XL.—*On the Action of Air upon Peaty Water.*

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IN his paper on river water (*Chem. Soc. Jour.*, 1880, 295), Dr. Tidy contends that the peaty matter in running water is rapidly oxidised. He instances the water of the Shannon, which he alleges loses more than 38 per cent. of its organic elements by oxidation during a flow of only one mile, and the water supply of a town in the north of England, which, as appears from the analysis of two samples similarly loses 50 per cent. of its organic carbon during a flow of less than four miles through an open brickwork conduit.

* In this instance the precaution was not taken of passing the carbonic anhydride through the apparatus after the termination of the combustion for the same length of time as when expelling the air.

If peaty matter in solution in water possesses this extraordinary affinity for oxygen at ordinary temperatures, it cannot be necessary to appeal for proofs of it to large bodies of water, which are always more or less liable to alterations in the proportion of their organic elements, from other causes.

We have therefore studied, upon an experimental scale, the action of exceptionally strong peaty water upon atmospheric air, so as to ascertain how far air loses oxygen by contact with such water. For this purpose, we have submitted to eudiometrical analysis limited volumes of atmospheric air which had been exposed for periods of varying duration to the action of large volumes of peaty water from unpolluted mountain sources.

Before describing the results of these experiments, however, we will here interpolate two analyses of the same sample of unpolluted peaty water. The second was made after an interval of 70 days, the water having half filled a colourless glass bottle, 10 inches high, and $5\frac{3}{4}$ inches in diameter, closed only by a piece of thin filter paper, so as to exclude dust but secure a continued interchange between the internal and external air, if there should be any variation in the composition of the former. The bottle and its contents were freely exposed to the strongest daylight obtainable through a window about 12 feet square.

Results of Analysis expressed in parts per 100,000.

	Total solid matters.	Organic carbon.	Organic nitrogen.	Ammonia.	Nitrogen as nitrates and nitrites.	Total combined nitrogen.	Chlorine.	Hardness.	Remarks.
Composition of the peaty water used.	4.58	0.759	0.033	0	0	0.033	0.70	2.6	Yellow and turbid.
Ditto after exposure to air and light for 70 days.	4.26	0.718	0.026	0	0	0.026	0.70	2.7	Yellow and clear.

Thus after a free exposure of 70 days to air and light, in a stratum only 5 inches deep, this peaty water had suffered a loss of only 6 per cent. of its organic elements. We could not with certainty, however, attribute this loss to oxidation, because the water submitted to the first analysis was turbid, whilst that used for the second was clear, a slight brownish sediment having been deposited at the bottom of the bottle.

Effect upon Air of prolonged Exposure to Peaty Water in Daylight, but without Agitation.

These experiments were made upon air which had been in contact with comparatively large volumes of unpolluted mountain water (containing between 0·4 and 0·5 part of organic elements per 100,000), in accurately stoppered bottles for more than a year. The small quantity of air required for analysis was expelled by the injection of distilled water to the bottom of the bottles. The gases were collected, and their analyses performed over mercury.

I. Analysis of air which had been standing in contact with upland surface water from March 24th, 1879, to May 3rd, 1880 :—

	Pressure.	Temperature.
Original gas (dry)	204·5 mm.	17·7°
After absorption of CO ₂ (dry).	204·3 „	„
After admission of H (dry)	439·9 „	„
After explosion (dry)	312·4 „	„

These numbers correspond to the following percentages by volume :—

CO ₂	0·10
O	20·78
N	79·12
	<hr/> 100·00

The water, after admixture with the distilled water used to expel the air, still contained 0·354 part of organic carbon, and 0·069 of organic nitrogen in 100,000 parts. Originally the unmixed water contained 0·399 part of organic carbon, and 0·074 of organic nitrogen in 100,000 parts. It is the only one of the four samples used in this series of experiments, of which an initial analysis was made.

II. Analysis of air which had been in contact with upland surface water, from March 25th, 1879, to May 5th, 1880. The contents of this bottle were well shaken up several times during the 48 hours immediately preceding the examination of the air.

