Wohlmann, water and whisky

Peter Hodder

Hodder Balog Social and Scientific Research, Wellington and Victoria Business School, Victoria University of Wellington (email: *peterh@hodderbalog.co.nz*)

Introduction

Bottles of Lemon & Paeroa on supermarket shelves and television advertisements that include pictures of bathers in hot pools are the legacy of a nineteenth century Government initiative to exploit the numerous occurrences of geothermal springs as spas in the European tradition: bathing in hot waters and drinking cooled waters for the relief and possible cure of a variety of ailments. Central to this initiative was the appointment of Arthur Stanley Wohlmann in 1902 as the Government balneologist (Fig. 1).[1] His first task was to undertake a survey of New Zealand's hot springs in order to determine which might be most effectively used (Table 1).[2]

Fig. 1. A.S Wohlmann. Appointed as Government balneologist in 1902, he was responsible for chronicling the chemical composition and alleged curative properties of New Zealand's hot springs. He is particularly remembered for his work in developing Rotorua as a spa town. Although he may have intended Rotorua to rival the spas of Europe, the reality was different: Rotorua, Te Aroha and Hamner instead provided an impetus to the fledgling tourism industry. [Photo: *New Zealand Illustrated Magazine*, vol. 7, issue 1, 1 October 1902, p. 4. Used with permission.]

Immersion in the waters

Ultimately the three occurrences of hot water that were identified as suitable for spa purposes were Rotorua and Te Aroha in the North Island and Hanmer Springs in the South Island, of which Rotorua attracted most of the investment.[3] All were used for bathing, but it remains un-

Table 1. The range of thermal waters investigated and classified by A.S. Wohlmann, Government balneologist [2]

Class	Description	Essential chemistry	No. of waters investigated
Simple thermal waters		Weakly mineralized	15
Muriated[a] waters		Chloride (Cl^-)	
I	Sodic muriated waters	Sodium (Na^+), chloride (Cl^-)	13
II	Calcic sodic muriated waters	Calcium (Ca^{2+}), Na^+, Cl^-	11
III	Iodide muriated water	Iodide (I^-) 25 grains per gallon (0.036 $g.litre^{-1}$), generally shown by the presence of iodine gas (I_2)	27
IV	Magnesic sodic muriated water	Magnesium (Mg^{2+}), Na^+, Cl^-	1
Simple alkaline waters[b]		Sodium bicarbonate (Na^+, HCO_3^-)	2
Muriated alkaline waters		Na^+, Cl^-, HCO_3^-	2
Muriated sulphated waters		High in Cl^-, with moderate Mg^{2+} and SO_4^{2-}	1
Chalybeate waters		Iron (Fe^{2+}), HCO_3^- and CO_2 gas; only 6 of the 30 occurrences have all three components	30
Sulfur waters			
I	Alkaline sulfur[c]	High dissolved silica ($SiO_{2(aq)}$)	21
II	Acid sulfur[d]	Less dissolved silica; acidic because of sulfuric acid (H_2SO_4)	3 of 'innumerable'
III	Muddy waters	Quartz, amorphous silica, little feldspar; mud also contains 5 grains of gold and 6 dwt (24 grains) of silver per ton	unspecified
Arsenical waters[e]			unspecified
Borated waters[f]		Na^+, borate	3
Mercurial[g]		Associated deposit contain globules of mercury	1
Minimum total of waters investigated			130

[a] Muriatic acid is an old name for hydrochloric acid; thus, 'muriates' are 'chlorides'
[b] Typical of Te Aroha
[c] Typical of Rachel Spring, Rotorua
[d] Typical of numerous springs in Rotorua, Wairakei, and Waiotapu
[e] Only on White Island, although later found at Te Aroha
[f] Typical of Hanmer, where the concentration of sodium borate was reported as five times that in similar waters elsewhere; also later found at Te Aroha (see text)
[g] Only at Ohaewai, in Northland

certain whether the specific composition of the water or simply the fact that the waters were warm was responsible for the waters' alleged curative properties when a human body afflicted by one or more of a wide range of medical conditions was immersed in the water.

