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Title: **THE CARBON FLUX IN IRISH RIVERS**
Estimation of its magnitude and a discussion
of its significance in the environmental and
water supply contexts

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INTRODUCTION

Natural waters transport organic and inorganic carbon in both dissolved and suspended forms. This paper is concerned specifically with the inorganic carbon transported by Irish rivers at their freshwater limits. This carbon burden comprises free carbon dioxide, bicarbonate and carbonate ions that together constitute the carbonate system. The carbonate system has a key influence on natural fresh water chemistry, regulating parameters such as pH, alkalinity and hardness. Rainwater has a very low inorganic carbon content and a very low capacity to dissolve the solid phase carbonates with which it comes into contact following precipitation. Despite this fact many rivers carry a very significant carbon burden, representing a more than one hundred-fold increase over that contained in the catchment rainfall. This enhanced dissolution capacity is brought about by the uptake of carbon dioxide from carbon dioxide enriched environments with which the water comes in contact during the runoff process.

The paper reviews this natural phenomenon as it relates to the major Irish rivers. It is of environmental interest in so far as very significant quantities of carbon dioxide are sequestered and large amounts of calcium and magnesium carbonates are leached from soils and rock formations. Likewise, the carbonate system plays a key role in the treatment processes used to produce drinking water from surface waters, particularly in respect of water stability and its corrosive and/or scale-forming capacities.

THE CARBONATE SYSTEM

Role of carbon dioxide

Although it is not obvious at first glance, carbon dioxide (CO₂) is a primary determinant of the solute content of natural waters. The very extensive interfacial exposure of rainfall to air ensures that it becomes saturated with carbon as determined by the partial pressure of the latter in the atmosphere. Since CO₂ constitutes only about 0.03% of atmospheric air by volume (partial pressure 0.0003 atm), the equilibrium concentration of CO₂ in water in contact with atmospheric air, within the normal natural water ambient temperature range, is less than 1 mg/l, as shown in Fig 1.

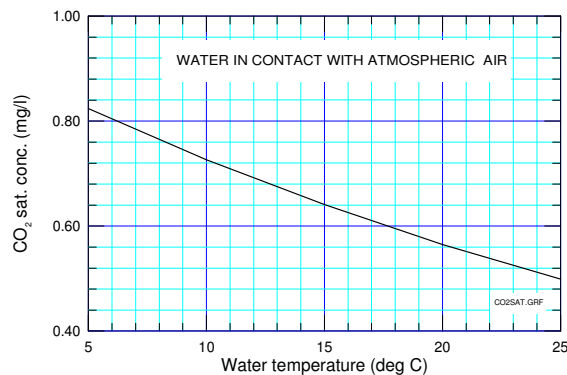


Fig 1 **Equilibrium concentration of CO₂ in water**

As well as the CO₂ derived from rainfall, water takes up additional CO₂ along its flow pathway to surface waters due to contact with gaseous environments that are enriched with CO₂, relative to atmospheric air, for example, the inorganic carbon content of most Irish surface and groundwaters is greatly in excess of the atmospheric equilibrium value. The total inorganic carbon (TIC) in water is made up of free CO₂, bicarbonate ions (HCO₃⁻) and carbonate ions (CO₃²⁻). In the pH range of most Irish natural waters, bicarbonate is the predominant anion. Aqueous bicarbonate and carbonate are derived almost exclusively from reaction between water containing free CO₂ and a solid phase containing calcium (or magnesium) carbonate according to the reactions:



Thus, on the basis of the forgoing reactions the inorganic carbon in natural waters is derived in equal proportions from gaseous CO₂ taken into solution and from the dissolution of solid phase carbonates.

The carbonate species provide the main buffering capacity of natural waters as measured by the universally used alkalinity parameter. Other species often present in small concentrations such as silicates, ammonia and phosphates also contribute to alkalinity. As the concentrations of these bases are generally negligibly small relative to the carbonates in Irish rivers their contributions to alkalinity are neglected in the following analysis for the purposes of which alkalinity is defined as follows:

$$\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \text{ eq/l}$$

$$\text{Alkalinity (mg/l CaCO}_3) = \text{Alkalinity (eq/l)} \times 50,000$$

The individual concentrations of the inorganic carbon species (CO₂, HCO₃⁻ and CO₃²⁻), which together constitute the total inorganic carbon concentration (TIC) in water, can be calculated from known values of water pH and alkalinity (refer Appendix A for computational details). For current descriptive purposes the CO₂ that has been converted to bicarbonate and carbonate anions during the runoff process is designated as *carbonated* CO₂. Carbonated CO₂ is stoichiometrically correlated with alkalinity as follows:

$$\text{carbonated CO}_2 \text{ (mg/l)} = 0.44 \times \text{alkalinity (mg/l CaCO}_3)$$

The net CO₂ uptake of water subsequent to precipitation is the sum of the free and carbonated forms:

$$\text{CO}_2 \text{ uptake} = \text{free CO}_2 + 0.44 \times \text{alkalinity}$$

ESTIMATION OF CARBON FLUX IN IRISH RIVERS

The following analysis encompasses sixteen major Irish rivers, the catchment boundaries of which are mapped in Fig 2. The river catchment areas and specific runoff rates are given in Table 1.

The basic water quality data used to estimate the carbon flux in the selected Irish rivers are presented in Table 2, in the form of estimated mean values at the respective river freshwater limits for the parameters, pH, alkalinity, hardness and conductivity. It is emphasized that these data should be regarded as approximate as they are based on arithmetic means of somewhat limited water quality data sets that may in most cases be insufficient to establish accurate mean parameter values. Empirical correlations of conductivity, alkalinity and hardness for Irish river waters are presented in Appendix B. As it is deemed likely that the magnitudes of water quality parameters such as alkalinity, hardness and conductivity may have an inverse relationship with flow rate, a more comprehensive study than has been carried out would be necessary to establish mean values with an acceptable level of confidence.

