries

suggest that their Sr was derived from ≈ 14 - to 19-Ma-old marine sediments (see [6,38]), such as carbonates. Miocene sediments of the Alpine molasse are thus the likely source of the ions in the dissolved load of the Upper Rhine. The highly radiogenic tributaries of the Middle Rhine have no discernible impact on the $^{87}\text{Sr}/^{86}\text{Sr}$ evolution of the Rhine water, probably because their input of Sr (and other ions) into the Rhine is negligible, due either to small water volume or, more likely, to their low concentrations of dissolved solids. In fact, the largest ^{87}Sr spike in the Rhine appears where the tributaries (Aare, Ill) are less radiogenic than the Rhine itself. The second largest spike, in the Emscher-Lippe area, also appears where the radiogenic component in the tributaries is significantly reduced. It is clear therefore that these spikes have entirely anthropogenic sources. At Breisach, and in the Mosel, they originate from waste discharge of Alsatian salt mining. The brine discharged into the Grand Canal near Fessenheim has $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70947 and results in a considerable ^{87}Sr jump downflow in the Grand Canal and eventually in the Rhine below their confluence at Breisach (Fig. 6, Table 2). The observed jump between Rhine localities 6 and 7 requires that $\approx 26\%$ of Sr downriver originates from the Alsatian brines. In the Lower Rhine area the culprits are the saline waters from coal mines of the Ruhr area. To account for the ^{87}Sr increase between Rhine localities 24 and 25 (Fig. 6, Table 2), 31% of Sr downriver must originate from the Emscher. Based on these observations, the role of natural factors on the downriver Sr isotopic evolution of the Rhine water is negligible. By inference, such an explanation may also be advocated for other anthropogenic components, a conclusion in general agreement with the evaluation of Zobrist and Stumm [42]. The only discrepancies between their and our conclusions appear for mobilized, dissolved K and PO_4 . Our data, in contrast to [42], suggest that K is almost entirely an anthropogenic component while PO_4 , although $\approx 60\%$ anthropogenic, indicates also some geogenic tendencies (cf. [5,23]).

Geogenic Trends

The second group of elements, controlled by a combination of natural and anthropogenic causes, includes Ca, Mg, PO_4 , Fe, Mn, Zn, and, as discussed previously, also Al. For most of these elements, an overall downriver increase is discernible, but usually less than one order of magnitude, the latter characteristic of the anthropogenic ions. The only clear exception from such a pattern is the spring 1989 downriver decline in Ca (Table 1), a trend for which we have no explana-

tion. In the absence, in our data base, of measurements for tributaries, we prefer to close the discussion of the relative importance of natural vs anthropogenic causes at this point.

CO_2 in the River

The overall CO_2 river budget and its downriver buildup (Fig. 2) have been discussed by Kempe [16,17]. This buildup is reflected in our data set by a decrease in pH, particularly visible in the fall 1989 data (Table 2). Note also that many tributaries sampled in the fall of 1988 have a pH lower than the Rhine itself (Tables 2, 3).

The carbon isotopic composition of the total dissolved inorganic carbon (DIC) mirrors the trend for pH. Firstly, the $\delta^{13}\text{C}$ decreases downriver from -4 to about -9‰ PDB, with a minimum of -10.7‰ encountered below the confluence with the Main river (Table 2, Fig. 7). Secondly, the $\delta^{13}\text{C}_{\text{DIC}}$ of the tributaries, with only a few exceptions, is more negative than that of the Rhine. Rivers with particularly low $\delta^{13}\text{C}$ and pH include the Main, the Wupper, and the Emscher (Fig. 8).