As an example, there were suggestions that the waters in particular springs at Te Aroha were useful in relieving specific ailments: for example, water from Spring No. 8 "would relax the bowels", while water from Spring No. 15 would "confine" them; water from No. 2 bath was allegedly helpful in cases of rheumatic fever, while water from No. 3 bath was said to be helpful for eczema. However, it is difficult to find any single chemical characteristic of these waters (Table 2) that justifies these particular therapeutic claims.

Despite initial claims about the therapeutic value of bathing in hot water, until well into the 20th century, the spas were effectively under the control of the Tourist Department for most of their existence, and ultimately it was their recreational and tourist use that ensured their survival, whether under the control of local bodies or under private management.

Drinking the waters

The waters from Te Aroha were and are pleasant enough to drink (Fig. 2). Indeed, it was advertised by its bottler – Hancock and Company – as the 'autocrat of the dinner table'. Because the acidic water at the Rotorua baths was not drinkable, Te Aroha water was sold at the baths for a penny a cup, and a shilling a bottle at the nearby Grand Hotel.[3] As well as chronicling the attendance at the baths, particularly at Rotorua, Te Aroha and Hanmer, sales of bottled Te Aroha water – some of which was exported to Australia – were reported annually by the Government Balneologist for a decade from 1926 to 1936 (Table 3). Drinking the waters was essentially the lifeline for Te Aroha, since there was never sufficient water available either from the natural springs or as a result of drilling for a large bathing establishment.[4]

Fig.2. The gazebo built for No. 15 Spring at Te Aroha: "View of a man and two children in the summer house, a wooden gazebo with a thatched roof, at the `No. 15' mineral spring in the Government Tourist Domain at Te Aroha. A hand pump for providing drinking water is in the centre, with a sign above it that reads: `The public are warned against removing mineral water in bulk or using it at the spring for other than drinking purposes / by order'. Photograph taken circa 1910s, by Frederick George Radcliffe." [Photo: Alexander Turnbull Library, Ref.: 1/2-006352-G]

Wohlmann made copious comments about the suitability of the waters he encountered as potentially useful as medicinal waters, and as table waters, many of which have been reported in later works.[3]

Rather more recently, a classification scheme for the taste of mineral waters has been developed based on the contribution of six 'concepts': 'balance' ('carbonation', effectively the amount of CO_2),[5] 'virginality' (NO_3^-), 'minerality' (total dissolved solids), 'orientation' (pH), 'hardness' (Ca and Mg), and 'vintage'(age).[6] For geothermal waters obtained from wells or fast-flowing springs, the concentration of nitrate is expected to be very low.

Table 2. Composition of selected waters at the Te Aroha spa [11]

	Bath No. 2	Bath No. 3	Spring No. 8	Spring No. 15
	Concentrations (in grains/gallon)			
$NaHCO_3$	426.29	429.19	451.97	331.76
NaCl	60.45	60.51	66.14	43.11
KCl	1.90	Trace	1.96	-
Na_2SO_4	32.67	32.82	32.91	22.16
$CaCO_3$	7.12	7.24	7.47	6.91
$MgCO_3$	4.21	4.20	4.21	3.61
silica	7.12	7.21	8.60	7.05
Al, Fe	Trace	Trace	Trace	Trace
Sum	539.76	541.17	573.26	414.60
Temperature (°F)	112	90 – 112	109	139

Table 3. Number of bottles of No. 15 spring water from Te Aroha sent to Rotorua and sold there, 1926-1936

Year	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936
No. of bottles	196	138	96	80	78	62	50	46	44	51	42
*Data from *Appendices to the Journal of the House of Representatives*											

Thus, the influence of 'virginality' on their taste can be ignored. Moreover, most geothermal waters are hundreds to thousands of years old, so 'vintage' can also be ignored. The modern chemical compositions of a selection of geothermal waters considered by Wohlman to be particularly suitable as 'table waters' are mapped against balance, minerality, orientation and hardness concepts in Table 4.[7] Of these 'concepts', balance, minerality and orientation are the characteristics of water believed to be most responsible for its taste, these three 'concepts' contributing 75%, 20%, and 5% to the taste respectively. The geothermal waters in Table 4 are shown on a 'balance' versus 'minerality' grid (Fig. 3). This grid shows that most of the waters contain high concentrations of total dissolved solids, and that they collectively encompass a wide range of dissolved carbon dioxide concentrations.