Table 1
Annual runoff volumes and mass flux rates
(EPA, 2001)

River	Catchment area at freshwater limit (km ²)	Specific runoff rate (mm/y)
Avoca	652	973
Bandon	608	1091
Barrow	3067	385
Munster Blackwater	3324	845
Boyne	2695	454
Corrib	3138	1053
Deel	486	478
Fergus	1042	567
Lee	1253	994
Liffey	1256	452
Maigue	1052	494
Moy	2086	929
Nore	2530	535
Shannon	11628	563
Slaney	1762	669
Suir	3610	672

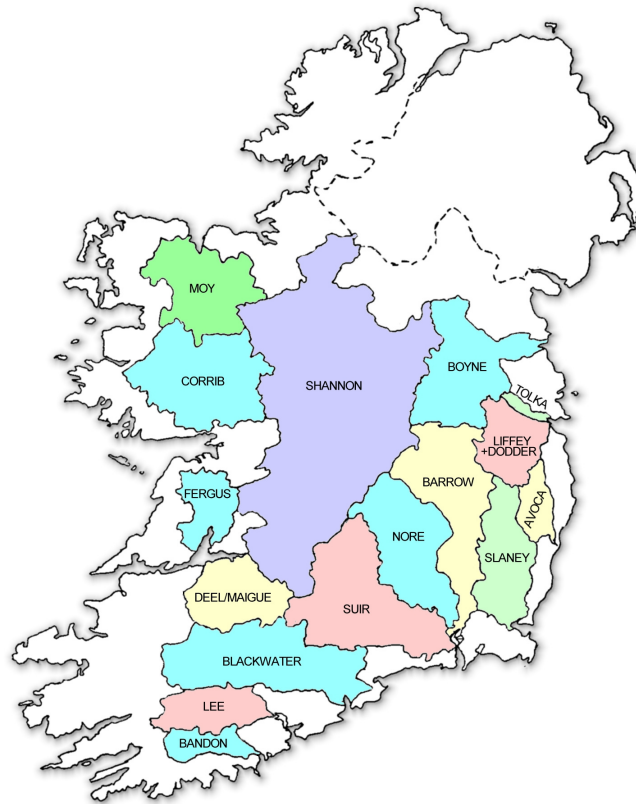


Fig 2

River catchment map

Table 2
River water quality
Mean parameter values at river freshwater limit
(Estimated from data supplied by the EPA)

River	Mean values			
	pH	Alkalinity (mg/l CaCO ₃)	Hardness (mg/l CaCO ₃)	Conductivity (µS/cm)
Avoca	7.2	18*	29	96
Bandon	7.5	36*	54	176
Barrow	8.1	230	286	529
Munster Blackwater	7.8	73*	99	246
Boyne	8.2	257*	296	541
Corrib	8.2	129*	162	330
Deel	8.2	187*	224	479
Fergus	7.8	143*	178	370
Lee	7.5	54	58	159
Liffey	8.2	215*	253	480
Maigue	8.2	230*	269	531
Moy	7.8	122	135	282
Nore	8.1	234	251	458
Shannon	8.2	185	212	403
Slaney	7.7	74	95	233
Suir	8.1	197	198	400

Footnote: Alkalinity values marked * have been calculated from measured hardness values on the basis: $\text{Alkalinity (mg/l CaCO}_3\text{)} = 0.37 \times \text{H}^{1.15}$, where H is the hardness as mg/l CaCO₃ (refer Appendix B).

The distribution of the carbonate species was calculated (O'Connor, 1982), using the parameter values in Table 2 and the chemical equilibrium equations given in Appendix A. The results are presented in Table 3. The TIC concentrations are plotted in bar chart format in Fig 3.

Table 3
Calculated inorganic carbon species
concentrations at the river freshwater limit

River	mg/l as CO ₂			
	CO ₂	HCO ₃ ⁻	CO ₃ ²⁻	TIC
Avoca	2.75	15.8	0.02	18.57
Bandon	2.7	31.6	0.1	34.4
Barrow	4.0	200.0	2.7	206.7
Munster Blackwater	2.7	63.9	0.4	67.0
Boyne	3.5	222.8	3.8	230.1
Corrib	1.8	111.9	1.8	115.5
Deel	2.6	162.1	2.7	167.4
Fergus	5.1	125.1	0.8	131.0
Lee	4.0	47.4	0.1	51.5
Liffey	3.0	186.4	3.1	192.5
Maigue	3.1	199.4	3.4	205.9
Moy	4.4	106.7	0.7	111.8
Nore	4.1	203.5	2.7	210.3
Shannon	2.6	160.5	2.6	165.7
Slaney	3.4	64.8	0.3	68.5
Suir	3.5	171.4	2.2	177.1

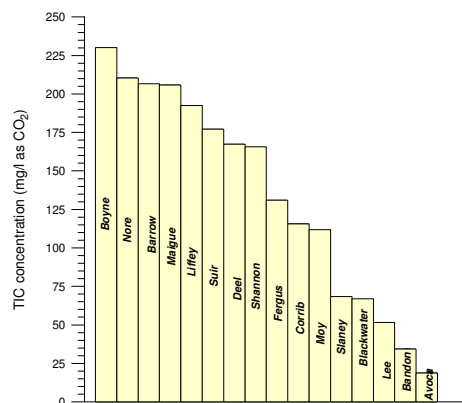


Fig 3 Estimated river TIC concentrations

The annual mass flux rates for species transported in river water are calculated as the product of mean concentration and annual flow volume. Based on the concentration data in Table 3 and the catchment hydrological data in Table 1, the calculated river flux rates for CaCO₃ and TIC are given in Table 4. The calculated catchment CO₂ uptake that enabled the dissolution of CaCO₃ is also given in Table 4.