	Pressure.	Temperature.
Original gas (dry)	460·8 mm.	17·5°
After absorption of CO ₂ (dry)	460·1 „	„
Ditto new measurement for combustion (dry)	183·9 „	„
After admission of H (dry)	342·2 „	„
After explosion (dry)	227·2 „	„

The following percentages by volume are calculated from these readings :—

CO ₂	0·15
O	20·81
N	79·04
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	100·00

The water, after the addition of the distilled water, still contained 0·354 part of organic carbon, and 0·09 part of organic nitrogen in 100,000 parts.

III. Analysis of air which had been standing in contact with upland surface water, from March 26th, 1879, to May 7th, 1880. This bottle was nearly full of water, and consequently contained but very little air.

	Pressure.	Temperature.
Original gas (dry)	417·4 mm.	20·0°
After absorption of CO ₂ (dry).	416·6 „	„
Ditto new measurement for combustion (dry)	300·9 „	20·4°
After admission of H (dry) ..	509·0 „	„
After explosion (dry)	320·6 „	„

These numbers correspond to the following percentage volumes :—

CO ₂	0·19
O	20·83
N	78·98
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	100·00

After admixture of distilled water as before, the water contained 0·471 part of organic carbon and 0·075 part of organic nitrogen in 100,000 parts.

IV. Analysis of air which had been standing in contact with unpolluted mountain water, from April 17th, 1879, to April 30th, 1880 :—

	Pressure.	Temperature.
Original gas (dry)	536·0 mm.	18·1°
After absorption of CO ₂ (dry).	535·2 „	„
Ditto, new measurement for combustion (dry)	219·5 „	„
After admission of H (dry) ..	357·6 „	„
After explosion (dry)	221·1 „	„

From these numbers the following percentage volumes are calculated :—

CO ₂	0.15
O	20.69
N	79.16
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	100.00

100,000 parts of the mixture of original water and distilled water left in the bottle still contained 0.408 part of organic carbon, and 0.070 part of organic nitrogen.

All these results prove that the extent to which the peaty matter of the upland water was oxidised, in periods of more than a year, was very small indeed; for the carbon alone of the peaty matter in each bottle was more than sufficient to take up the whole of the oxygen from at least 100 c.c. of air, whilst, as the analyses show, not more than $\frac{1}{100}$ at the maximum, was removed from less than 1 litre of air.

Effect upon Air of Violent Agitation with Peaty Water.

For these experiments, bottles of about 500 c.c. capacity, with accurately fitting stoppers, were half filled with very strong peaty water, collected from a mountain bog, and containing in 100,000 parts, 2.912 parts of organic carbon and 0.168 part of organic nitrogen, but no ammonia and no nitric nitrogen. The stoppers were greased with resin cerate and carefully secured, and the bottles were kept in an inverted position throughout the whole course of the experiments. At the conclusion of each experiment, the air was expelled by distilled water, as before, and collected over mercury. Immediately before use 100 volumes of this peaty water contained, according to Mr. Frank Hatton's analysis, 2.01 volumes of air in solution, possessing the following percentage composition:—

CO ₂	1.99
O	31.96
N	66.05
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	100.00

V. Analysis of air which had stood over an equal volume of peaty water for 19 hours in darkness, with frequent agitation. Temperature about 18°. The water remained clear and unchanged in colour.

	Pressure.	Temperature.
Original gas (dry)	469.6 mm.	16.1°
After action of KHO (dry) ..	468.5 „	„
Ditto remeasured for combustion (dry)	354.8 „	21.4
After admission of H (dry) ..	595.7 „	„
After explosion (dry)	374.1 „	„

From these readings the following percentage volumes result :—

CO ₂	0·23
O	20·77
N	79·00
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	100·00

VI. Analysis of air which had been frequently shaken up with an equal volume of peaty water for 64 hours, viz., 30 hours in darkness, 28 hours in daylight, and 6 hours in sunlight. Temperature about 18°. The water remained clear and unchanged in colour.