In a few cases, more exotic chemical components in or associated with the geothermal waters were identified and promoted. Wohlmann prescribed several glasses of 'radioactive water' each day for some visitors to Rotorua. However, the radioactivity was not derived from the geothermal water itself; rather, water was irradiated with radon derived from the decay of a small amount of radium bromide, rather than being naturally radioactive.[8] In fact, the water from Te Aroha, which as mentioned above, was sold in Rotorua, could have been used instead, since it was found to be naturally radioactive in 1911: the radium content of Spring No. 8 being cited as 1.0×10^{-14} g cm^{-3}, and that of Spring No. 15 as 3.1×10^{-14} g cm^{-3}, respectively.[9] As analytical techniques improved other potentially harmful chemical elements were identified, which began to cast doubt on the advisability of drinking these waters. Prominent among these was boron. For example, analysis of the water at Te Aroha indicated that it contained significant boron and arsenic,[10] and a sign was later erected advising against drinking it.[11]

Among the warm and hot springs visited by Wohlmann, 27 were noted as containing iodine. In his particular classification of waters, these were "Class III – Iodide muriated waters"; and of the iodide in them he noted that there was "seldom more than 2.5 grains per gallon, but even this small quantity exceeds the amount present in most similar European waters".

In Wohlmann's time the therapeutic value of iodine for the thyroid was recognised, if not understood, and he further speculated that if the waters containing iodide had any benefit, it was because of iodine rather than iodide:

"There remains the possibility, however, that the essentially active factor is not the iodide, but the free nascent iodine which is almost always present. The pungent smell of the mineral may generally be detected for some distance around the source of an iodide spring, and where the thermal water is broken up by a fall into a spring or douche, under which circumstances free iodine seems to be liberated, the odour is particularly strong. It is conceivable that apart from the iodine that is taken into the system

Balance (as CO_2)	Super low	Low	Medium	High	Very high
Still					
Effervescent		❼	❾		❸❺
Light					
Classic			❹		❷
Bold				❽	❶❻❿
	Minerality (as total dissolved solids)				

❶ Te Aroha (Mokena well) – "the autocrat of the dinner table"; ❷ Morere (spring), East Coast of North Island; ❸ Waiwera (well), Auckland, said by a visiting doctor to be "not disagreeable, resembling diluted Wiesbaden water"; ❹ Okauia – Crystal Springs, Matamata, of which Wohlmann noted this water was 'Without medical value" but "would make an excellent and palatable table water"; ❺ Parakai (well), Auckland; ❻ Kamo, Northland, of which Wohlmann noted that the water was "foaming with a fierce effervescence of gas"; ❼ Sapphire (well), near Tauranga, of which Wohlmann commented, "the fairly neutral water could be bottled as excellent table water"; ❽ Paeroa (well), now combined with lemon juice or extract to make Lemon & Paeroa; ❾ Jerusalem (spring), proxy for Pipiriki Spring, Whanganui River; ❿ Puriri (spring), Coromandel Range, from which water was shipped to Auckland in kegs, bottled by Campbell & Ehrenfried and sold until the 1960s.

Fig. 3. Minerality *vs* balance for a selection of geothermal waters considered by Wohlmann to have potential as table waters.

Fig. 4. Left: Hatrick's Accommodation House at Pipiriki, *ca.* 1900. [Photo: Alexander Turnbull Library, Ref: 1/1-020952-G used with permission]. ***Right:*** The paddle steamer 'Waimari' and passengers, on the Whanganui River, below Pipiriki, *ca.* 1900. [Photo: Alexander Turnbull Library, Ref: PA1-q-014-4405 used with permission].