The calculated post-precipitation CO₂ specific uptake rates (t CO₂/km².y) in the course of the runoff in the respective river catchments are plotted in bar chart form in Fig 4.

Table 4
 Annual runoff volumes and mass flux rates

River	CaCO ₃ flux (10 ³ t/y)	TIC flux as CO ₂ (10 ³ t/y)	CO ₂ uptake (10 ³ t/y)
Avoca	18.4	11.8	6.8
Bandon	35.8	22.8	12.3
Barrow	337.7	244.1	124.4
Munster Blackwater	278.1	188.2	97.9
Boyne	362.2	281.5	142.9
Corrib	535.3	381.6	193.8
Deel	52.0	38.9	19.7
Fergus	105.2	77.4	40.2
Lee	72.2	64.1	34.6
Liffey	143.6	109.3	55.5
Mague	139.8	107.0	54.3
Moy	261.6	216.7	112.6
Nore	339.7	284.7	145.1
Shannon	1387.9	1084.8	550.9
Slaney	112.0	80.7	42.4
Suir	480.3	429.6	219.1
Totals	4661.9	3623.2	1852.4

EVALUATION OF RESULTS

CO₂ Uptake

As chemical reaction (1) indicates, the carbonate species in natural waters result from the dissolution of solid phase calcium and magnesium carbonates by water containing free CO₂ in solution. Thus, the generation of dissolved carbonates is dependent on both the availability of free CO₂ in solution and the availability of solid phase carbonates. The amount of CO₂ in rainwater is unlikely to exceed 1 mg/l at normal precipitation temperatures (refer Fig 1). However, it would appear that in the course of its downward movement through soils the infiltrating rainwater absorbs large amounts of CO₂ from the

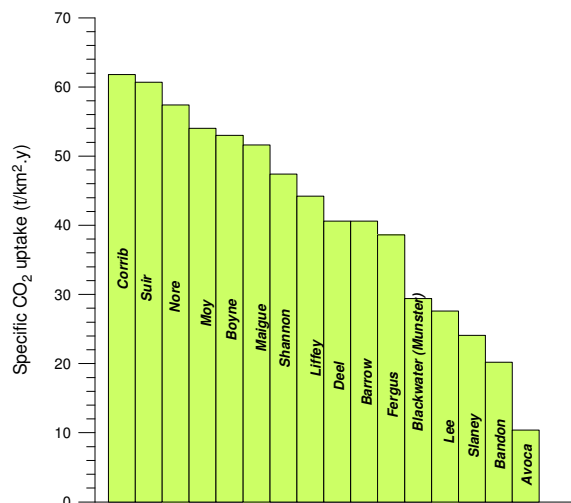


Fig 4 Calculated specific CO₂ uptake rate in Irish river catchments

CO₂-enriched soil atmosphere generated by microbial and root respiration. Some of this dissolved CO₂ reacts with solid phase carbonates thereby creating ionic carbonate species in solution, some is retained as free CO₂ and the remainder is desorbed back to the atmosphere. The foregoing analysis presents estimates of the sum of the free CO₂ retained in solution and that converted to ionic carbonate species (CO₂ uptake column in Table 4 and specific CO₂ uptake in Fig 4). The Corrib catchment exhibits the highest specific CO₂ uptake amounting to about 62 t/km².y, while the lowest specific uptake was found to be in the Avoca catchment at about 10 t/km².y. It is reasonable to surmise that the generation of CO₂ by microbial and root respiration is significantly in excess of these values as there is inevitably a substantial loss of CO₂ from the enriched soil atmosphere to atmospheric air. Lieth (1963) estimated maximum respiration rates for different vegetation types at steady-state condition. For a humid area with abundant vegetation in a temperate climate, such as a European forest, he estimated a specific respiration rate of 1500 t/km².y, while the amount produced by grassland he estimated to be in the range 100-200 t/km².y.

Where the uptake of CO₂ is low, as is the case in the Avoca, Bandon, Lee and Slaney rivers, the local geology would suggest the non-availability of solid phase carbonates in the catchments as the probable cause rather than a low availability of dissolved CO₂. There is no reason to presume that the level of microbial and root respiration is less in these catchments than in the catchments of the high alkalinity rivers. In this circumstance it might be expected that the free CO₂ in the low alkalinity rivers would be higher than in the high alkalinity rivers since much less CO₂ is consumed by reaction with solid phase carbonates. However, somewhat surprisingly, this appears not to be the case as examination of the calculated free CO₂ concentrations for the 16 rivers examined (Table 3) does not reflect such a trend. It would appear therefore that most of the CO₂ dissolved during infiltration is lost to the atmosphere in those catchments where it is not consumed by reaction with solid phase carbonates.

As the data in Table 3 indicate, bicarbonate (HCO₃⁻) is the predominant carbonate species, particularly in the high alkalinity rivers. It is also noteworthy that free CO₂ is at super-saturation in all the rivers with calculated concentrations ranging from 2 to 5 mg/l or some 3 to 7 times the saturation concentration at 10 °C (refer Fig 1). The carbonate ion (CO₃²⁻) concentration is a function of both pH and alkalinity, increasing as these parameter values increase. The calculated values for the rivers examined (Table 3) ranged from 0.02 mg/l in the low alkalinity Avoca river to 3.8 mg/l as CO₂ in high alkalinity Boyne river.

As indicated in Table 4, the 16 rivers in combination transport an estimated 1.85Mt (million tonnes) CO₂ of respiratory origin to sea annually. It is of interest to note that the estimated carbon flux for the

Shannon is 0.551 Mt/y (as CO₂), which is about twice the CO₂ emission saving due to the Ardnacrusha Hydro Power Station.

