

## ORIGINAL ARTICLE

# Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers

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## Abstract

*Scaling is an integral component of ecology and earth science. To date, the ability to determine the importance of air–water gas exchange across large spatial scales is hampered partly by our ability to scale the gas transfer velocity and stream hydraulics. Here we report on a metadata analysis of 563 direct gas tracer release experiments that examines scaling laws for the gas transfer velocity. We found that the gas transfer velocity scales with the product of stream slope and velocity, which is in alignment with theory on stream energy dissipation. In addition to providing equations that predict the gas transfer velocity based on stream hydraulics, we used our hydraulic data set to report a new set of hydraulic exponents and coefficients that allow the prediction of stream width, depth, and velocity based on discharge. Finally, we report a new table of gas Schmidt number dependencies to allow researchers to estimate a gas transfer velocity using our equation for many gasses of interest.*

Keywords: CO<sub>2</sub>, gas exchange, O<sub>2</sub>, reaeration, turbulence

## Introduction

[1] Accurate determinations of the exchange of gasses across the air–water interface of streams and rivers are an important component of biogeochemical budgets (McCutchan et al. 1998; Laursen and Seitzinger 2005; Aristegi et al. 2009) and metabolic rates (Marzolf et al. 1994; Young and Huryn 1998; Bott 2006). The air–water flux ( $F$ ) of a gas is driven by the product of the concentration difference between a gas (e.g., CO<sub>2</sub>) in water ( $[ ]_{\text{water}}$ ) and air ( $[ ]_{\text{air}}$ ) and the gas transfer velocity such that

$$F(g) = ([ ]_{\text{water}} - [ ]_{\text{air}})k, \quad (1)$$

where  $k$  is the gas transfer velocity with a unit of length per unit time. Both the concentration difference and an accurate measurement or

model of  $k$  must be made at appropriate temporal and spatial scales to constrain estimates of  $F$  (Raymond and Cole 2001).

[2] For most gasses, the measurement of the concentration difference is easier than the measurement of  $k$ . Past research has demonstrated that the gas transfer velocity is controlled by the turbulent dissipation rate at the air–water interface (Zappa et al. 2007), and therefore,  $k$  can theoretically be modeled based on physical characteristics of a site that correlate with surface turbulence. To date, most of the research on streams has focused on the reaeration coefficient ( $K$  or  $k_2$ ; unit of time<sup>-1</sup>), a parameter similar to the gas transfer velocity ( $k$ ) that is not corrected for depth. Previous studies have modeled  $k_2$  based on first principles or by fitting field

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measurements to stream characteristics (O'Connor and Dobbins 1958; Tsivoglou and Wallace 1972; Wilcock 1988). These studies have been useful in the field of environmental engineering because they provide an understanding of the ability of streams to reoxygenate after high rates of organic matter loading associated with sewage inputs.

[3] A difficulty with these models is that depth becomes a major predictor of  $k_2$  because of the relationship between depth and the mass of a gas that needs to be "reaerated" in a given system. Models of the gas transfer velocity, on the other hand, directly probe the physical processes that control turbulence at the water surface (Zappa et al. 2007). In addition, many previous efforts that have reported  $k_2$  models have not scaled their results to a common Schmidt number (defined below), making it difficult to utilize proposed models due to the dependence of the gas transfer velocity on diffusivity, which is temperature dependent.

[4] Here we report results of a meta-analysis of measurements of gas exchange and the gas transfer velocity ( $k$ ) made by direct gas tracer releases to analyze the controls of the gas transfer velocity across different streams and rivers. For all measurements we normalized for depth and converted to a common Schmidt number of 600 ( $k_{600}$ ). We found a correlation between  $k_{600}$  and the product of slope and water velocity, which are related to the rate of stream turbulent energy dissipation. Finally, we utilized this relationship with stream hydraulic data collated by this study to probe how  $k$  scales across stream orders for different regions of the United States.