	Pressure.	Temp.	Pressure.	Temp.
Original gas (dry) ..	424·0 mm.	20·0°	340·2 mm.	21·6°
After absorption of				
CO ₂ (dry)	422·9 "	"	339·5 "	"
Ditto remeasured for				
combustion (dry) ..	301·8 "	"	241·5 "	"
After admission of H				
(dry)	459·1 "	"	382·2 "	"
After explosion (dry).	270·5 "	"	231·2 "	"

These numbers denote the following percentage volumes :—

	I.	II.	Mean.
CO ₂	0·26	0·20	0·23
O	20·78	20·80	20·79
N	78·96	79·00	78·98
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	100·00	100·00	100·00

VII. In this experiment the bottle containing equal volumes of air and peaty water was securely tied to a wooden cradle, which was fastened to the connecting rod of a horizontal steam engine making 100 strokes per minute. Thus, in $10\frac{1}{2}$ hours, the contents of the bottle received 126,000 violent concussions. The engine was in a well lighted workshop, and for more than 9 out of the $10\frac{1}{2}$ hours the shaking took place in daylight. Altogether the contents of the bottle were 48 hours in darkness, $75\frac{1}{2}$ hours in daylight, and $8\frac{1}{2}$ hours in sunlight. The water was scarcely changed in colour, but it was slightly turbid when it came off the engine, and a very small quantity of dark brown sediment was rapidly deposited. The temperature near the engine was about 26° C., but during the rest of the time, it varied from 17° to 20°. An analysis of the enclosed air at the end of the experiment, gave the following results :—

	Pressure.	Temperature.
Original gas (dry)	405·0 mm.	17·3°
After absorption of CO ₂ (dry).	404·5 „	„
Ditto remeasured for combustion (dry)	289·0 „	„
After admission of H (dry)	478·9 „	„
After explosion (dry)	298·8 „	„

These readings correspond to the following percentage volumes :—

CO ₂	0·12
O	20·75
N	79·13
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	100·00

VIII. The next experiment was made with the view of testing the effect of an increase of temperature. The bottle and its contents were kept during the day as nearly as possible at a temperature of 30°, by being immersed in warm water contained in a clear glass vessel. During the night, however, the temperature fell to 16° or 17°. Altogether the contents of this bottle were 64 hours in darkness, 112 hours in daylight, and 16 hours in sunshine. The water at last was slightly turbid, and deposited a small quantity of a brownish sediment, but its peaty tint was not perceptibly affected. At the end of these periods a sample of air was withdrawn and submitted to analysis with the following results :—

	Pressure.	Temperature.
Original gas (dry)	395·5 mm.	21·9°
After absorption of CO ₂ (dry).	394·7 „	„
Ditto new measurement for combustion (dry)	279·8 „	20·1
After admission of H (dry)	438·8 „	„
After explosion (dry)	263·9 „	„

These numbers lead to the following percentage volumes :—

CO ₂	0·20
O	20·79
N	79·01
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	100·00

Effect upon Air of Violent Agitation with Waters free from Oxidisable Organic Matter.

For the sake of comparison we have extended these experiments to the deep well waters of the Kent and Colne Valley Companies, and to

organically pure distilled water. The small quantity of organic matter which these deep well waters contain having survived the oxidising effect of percolation through vast thicknesses of chalk, may be regarded as unattackable at ordinary temperatures by free oxygen. The Kent Company's water contains a large proportion of bicarbonate of lime, the hardness of this sample being no less than 26° , of which a large portion is temporary. The Colne Valley Company's water, on the other hand, having been softened by Clark's process, retained a hardness of only $3\cdot7^{\circ}$, and was presumably deprived of carbonic acid both free and combined. The organically pure distilled water was allowed to aërate itself by being put into a large beaker, covered with filter-paper to exclude dust.