Leaching of calcium and magnesium carbonates

The uptake of CO₂ during the infiltration process enables the leaching of calcium and magnesium carbonates in catchments where ample sources are available resulting in hard alkaline river waters. The river waters are soft and of low alkalinity in catchments where such sources are scarce or absent. The mean river water hardness parameter values given in Table 2, although expressed as equivalent CaCO₃, are inclusive of both calcium and magnesium. The ratio of Ca:Mg in Irish river waters typically varies in the range 5% to 15% on a mg/l basis.

The estimated average mass leaching rate of calcium/magnesium carbonates in the 16 rivers reviewed varied in the range 28-171 t/km².y, the average rate across the catchments being 116 t/km².y. The overall annual mass flux is estimated to be some 4.66 Mt/y, much of which is presumably lost from soils and is therefore of environmental significance for soil fertility. The variation in specific leaching rate across the catchments is illustrated graphically in Fig 5. The Corrib catchment has the highest specific leaching rate (171 t/km².y) arising from a combination of fairly high average concentration (162 mg/l) and a very high specific runoff rate (1053 mm/y). The Boyne, Nore, Suir and Maigue, on the other hand, have significantly higher average hardness concentrations than the Corrib, but because of their lower specific runoff rates, their specific leaching rates (ca. 134 t/km².y) are lower than that of the Corrib.

It would appear that the catchment aquifers of the Avoca, Bandon, Lee and Slaney rivers contain very little leachable calcium and/or magnesium carbonates. For example, the estimated specific CaCO₃ flux for the Bandon is only about one third that for the Corrib, even though the two catchments have roughly the same specific runoff rate.

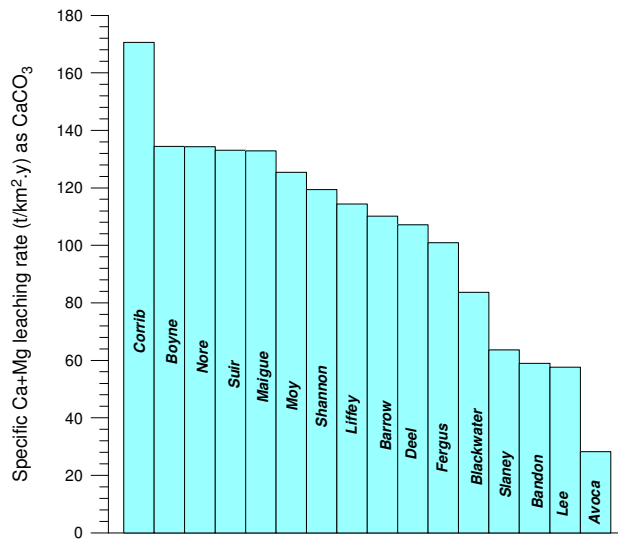


Fig 5 Calculated specific Ca + Mg leaching rates in Irish river catchments

Empirical parameter correlations

Empirical correlations of the parameters, *conductivity, hardness and alkalinity* provide a useful reference guide for technical personnel working in the general area of river water quality management and water supply treatment technology. Two such correlations for Irish river waters are presented in Appendix B.

Fig B1 illustrates the relationship between river water alkalinity (Alk) and hardness (H), which is quantified by the following empirical expression:

$$\text{Alk} = 0.37 H^{1.15}$$

where both parameters are expressed as mg/l CaCO₃.

Fig B2 illustrates the relationship between river water hardness (H) and conductivity (C), which is quantified by the following empirical expression:

$$H = 0.54(C-60)$$

where H is expressed as mg/l CaCO₃ and C is expressed as μS/cm.

The foregoing correlations are useful for the approximate general chemical categorization of river waters on the basis of conductivity measurements, which are relatively simple and inexpensive to carry out. They also provide a useful tool for checking analytical water quality data and identifying anomalies in data sets. However, it is emphasized that they are empirical approximations and, as such, due caution should be exercised in their analytical use.

IMPACT ON WATER SUPPLY USE

Surface waters are the main source of drinking water in Ireland, accounting for over 70% of the supplied volume. Hence, the carbon flux in Irish rivers has a major influence on the chemical composition of drinking water in Ireland. In particular, it affects the treatment processes that are required to convert raw river waters to drinking water quality and it also affects the chemical stability of the supplied water. In the water supply context, chemical stability is concerned with minimizing the reactivity of water relative to the materials with which it comes into contact between source and consumer. Ideally, it should not take any of these materials into solution nor should it precipitate any material from solution. The latter is particularly a problem with hard waters i.e. waters that have high concentrations of calcium and magnesium, which tend to precipitate hard scale deposits on pipe walls and in hot water systems. Stability criteria and water hardness are discussed in the following sections.

Chemical stability criteria

In the water supply context, chemically stable water is characterized by a minimal reactivity with the materials it contacts in the course of its delivery to the consumer. These materials may include concrete and cementitious materials, various plastics, metals including ductile iron, steel, lead, copper, brass, zinc coatings aluminium and other miscellaneous materials, used in distribution networks and domestic plumbing systems. It has been found (Mons et al., 2007) that water complying with the following criteria has a high level of chemical stability:

$$\begin{array}{ll} \text{pH:} & 8.2 > \text{pH} > 7.8 \\ \text{Saturation Index (SI):} & -0.2 < \text{SI} < +0.3 \\ \text{Ion balance:} & \{[\text{Cl}^-] + [\text{NO}_3^-] + 2[\text{SO}_4^{2-}]\} / [\text{HCO}_3^-] < 1 \end{array}$$

where [] indicates concentration in mmol/l. The Saturation Index (SI; also known as the Langelier Index) relates to the saturation status of the water with respect to CaCO₃; it is defined as follows:

$$\text{SI} = \log \left(\frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_s} \right) = \text{pH} - \text{pH}_s$$

where

K_s is the solubility product for calcium carbonate (refer Appendix A for value)
 pH_s is the saturation or carbonate equilibrium pH of the water based on its Ca²⁺ and HCO₃⁻ concentrations

The foregoing criteria, taken together, ensure that the corrosivity of water is minimized and its scale-forming potential is moderated to a satisfactory degree. The alkaline pH range in conjunction with a near to zero SI value results in a low free CO₂ concentration.