Kempe [16,17] concluded that the “excess” CO_2 in the Rhine river derived from internal microbial respiration of C_{org} , fuelled by nutrient pollution. He proposed that NO_3 was the donor of oxygen necessary for respiration of C_{org} to CO_2 . In his correlation matrices either NO_3 or PO_4 may correlate with pH and P_{CO_2} . In our data set, the section of the Rhine that has a low pH also has high PO_4 concentrations (Tables 1, 2). This section starts at the confluence with the Main river (Fig. 5). Thus, nutrient pollution may indeed fuel the internal riverine respiration process, a conclusion supported by the $\delta^{13}\text{C}_{\text{DIC}}$ data. Organic carbon sources yield $\delta^{13}\text{C}$ of about -25‰ , while the dissolution of carbonates and exchange with atmospheric CO_2 introduce $\delta^{13}\text{C}$ of about 0‰ PDB. Balance calculations based on these end members suggest that the proportion of DIC that is derived from organic sources increases from at least 18% in the Alpine Rhine to 43% at the confluence with the Main river. This tributary derives about 60% of its DIC from an organic source. Note that these are minimal estimates, because of continuous equilibration with atmospheric CO_2 that tends to shift the $\delta^{13}\text{C}$ of DIC to heavier values (cf. Chap. 5 in [4]), thus underestimating the organic contribution. Overall, the carbon isotope data support the proposition of Kempe [17] that the production of excess CO_2 in the river is a result of increased respiration fuelled by nutrient pollution. However, the problem is much more serious for the tributaries, such as the Wupper, Emscher, Sieg, and particularly the Main. It is therefore entirely feasible that it is the tributaries that control, or at least strongly influence, the CO_2 budget of the Rhine.