Table 4. Masha's 'concepts' for fine drinking waters applied to selected New Zealand geothermal waters

Mascha's 'Concept'	Chemical characteristic			Selected North Island geothermal waters identified with potential for medicinal purposes or table waters*									
				Te Aroha ❶	*Morere* ❷	*Waiwera* ❸	*Okauia* ❹	*Parakai* ❺	*Kamo* ❻	*Sapphire* ❼	*Paeroa* ❽	*Pipiriki* ❾	*Puriri* ❿
Balance	Carbonation*	***Category***	***CO_2† /(mg.l^{-1})***										
		Still	0										
		Effervescent	0-2.5			0.07		0.76		1.87		1.03	
		Light	2.5-5.0										
		Classic	5.0 -7.5		6.06		7.54						
		Bold	>7.5	56.3					54.2		1676		514
Minerality	Total dissolved solids	***Category***	***TDS‡/(mg l^{-1})***										
		Super low	0-50										
		Low	50-250							97.5			
		Medium	250-800				336					766	
		High	800-1500								1452		
		Very high	>1500	7249	26074	1933		1532	1635				4707
Orientation	pH	***Category***	***pH-range***										
		Acidic	5.0-7.0								6.29		
		Neutral	6.7-7.3		6.95				6.73				
		Hint of sweet	7.3-7.8										7.30
		Alkaline	7.8-10.0	8.03		8.57	7.84	7.83		7.88		8.78	
Hardness	Calcium and Magnesium	***Category***	***Hardness#/(mg l-1)***										
		Soft	0-17.1									7.27	
		Slightly hard	17.1-60.0	28.6						53.3			
		Moderately hard	60-120			108	79.8						
		Hard	120-180					134.8					
		Very hard	>180		6328				804.5		937		404

Notes to Table 4

*For further details of these waters, see legend to Fig. 3.

†CO_2 calculated from $a_{H2CO3}/a_{HCO3-} = a_{H+}/K_1$, using K_1 values extrapolated and interpolated for values given in Drever (1982, p. 36) for the temperature range 0 – 50°C, assuming a logarithmic relationship between log K_1 and temperature

‡TDS calculated as the sum of concentration of cations Na^+, K^+, Ca^{2+}, Mg^{2+}; plus sum of concentration of anions SO_4^{2-}, Cl^-, and half of the concentration of HCO_3^-

#Hardness of water is calculated as {[Ca (in mg.l^{-1}) x 2.5] + [Mg (in mg l^{-1}) x 4]}

when the water is drunk, quite an appreciable amount, and that in a highly active condition, may be inhaled with the water vapour and spray by the bather."[2]

At the request of the firm A. Hatrick and Co., which operated river steamers on the Whanganui River, Wohlmann investigated a hot spring near Pipiriki, recommending the water as a medicinal drinking water because of the presence of iodine. This information was used by Hatrick in 1906 to recommend to the Government that he erect a bath-house at the spring at his own expense and contribute to the cost of extending a nearby track to improve access. An extract from the Report on Scenery Preservation for 1907-1908 indicates that his request had fallen on responsive ears: "A spring of water near to Pipiriki on the banks of the Wanganui River was taken under the [Public Works] Act and has now been leased to Mr Hatrick, owner of the Pipiriki Accommodation House, who has by the terms of his lease, to keep it in order and erect a suitable drinking-fountain and bath-house thereon, which the public, on payment of a small charge can use. This will considerably popularize the spring which hitherto has been little known." [12] In fact, Hatrick did just that: the spring was advertised as a two-mile walk or boat-ride up-river along 'the Rhine of Maoriland' from his accommodation house (Fig. 4)[13], and by the 1930s, posters promoted Pipiriki as important a tourist destination as the Chateau Tongariro and Waitomo Caves.[14] Wohlmann's findings were highlighted in Hatrick's advertisements, an example of which is reproduced as Fig. 5. At the high pH of the Pipiriki Spring water (pH 8.78),[7] the iodine is expected to be in the form of IO_3^- rather than I^-, and little I_2 would be expected on the basis of the Eh-pH diagram of Fig. 6.[15]

Morere Springs on the East Coast of the North Island contains 1700 times the amount of iodide present in seawater: it "made the water so brown that bathers often thought it wasn't clean. People suffering from goitre drank Morere's special water; it was also drunk for the last stages of syphilis. The waters are now used for less desperate purposes."[3] The lower pH of these waters (viz., 6.95),[7] means that the brown colour is unlikely to be caused by iodine dissolved in the water if the Eh-pH diagram for iodine under standard conditions is considered valid (see Fig. 6); but may result from the reaction $I_2 + I^- \rightarrow I_3^-$.