Chloride and sulphate ions are known to accelerate corrosion of ductile iron and steel. The third criterion above, which is applied in German water supply practice, is based on the assumption that carbonates are effective in counter-acting the corrosive influence of other commonly occurring aqueous anions such as chlorides, sulphates and nitrates.

It should also be noted that compliance with the foregoing pH and SI value ranges limits the feasible Ca²⁺ concentration and thus the hardness level as discussed in the following section.

Hardness

Calcium and magnesium ions are mainly responsible for hardness in water. They precipitate soaps, hindering lather formation and may also cause a hard scale in hot water distribution systems and boilers. Water hardness is generally expressed as equivalent CaCO₃ in mg/l. While there is no universally accepted classification of water hardness, the following is a typical classification:

0 –100 mg/l	soft
100 –250 mg/l	moderately hard
250 – 400 mg/l	hard
> 400 mg/l	very hard

Based on the hardness data in Table 2 and the foregoing categorization, the hardness classification of the rivers in this study is set out in Table 5. It should be noted that the hardness parameter values in Table 2 relate to locations near the freshwater limits of the rivers. This is of significance in the current context as, in general, the hardness of Irish river waters is found to increase with distance from source. Hence, for example, while the Liffey water is classified as a marginally hard water at its freshwater limit, it is in the moderately hard category in its middle reach (Leixlip Waterworks) and in the soft category at its upstream end (Ballymore Eustace Waterworks).

Table 5
 River hardness classification at freshwater limit
 (mg/l as CaCO₃)

Soft (<100)	Moderately hard (100-250)	Hard (250-400)
Avoca (29)	Corrib (162)	Barrow (286)
Bandon (54)	Deel (224)	Boyne (296)
Munster Blackwater (99)	Fergus (178)	Liffey (253)
Lee (58)	Moy (135)	Maigue (269)
Slaney (95)	Shannon (212)	Nore (251)
	Suir (198)	

A positive SI value indicates a potential to precipitate calcium carbonate, while a negative SI indicates a capacity to dissolve calcium carbonate. The calcium carbonate precipitation potential (CCPP), which is the actual CaCO₃ saturation concentration minus the CaCO₃ saturation concentration, is a useful complementary parameter to the SI value. The calculated values for these two parameters for the 16 river waters examined in this study are given in Table 6.

It will be noted that the soft river waters have a negative SI value and a capacity to dissolve additional CaCO₃, reflecting a low availability of solid phase carbonates in their catchments. The hard river waters, on the other hand, have positive SI values and significant super-saturation with respect to CaCO₃. The super-saturated state arises from the loss of free CO₂ (with an accompanying increase in pH) subsequent to CaCO₃ dissolution.

Table 6
 Calculated SI and CCPP values for river waters
 at the freshwater limit at temperature of 10 °C

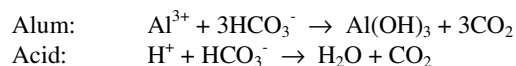
River	SI	CCPP (mg/l CaCO ₃)
Avoca	-2.0	-11.4
Bandon	-1.2	-9.1
Barrow	0.8	29.4
Munster Blackwater	-0.4	-4.4
Boyne	0.9	40.6
Corrib	0.4	7.3
Deel	0.7	19.7
Fergus	0.1	2.9
Lee	-1.1	-9.6
Liffey	0.8	27.8
Maigue	0.8	31.9
Moy	-0.1	-1.9
Nore	0.7	27.1
Shannon	0.6	16.3
Slaney	-0.6	-6.0
Suir	0.5	15.4

Water treatment

The treatment sequence used to convert surface waters to drinking water quality invariably includes a chemical coagulation process, the purpose of which is to convert colour and turbidity-causing solid matter in raw surface waters into non-colloidal suspensions that can be removed by sedimentation and filtration processes.

Aluminium sulphate (alum) is by far the most widely used coagulant in Irish water treatment practice. Alum coagulation is pH-sensitive. The optimum alum coagulation pH is typically found to be within the range 6.5-7.0. Research on Irish river waters (Chua, 1996) has shown that, in this pH range, there is efficient removal of the organic precursor material that may react with chlorine to form trihalomethanes (THMs), which are suspected carcinogens.

Alum reacts with water alkalinity, releasing free CO₂ and thereby reducing pH. Thus, for waters of moderate alkalinity it is economically feasible to achieve a satisfactory coagulation pH using alum on its own. For low alkalinity waters it may be necessary to add an alkali (such as lime, sodium hydroxide, sodium carbonate) in conjunction with alum to achieve the desirable coagulation pH range. For high alkalinity waters it may be economically advantageous to use a strong acid in conjunction with alum to achieve the desirable coagulation pH range. The reactions are as follows:



The amount of CO₂ released in reducing the pH to the optimum coagulation value depends on the pH and alkalinity of the raw water. This is illustrated in Fig 7 where the released CO₂ is plotted as a function of coagulation pH for a hard river water (Boyne), a moderately hard river water (Corrib) and a soft river water (Lee) - refer Table 2 for pH and alkalinity values at the river freshwater limit locations.