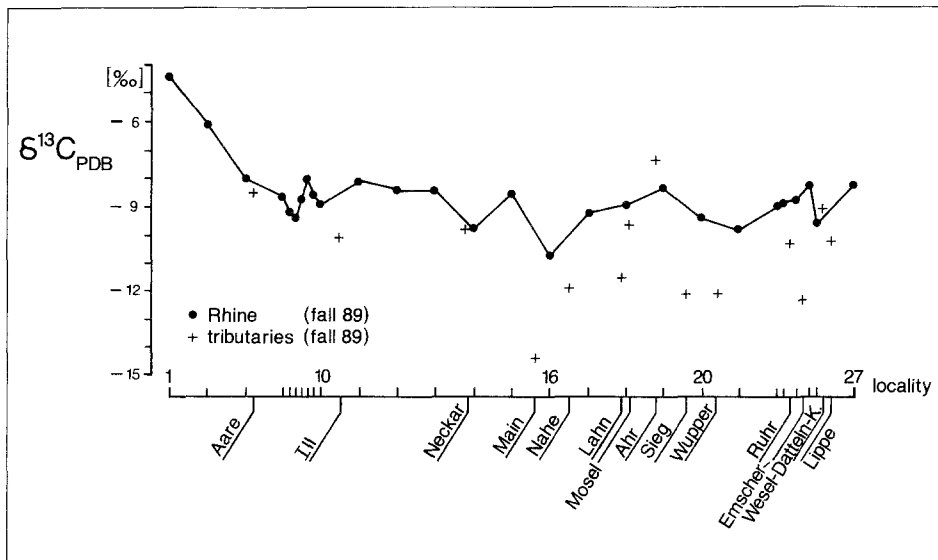


Fig. 7. $\delta^{13}\text{C}$ of DIC in the Rhine river and its tributaries

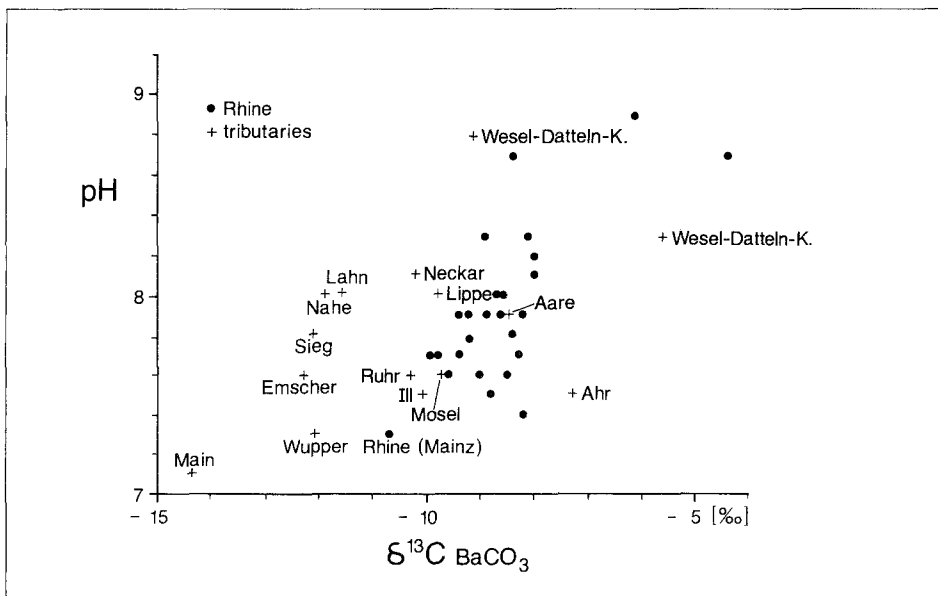


Fig. 8. $\delta^{13}\text{C}$ vs pH scatter diagram for the Rhine river and its tributaries

Growth of Mollusc Shells

The fresh-water mollusc, *Dreissena polymorpha*, precipitates its shell in isotopic equilibrium with the DIC and oxygen of the ambient water, a conclusion evident from the general agreement of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements for shells and water (Tables 2, 3). Larger discrepancies appear only in the Upper Rhine specimens, particularly for oxygen. The agreement of $\delta^{18}\text{O}_{\text{aragonite}}$ (PDB) with the $\delta^{18}\text{O}_{\text{water}}$ (SMOW) suggests that the bulk of the shell growth has been accomplished at an average temperature of about 16 °C. In the Upper Rhine, the indicated growth temperatures could have been up to 10 °C colder. Taking into ac-

count, however, that the shells grow over a prolonged time, and that our water sampling reflects only 2 days of the year, the Upper Rhine "anomalies" may not be real.

Conclusions

The downriver chemical evolution of water in the Rhine is influenced by a combination of anthropogenic and geogenic factors. The former control predominantly the observed increase in conductivity (Total Dissolved Solids), Na, K, PO_4 , and partly also Ca. The geogene factors complementarily control anthropogenic influences for Ca, Mg, PO_4 , Fe, Zn, and Mn. The

downriver evolution of ionic species is mimicked by the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the river water and mollusc shells found in the river. Sr isotope data indicate that the bulk of the dissolved load in the Upper Rhine is derived from Miocene marine sediments of the Alpine molasse. This natural input is, however, entirely swamped by waste products of Alsatian salt-mining activities that reach the Rhine at Breisach and salt the river along its entire subsequent course. Superimposed on the Alsatian load are secondary peaks from diffuse industrial pollution in the Mannheim to Frankfurt area and particularly from mine waters of the Ruhr area, the latter discharged into the Rhine via Emscher. The Sr isotopic composition of Rhine tributaries faithfully reflects their basement area geology, but – compared to the importance of anthropogenic sources – tributaries appear to exert only subordinate control on the Sr (and presumably TDS) budget of the Rhine river.

The Rhine is a net source of CO_2 , with concentrations increasing downriver by an order of magnitude. A substantial proportion of this CO_2 originates from microbial respiration of organic matter, as indicated by $\delta^{13}\text{C}$ of the dissolved inorganic carbon. The ultimate source of the enhanced productivity is the nutrient pollution from agricultural, industrial, and urban sources. The data indicate, however, that the CO_2 budget of the Rhine is controlled more by some of its tributaries than by its internal sources. In particular the Main, and to a lesser extent the Wupper, Emscher, Sieg, Nahe, and Lahn, appear to be significantly affected by nutrient pollution.

The fresh-water mollusc, *Dreissena polymorpha*, living in the Rhine and in some of its tributaries, appears to have precipitated its shell at temperatures of about 16°C in isotopic equilibrium with the $\delta^{18}\text{O}$ of ambient water as well as with $\delta^{13}\text{C}$ of the dissolved inorganic carbon.

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