Although Morere Springs are somewhat unusual among geothermal springs in that they contain methane (which was used in gas lighting for the bath-house), natural gas seeps are common along the East Coast of the North Island.[16]

Whisky and water

A recent study has found that mixing iodide-containing water with whisky does affect its taste.[17] Wohlmann made no comment about this, but he did note that water from Paeroa, 'blackened whisky', presumably on the basis of an experiment. He attributed this 'blackening' to the iron content of the water, going on to comment, "I am afraid that the universal use of tea in the Colony makes the demand for such a water very limited".[3] This comment may seem strange until it is realised that water with a high iron content turns black when mixed with tannin-containing tea, coffee, or alcoholic beverages.[18] This includes whisky

PIPIRIKI
Thermal Spring
BATHS.

Towels and Keys for Bath Rooms can be obtained from the Manager, Pipiriki House.

ANALYSIS OF WATER.

Sodium Chloride		121·88
Potassium Chloride	Traces	·52
Magnesium Iodide	Traces	
Calcium Sulphate		1·88
Aluminium Chloride		1·22
Sodium Carbonate		·48
Magnesium Carbonate		2·22
Silica		2·41
Total Solids		130·61

Dr. Wohlmann, Govt. Balneologist, states:

"Taken in regular doses, and on an empty stomach, it would act as a very gentle tonic in certain forms of Dyspepsia, by cleansing the stomach, and stimulating the gastric and intestinal mucous membranes. For internal administration the water is specially adapted. For this purpose it should be taken fresh at the spring before the three principal meals, the walk back to Pipiriki afterwards being rather an advantage, except in debilitated subjects. Aerated it should make an excellent table water.

The small amount of Silica present is an especial advantage in a country where most of the mineral springs are too Siliceous. The water would be classed as 'muriated' the chief constituent being Sodium Chloride; but the small quantity of Magnesium Iodide present is of much more importance than would be indicated by the analysis, as this Iodide tends to decomposition at the source, with the consequent liberation of free Iodine. Iodide in this 'nascent' condition has more powerful properties than in its ordinary state."

THERE IS A DRINKING FOUNTAIN AT THE SPRING
Also Bathrooms for Ladies and Gentlemen.

A. HATRICK & Co.,
Proprietors Wanganui River Steamer Fleet.

Fig. 5. Advertisement for Pipiriki Thermal Springs (National Archives, Ref. No. T0164, Item Ref. No. 1906/314). The second paragraph of Wohlmann's statement in the advertisement also featured in 'Advance Wanganui River', *Wanganui Herald* (1907, November 20).

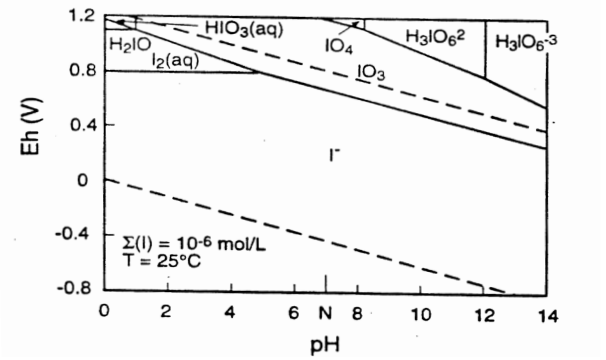

Fig. 6. Eh-pH diagram for iodine at 25°C .[15]

because even though iron-free calcium-bearing waters are sought in the making of the beverage,[19] it is generally aged in wooden barrels, from which tannins enter the whisky.