The chemical stabilization of water following chemical coagulation requires the removal of CO₂ to meet the pH and SI criteria as earlier defined. This is most commonly achieved in water treatment practice by the addition of lime (Ca(OH)₂) or soda ash (Na₂CO₃), both of which react with free CO₂ to form bicarbonate. Lime is the most widely used chemical for this purpose because of its effectiveness and relatively low cost. However, it is a difficult chemical to handle and accurately dose. In particular, it is not suitable for use where the raw water is already hard, as it adds to water hardness and makes it impossible to simultaneously satisfy the stabilization criteria in respect of the pH and SI values.

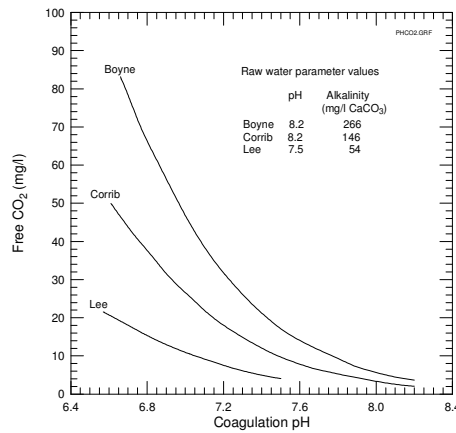


Fig 7 Calculated CO₂ release as a result of pH reduction due to chemical coagulation process reactions

While soda ash is widely used in water treatment, high concentrations of sodium ions in drinking water are considered to be hygienically undesirable because of potential adverse health impact on consumers with high blood pressure. In this regard it is pointed out that the intake of sodium in drinking water is generally a small fraction of the total daily intake of this ion.

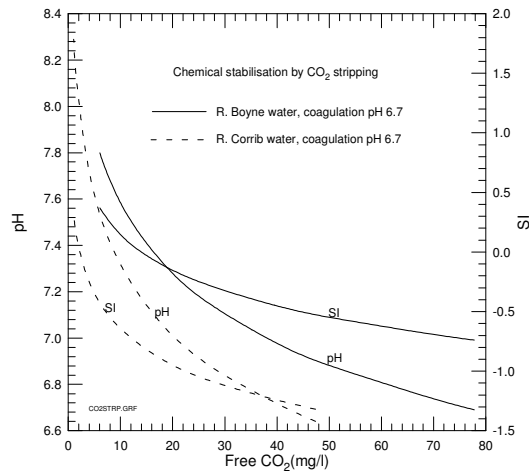


Fig 8 Chemical stabilization by CO₂ stripping

Stripping out of the excess CO₂ generated by chemical coagulation is a feasible alternative to the use of either lime or soda ash, particularly for hard waters where large amounts of CO₂ may be generated. The influence of CO₂ stripping on pH and SI value for the Boyne and Corrib chemically coagulated waters (Fig 7) is illustrated in Fig 8. The degree of super-saturation is the driving force for the stripping process. In the case of the Boyne water, the calculated CO₂ concentration at a coagulation pH of 6.7 is about 77 mg/l or about 100 times the equilibrium concentration relative atmospheric air at 10 °C.

DISCUSSION

The carbon flux in rivers is enabled by the passage of rainfall through CO₂-enriched environments during infiltration, resulting in the dissolution of a considerable mass of CO₂. The estimated carbon flux in Irish rivers, presented earlier in this paper, reflects the amount of CO₂ retained in solution,

mostly through conversion to ionic species by reaction with solid phase carbonates. The CO₂ lost to the atmosphere by natural stripping has not been quantified. However, the fact that there is no marked difference in free CO₂ concentrations between rivers with a low carbon flux (soft, low-alkalinity waters) and rivers with a high carbon flux (hard, high-alkalinity waters), provides strong evidence of the very considerable potential for natural stripping of CO₂ from surface waters. If the latter were not the case the low alkalinity rivers would have significantly higher free CO₂ concentrations than the high alkalinity rivers, assuming similar CO₂ environments in the catchment soils. The following parametric values for the Barrow river, which has a high TIC concentration, and a borehole water from the Barrow catchment, are of interest in this context.

Parameter	R. Barrow	Borehole
pH	8.1	7.12
Alkalinity (mg/l CaCO ₃)	230	377
Hardness (mg/l CaCO ₃)	286	428
Free CO ₂ (mg/l)	4	62
TIC (mg/l CO ₂)	205	395

The borehole water reflects the high availability of CO₂, presumably mainly of respiratory origin, for the dissolution of solid phase carbonates. In the above example the calculated amount of CO₂ required to deliver the TIC burden in the groundwater is roughly twice that required to deliver the TIC burden in the river water. Thus, even in a comparatively hard high-alkalinity river water, such as the Barrow water, there would appear to be a substantial loss of CO₂ from water to the atmosphere in the course of the runoff process. It is therefore concluded that the availability of solid phase carbonates in the geological formations in Irish river catchments is the critical factor in regulating the alkalinity and hardness levels in the river waters.

Fate of freshwater carbonates in the marine environment

The fate of river-borne carbonates in the marine environment is of considerable significance in view of the current environmental imperative to reduce carbon emissions. This is a complex issue, the full exploration of which is outside the scope of this paper. However, as discussed briefly in the following paragraphs, it would appear that, due the impact of increased atmospheric CO₂ on the carbonate system of the oceans, the carbon dioxide sequestered in the freshwater segment of the hydrological cycle remains as non-gaseous carbon species in the marine environment i.e. is effectively removed from the carbon cycle.

It is known that the largest reservoir of carbon is in the deep ocean, which contains close to 40,000 Gt C, compared to about 2000 Gt C on land, 750 Gt C in the atmosphere and 1000 Gt C in the upper ocean. The atmosphere, biota, soils and the upper ocean are strongly linked. The exchange of carbon between this fast-responding system and the deep ocean takes much longer (several hundred years) (Hadley Centre, 2007).