The Kent and Colne Valley Company's waters actually used contained in 100,000 parts the following quantities of organic elements :—

	Kent.	Colne Valley.
Organic carbon.....	0·093	0·066
„ nitrogen.....	0·011	0·015

IX. Analysis of air which had been in contact with the Kent Company's water for 44 hours, the bottle having been in darkness for 16 hours, in bright diffused daylight for 22 hours, and in sunshine for 6 hours. The water remained bright and clear :—

	Pressure.	Temp.	Pressure.	Temp.
Original gas (dry) ..	296·8 mm.	20·0°	484·5 mm.	16·3°
After absorption of				
CO ₂ (dry)	296·1 „	„	483·2 „	„
Ditto, new measure-				
ment for combus-				
tion (dry)	296·6 „	„	290·7 „	„
After admission of H				
(dry)	462·6 „	„	446·6 „	„
After explosion(dry).	277·1 „	„	264·5 „	„

These readings correspond to the following percentage volumes :—

	I.	II.	Mean.
CO ₂	0·23	0·27	0·25
O	20·80	20·82	20·81
N	78·97	78·91	78·94
	100·00	100·00	100·00

X. Analysis of air which had been in contact with the Colne Valley Company's water for 63 hours, the bottle having been 24 hours in darkness, 35 in bright daylight, and 4 in sunlight :—

	Pressure.	Temp.	Pressure.	Temp.
Original gas (dry) ..	386·8 mm.	18·6°	—	—
After absorption of CO ₂ (dry)	386·8 „	„	—	—
Ditto, new measure- ment for combus- tion (dry)	257·2 „	17·0	278·0 mm.	20·6°
After admission of H (dry)	422·7 „	„	429·9 „	„
After explosion(dry).	260·9 „	„	255·0 „	„

These numbers express the following percentage volumes :—

	I.	II.	Mean.
CO ₂	0·00	—	—
O	20·97	20·97	20·97
N	79·03	79·03	79·03
	100·00	100·00	100·00

Like most deep well waters, the Colne Valley Company's probably arrives at the surface with mere traces of oxygen in solution; but if so, it had acquired its full complement of atmospheric oxygen before it was used for this experiment, since it scarcely withdrew an appreciable amount from the air with which it was shaken up. By undergoing Clark's softening process, however, this water is deprived of every trace of carbonic anhydride, and it can only, of course, reabsorb its full amount of this from the air with extreme slowness. Hence the air shaken up with this water was entirely deprived of its carbonic anhydride.

XI. Analysis of air which had been in contact with organically pure distilled water for 72 hours; the bottle was in darkness for 24 hours, in daylight 42 hours, and in sunlight 6 hours :—

	Pressure.	Temp.	Pressure.	Temp.
Original gas (dry) ..	479·0 mm.	19°	360·3 mm.	18·3°
After absorption of CO ₂ (dry)	478·6 „	„	359·9 „	„
Ditto, new measure- ment for combus- tion (dry)	342·0 „	19·8°	214·7 „	„
After admission of H (dry)	504·5 „	„	339·1 „	„
After explosion(dry).	289·2 „	„	203·9 „	„

These numbers give the following percentages by volume :—

	I.	II.	Mean.
CO ₂	0·08	0·11	0·10
O	20·97	20·97	20·97
N	78·95	78·92	78·93
	100·00	100·00	100·00

XII. Finally, a sample of air collected during the course of the experiments was submitted to analysis with the following results. An east or north-east wind prevailed during the whole time, and consequently the air at South Kensington had travelled across nearly the whole of London.

	Pressure.	Temp.	Pressure.	Temp.
Original gas (dry) ..	479.0 mm.	17.4°	734.4 mm.	18.1°
After absorption of CO ₂ (dry)	478.6 „	„	733.7 „	„
Ditto, new measure- ment for combus- tion (dry)	338.3 „	17.8	335.1 „	18.3
After admission of H (dry)	536.8 „	„	481.9 „	„
After explosion (dry).	324.1 „	„	271.1 „	„