The modern-day Lemon and Paeroa carbonated soft drink contains 160 mg kg-1 of sodium,[20] similar to the natural Paeroa spring water.[7] It also has lemon juice or lemon extract added. Adding strong tea to modern-day Lemon and Paeroa produces no 'blackening', suggesting that it is either not made from the natural Paeroa water, or that it is made from the Paeroa water from which the iron has been removed. Of course, had the experiment worked, the black material made from the combination of tannins and irons would have been gall ink[21] and could have been used in the writing of this article, had a computer not been available.

References

1. Johnson, R.H. *Medical History* **1990**, *Suppl. 10*, 114-126.
2. Wohlmann, A.S. *The Mineral Waters and Health Resorts of New Zealand*, 4th edition. Government Printer: Wellington, 1914.
3. Rockel, I. *Taking the Waters: Early Spas in New Zealand*. Govern-

ment Printing Office: Wellington, 1986.

4. McClure, M. *Wonder Country – Making New Zealand Tourism*. Auckland University Press: Auckland, 2004.
5. Drever, J.I. *The Geochemistry of Natural Waters*. Prentice-Hall, Englewood Cliffs, 1982, pp. 35-38.
6. Mascha, M. *Fine Waters: a Connoisseur's Guide to the World of Premium Water*.; see: http://www.finewaters.com (accessed 20 January 2014).
7. Reyes, A.G.; Christenson, B.W.; Faure, K. *J. of Volcanology and Geothermal Res.* **2010**, *192*, 117-141.
8. Priestley, R. *Mad on Radium: New Zealand in the Atomic Age*. Auckland University Press: Auckland, 2013, pp.2-3.
9. MacLaurin, J.S. *NZ Dominion Laboratory 44th Annual Report* **1911**, *Appendix*, 63-70.
10. White, D.E.; Hem, J.D.; Waring, G.A., 'Chemical composition of sub-surface waters', Chapter F in Fleischer, E. (ed.), *Data of geochemistry*, 6th edn., *Geological Survey Professional Paper*, *440-F*, F48, 1963.
11. Wells, K. *A postcard from Te Aroha. An account of taking the waters at Te Aroha's Hot Springs Domain*. Polygraphia: Auckland, 2003.
12. 'Pipiriki Thermal Springs. National Archives Ref. No. T0164, Item Ref. No. 1906/314, File title: Pipiriki Thermal Springs, 1906-1908.
13. 'A Hatrick & Co. : Timetable, subject to alterations without notice and circumstances permitting. Steamers, New Pipiriki house; What to do at Pipiriki' (*ca.* 1912), Alexander Turnbull Library**,** Ref.: Eph-A-TOURISM-Wanganui-1912-01-outside.
14. 'The 3 big tourist attractions of the North Island' – Waitomo Caves, Pipiriki and Chateau Tongariro, Advertisement by Newman Bros, New Plymouth (1931), Alexander Turnbull Library, Ref.: Eph-C-TOURISM-North-Island-1931-01.
15. Ticknor, K.V.; Cho., Y.H. *J. Radioanal. Nuc. Chem*. **1990**, *140*, 75-90.
16. Field, B.D.; Uruski, C.I.; *et al. Institute of Geological and Nuclear Sciences Monograph* **1997**, 19, map 4.
17. 'How different waters affect the flavor of whisky'; see: http://www.alcademics.com/2013/06/how-different-waters-affect-the-flavor-of-whisky.html. (accessed 20 January 2014).
18. 'Water that causes stains'; see: http://www.coh2o.com/water-that-causes-stains (accessed 23 January 2014).
19. 'How whisky is made'; see: http://www.madehow.com/Volume-2/Whiskey.html (accessed 23 January 2014).
20. 'L&P Lemon and Paeroa Soft Drink'; see: http://www.tesco.com/groceries/Product/Details/?id=277289896 (accessed 23 January 2014).
21. Smith, G. *ChemEd NZ [Chemistry Education in New Zealand]* **2009**, *115*, May, 12-15.