It has been observed that the carbon dioxide content of the atmosphere has increased from about 280 ppm to about 380 ppm since pre-industrial times (about 200 years ago). This increase has produced a corresponding increase in the amount of CO₂ absorbed by the oceans. It has been estimated (Royal Society, 2005) that the oceans have absorbed approximately half the CO₂ produced by fossil fuel production and cement manufacture. The resultant acidification has lead to an estimated reduction in the pH of the upper ocean of approximately 0.1 units. This reduction in pH has altered the carbonate balance, resulting in an increased TIC concentration and in a reduced CO₃²⁻ concentration.

It seems reasonable to postulate that a reduced CO₃²⁻ concentration in the upper oceans would permit an increased Ca²⁺ concentration, thereby tending towards an approximately constant ion product (IP). However, many factors influence the equilibrium concentration of calcium carbonate in seawater. The ion product at equilibrium or saturation concentration is defined as follows:

$$IP_{\text{sat.}} = [Ca^{2+}][CO_3^{2-}] = K'_{\text{SP}}$$

where K'_{SP} is the apparent solubility product, taking into account the influence of ion concentration on activity. The magnitude of K'_{SP} is influenced by temperature, salinity and pressure, increasing with both salinity and pressure and decreasing with temperature (Pytkowicz, 1969). The observed calcium carbonate profile in seawater is exemplified by the data listed in Table 7, which relates to a sampling location in the North Pacific.

Table 7
 Calcium carbonate saturation
 in seawater (Pytkowicz, 1969)

Depth (m)	IP/ K'_{SP}
0	2.3
190	0.61
468	0.62
753	0.59
1425	0.72
2262	0.74
3256	0.84
4499	0.73
7210	0.55

As the data in Table 7 show, the upper oceans are supersaturated with respect to calcium carbonate while there is an under-saturation of calcium carbonate in the deep ocean water.

It is evident that the potential exists for the removal of calcium carbonate from solution in the upper ocean by chemical precipitation and also by downward diffusion to under-saturated deep waters. Calcium carbonate is also removed by shell-forming marine organisms that depend on its availability at a super-saturation concentration for their survival.

In pre-industrial times, it would appear that an equilibrium condition obtained whereby the addition of calcium carbonate through river systems was balanced by its removal through the foregoing mechanisms. In such circumstances the sequestration of CO_2 in freshwater carbonates would have been effectively reversed when these freshwaters were discharged into the oceans. However, the reduction in the pH of the upper oceans through increased CO_2 uptake has increased the potential for retaining an increased Ca^{2+} concentration in solution and hence a permanent sequestration of CO_2 transported into the marine environment as freshwater bicarbonate. It is noteworthy that the same process, involving the reaction of granulated limestone rock and flue gas under aqueous conditions to produce bicarbonate, has been proposed (Rau et al, 2001) as a potential industrial scale process for the sequestration of the CO_2 produced by thermal power stations.

Thus, the carbon flux in Irish rivers may be regarded as a natural sequestration of CO_2 , the environmental significance of which may be gauged by its magnitude relative to the CO_2 released by anthropogenic sources. The estimated annual total emission of greenhouse gases (GHG) in Ireland in 2004 was 68.4 Mt CO_2 equivalent (EPA, 2006). As indicated in Table 4, the estimated average CO_2 sequestration in the 12 Irish rivers included in this study was calculated to be 1.85 Mt/y or about 2.7% of the national 2004 GHG emission.

It is also of interest to compare the CO_2 emission displaced by the generation of electricity from Irish renewable energy sources with the CO_2 amount sequestered in river discharge. For example, the average annual electricity output of the Shannon hydroelectric power station at the Ard na Crusha, which is located on the lower Shannon, is ca. 320 GWh (ESB, pers. com.), corresponding to a CO_2 saving of about 0.19 Mt (estimate based on a CO_2 emission from the conventional thermal plant mix of 600 t CO_2 eq/GWh (www.parliament.uk/post)). Thus, for the river Shannon the CO_2 saving through hydropower generation is about 35% of the river's estimated average annual natural sequestration of CO_2 (0.551 Mt, refer Table 4). Likewise, Irish wind power installations produced about 1790 GWh of electricity in 2007 (IEA, 2007), thereby displacing some 1.07 Mt of thermal CO_2 emission, which is about 58% of the estimated annual carbon flux in the twelve Irish rivers examined in this study.

While the carbon flux in rivers is small in the overall context of the carbon cycle, the associated alkalinity burden exerts a positive environmental influence in reducing ocean acidification, albeit to a minor degree.

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Appendix A Carbonate System Constants

Aqueous reactions



Carbon dioxide solubility

The concentration of free CO_2 in water is proportional to its partial pressure in air in accordance with Henry's law.

$$[\text{CO}_2] = K_H P_{\text{CO}_2} \text{ mol/l} \quad (\text{A4})$$

where K_H is the Henry's law constant and P_{CO_2} is the partial pressure (atm) of CO_2 in air.

At equilibrium, the ratio of $[\text{CO}_2]/[\text{H}_2\text{CO}_3]$ is about 631:1 (Snoeyink & Jenkins, 1980), hence it is convenient for computational purposes represent the sum of these two species by the hypothetical species H_2CO_3^* . Thus, equation (A4) becomes:

$$[\text{H}_2\text{CO}_3^*] \cong K_H P_{\text{CO}_2} \quad (\text{A5})$$

Dissociation constants for carbonate species

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = K_1 \quad (\text{A6})$$

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2 \quad (\text{A7})$$

Dissociation constant for water
$$[\text{H}^+][\text{OH}^-] = K_w \quad (\text{A8})$$

Calcium carbonate solubility

Calcium carbonate is poorly soluble in water, its solubility being defined by the equilibrium condition:

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_{\text{SO}} \quad (\text{A9})$$

Equations (A5) to (A9), inclusive, are used to calculate the distribution of the carbonate species in water. Two related composite parameters, namely total alkalinity (T_{alk}) and total inorganic carbon (TIC) are commonly used in such computations. They are defined as follows:

$$T_{\text{alk}} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \text{ eq/l} \quad (\text{A10})$$

$$\text{TIC} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \text{ mol/l} \quad (\text{A11})$$

The magnitudes of the dissociation and other constants are influenced both by the water temperature and ionic strength. Empirical expressions quantifying the temperature dependence of the carbonate system constants are given in Table A1.