These numbers give the following percentages by volume :—

	I.	II.	Mean.
CO ₂	0.08	0.09	0.09
O	20.94	20.95	20.94
N	78.98	78.96	78.97
	100.00	100.00	100.00

In the experiments with strong peaty water, the volume of air (corrected to 0° C.) contained in each bottle was 234.5 c.c., and from this the organic carbon alone in the water (0.00728 gram) would remove, during complete oxidation, 0.0194 gram or 13.5 c.c. of oxygen, leaving the residual air with only 15.1 per cent. of oxygen. Even a superficial inspection of the foregoing analytical numbers proves that in the most successful experiment in which the water travelled 20.4 miles in 10½ hours, whilst undergoing the most violent agitation with the enclosed air, there was but a very slight reduction of the proportion of atmospheric oxygen. Even in this instance, however, it is extremely unlikely that the oxygen thus absorbed was applied exclusively to the conversion of a minute fraction of the peaty matter into carbonic acid and water, and it is therefore almost certain that no trace of organic matter was really destroyed or “burnt up.” Such portions as were attacked by the oxygen were only transformed into more highly oxidised forms of organic matter. Hence it follows that the slight excess of carbonic anhydride found in the residual air was derived from dissolved gases in the water and not from the organic matter, and this conclusion is confirmed, first, by the fact that in Experiments Nos. V, VII, and VIII, in which, as we shall show, the merest traces of oxygen were absorbed, the carbonic anhydride found in the residual air was even slightly greater than in Experiment VIII;

and secondly, because in Experiment IX, with the Kent Company's water, which certainly contains no spontaneously oxidisable organic matter, the proportion of carbonic anhydride found in the residual air was quite as high as in any other case.

Rejecting then the carbonic anhydride from the analytical results as of no import, we have the following proportions of oxygen and nitrogen in the residual air of the bottles and in the atmosphere of the laboratory in which all the experiments were conducted:—

	I.	II.	III.	IV.	V.	VI.
O	20·80	20·84	20·87	20·73	20·82	20·83
N	79·20	79·16	79·13	79·27	79·18	79·17
	100·00	100·00	100·00	100·00	100·00	100·00
	VII.	VIII.	IX.	X.	XI.	XII.
O	20·77	20·84	20·87	20·97	20·98	20·96
N	79·23	79·16	79·13	79·03	79·02	79·04
	100·00	100·00	100·00	100·00	100·00	100·00

If we compare the percentage amounts of oxygen found in the different samples of air which had been in contact with peaty water with those found in the air which had been similarly shaken up in the Kent and Colne Valley Companies' waters, and in the organically pure distilled water, and lastly with the percentage of oxygen in the air of the room in which the experiments were made, it is evident that minute quantities of oxygen have been absorbed by nearly all the samples of peaty water; but even in an extreme case, viz., the one in which the sample travelled more than 20 miles on the connecting rod of a steam-engine making 100 strokes per minute, the amount of oxygen absorbed by 250 c.c. of extremely peaty water was only 0·345 c.c., which is scarcely $\frac{1}{39}$ of that required for the complete oxidation of the organic carbon alone; or, in other words, only $2\frac{1}{2}$ per cent. of the organic matter was oxidised. Even this result is arrived at by the most favourable assumption, viz., that the whole of the oxygen taken up was employed in the oxidation of organic matter; but we have seen that even the Kent and Colne Valley Companies' waters absorbed oxygen, although they probably did not apply it to such a purpose. If we take only the oxygen absorbed by the peaty waters in excess of that taken up by these waters which probably contain no oxidisable organic matter, then only 1·6 per cent. of the organic matter could have been oxidised in the steam-engine experiment.

We conclude therefore that if peaty matter dissolved in river water is spontaneously oxidised at all (of which we consider there is as yet no sufficient proof), the process takes place with extreme slowness,

and cannot be accomplished to any considerable extent in the flow of a river: for our results show that peaty matter is even less oxidisable than animal matters under the same conditions.

During the experiments we noticed a considerable precipitation of brown peaty matter when the strong bog drainage was mixed with a comparatively small bulk of distilled water. We intend to investigate the cause of this precipitation, which promises to throw light upon the amelioration in peaty waters which has been observed by Mr. Bateman and other engineers.