Table A1
Temperature dependence of carbonate system constants
(Loewenthal and Marais, 1976)

Parameters: $pK = -\log(K)$; $t = ^\circ\text{C}$; $T = \text{absolute temp. (K)} = 273 + t$

$$pK_1 = \frac{17052}{T} + 215.21 * \log(T) - 0.12675 * T - 545.56$$

$$pK_2 = \frac{2902.39}{T} + 0.02379 * T - 6.498$$

$$pK_w = \frac{4787.3}{T} + 7.1321 * \log(T) + 0.010365 * T - 22.801$$

$$pK_H = 0.0138 * t + 1.12 \quad \text{for } t = 0 \text{ to } 35 \text{ } ^\circ\text{C}$$

$$pK_H = 0.0069 * t + 1.36 \quad \text{for } t = 35 \text{ to } 80 \text{ } ^\circ$$

$$pK_s = 0.01183 * t + 8.03$$

Ionic strength correction

The adjustment of the values of the constants to allow for ionic strength is conveniently made on the basis of conductivity, which is a readily measurable parameter. The following empirical relation between ionic strength (μ) and conductivity is taken from Snoeyink & Jenkins (1980):

$$\mu = 1.6 \times 10^{-5} \times \text{conductivity } (\mu\text{S/cm}) \quad (\text{A12})$$

The following ionic strength corrections for the foregoing equilibrium constants are taken from Fair, Geyer & Okun (1968).

$$pK_{1\mu} = pK_1 - (\mu)^{0.5} / [1 + 1.4(\mu)^{0.5}] \quad (\text{A13})$$

$$pK_{2\mu} = pK_2 - 2(\mu)^{0.5} / [1 + 1.4(\mu)^{0.5}] \quad (\text{A14})$$

$$pK_{SO\mu} = pK_{SO} - 4(\mu)^{0.5} / [1 + 3.9(\mu)^{0.5}] \quad (\text{A15})$$

$$pK_{w\mu} = pK_w - (\mu)^{0.5} / [1 + 1.4(\mu)^{0.5}] \quad (\text{A16})$$

Reaction kinetics

The foregoing relationships define the carbonate system in its equilibrium state. When this state is disturbed by the addition of a strong acid or a strong alkali, the resultant reactions proceed rapidly to completion with the exception of reaction (A1), involving free CO_2 and H_2CO_3 (Snoeyink & Jenkins, 1980), which proceeds at a slower rate than the others. As a consequence there may be an initial overshoot in pH change, while the $\text{CO}_2:\text{H}_2\text{CO}_3$ equilibrium is being re-established. This is because the $\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^-$ interchange is more rapid than the $\text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$ interchange. For example, in the alum-based chemical coagulation process, used to remove colour and turbidity in the production of

drinking water, Al^{3+} reacts with HCO_3^- to form H_2CO_3 , thereby reducing the pH. Following the addition of alum, the pH is likely to temporarily drop below the equilibrium value, to which it then gradually returns as the $\text{H}_2\text{CO}_3:\text{CO}_2$ equilibrium ratio is re-established.

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Appendix B

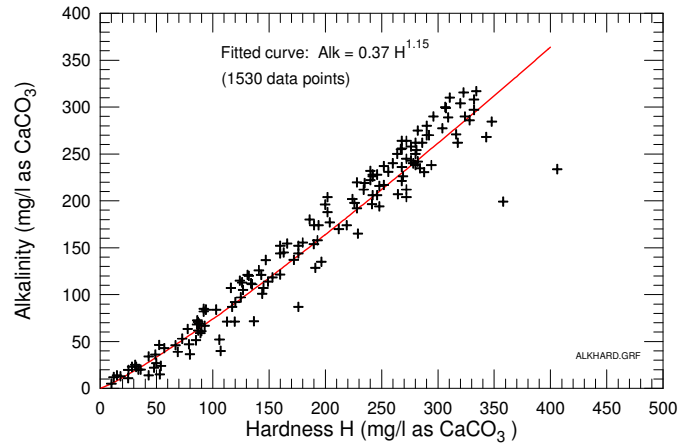


Fig B1 **Alkalinity/Hardness correlation for Irish river waters**
(Data source: Michael Neill, EPA Laboratory, Kilkenny)

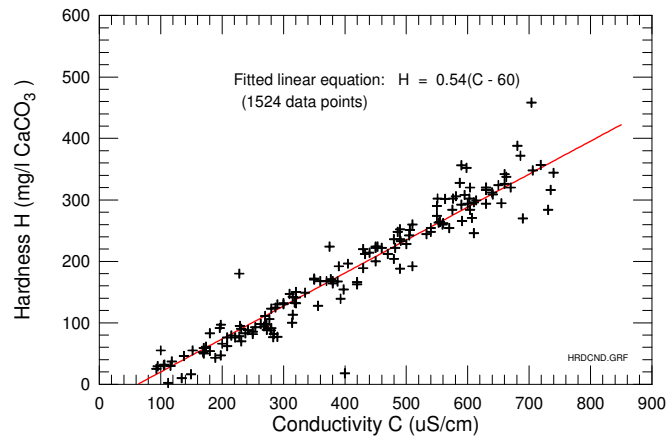


Fig B2 **Hardness/Conductivity correlation for Irish river waters**
(Data source: Michael Neill, EPA Laboratory, Kilkenny)