## Methods

### *Direct Tracer Studies*

[5] Direct tracer studies involve releasing a gas into a stream and measuring its loss over a defined reach. This study is based mainly on 5 data sets, each of which report temperature, stream width, stream depth, stream discharge, stream velocity, the slope of the reach, and a  $k_2$  normalized to  $O_2$ . The largest data set originates from measurements made by the U.S. Geological Survey (USGS) and was originally summarized in the context of reaeration coefficients (Melching and Flores 1999).

We reanalyzed this data set by revisiting the original USGS data reports to add temperature to the metadata already collated by Melching and Flores (1999). Of the original 493 independent reach measurements they reported, we were able to find reported temperature measurement from the original USGS reports in order to normalize to a Schmidt number of 600 for 250 independent stream reaches. Of these 250 estimates, 216 passed the data-screening protocols set forward by Melching and Flores. The data screening involved dropping tracer releases that had a low ratio of  $k_2$  to travel time of gas tracer (Melching and Flores 1999).

[6] The second set was measured by the Stroud Water Research Center for a variety of research projects. This data set had a total of 163 measurements, of which approximately 129 have been published. These studies used a propane injection that is detailed in Bott et al. (2006a, 2006b). Information on most of these sites is provided in the original publications (Bott et al. 2006a, 2006b; Arscott et al. 2008).

[7] Two data sets originate from the 2 Lotic Inter-site Nitrogen Experiments (LINX and LINX2). The LINX data set consisted of 12 measurements made by a propane addition previously published in Mulholland et al. (2001). The LINX2 data set consisted of 68 measurements made by either propane or  $SF_6$  additions and were previously used in metabolism calculations in Bernot et al. (2010).

[8] Finally, we also used 117 separate reach measurements in 5 stream/rivers found in Tsivoglou and Wallace (1972). These measurements were made using the release of krypton-85 and tritium. Similar to some of the USGS studies, they did multiple releases over separate reaches of the same stream in order to capture a large number of hydraulic features on the same system.

### *Gas Transfer Velocity Calculation*

[9] The gas transfer velocity is a function of the interfacial turbulence, the kinematic viscosity of water, and the diffusion coefficient of the gas of interest (Wanninkhof 1992). The Schmidt number is the ratio of the kinematic viscosity of water to the diffusion coefficient and is therefore sensitive to temperature. One can cal-

culate the gas transfer velocity of one gas (gas1) from another (gas2) using

$$k_{\text{gas1}}/k_{\text{gas2}} = (Sc_{\text{gas1}}/Sc_{\text{gas2}})^{-n}, \quad (2)$$

where  $Sc$  is the Schmidt number and  $n$  is the Schmidt number exponent, which is generally assigned a value of 1/2 to 2/3 depending on the surface state of the water (Jähne et al. 1987). A common approach when reporting  $k$  values is to normalize it to a Schmidt number of 600, which in freshwater corresponds to  $\text{CO}_2$  and  $\text{O}_2$  at a temperature of 20 and 17.5 °C, respectively.

[10] We first converted all reported oxygen reaeration coefficients ( $k_2$ ) to a gas transfer velocity ( $k_{\text{O}_2}$ ) by multiplying  $k_2$  by the reported depth. We determined the Schmidt number for this  $k_{\text{O}_2}$  ( $Sc_{\text{O}_2}$ ) using reported temperatures and the Schmidt number temperature dependency for  $\text{O}_2$  found in Wanninkhof (1992). We then used Eq. 2 to standardize all  $k$  values to a constant temperature by converting all  $k_{\text{O}_2}$  to a gas transfer velocity with a Schmidt number of 600 ( $k_{600}$ ) using the following equation:

$$k_{600} = (600/Sc_{\text{O}_2})^{-0.5} \times k_{\text{O}_2}. \quad (3)$$

As part of this analysis, we also reevaluated and report the Schmidt number temperature dependencies for many gasses of interest to the stream community. This will allow for the determination of  $k$  for a given gas from the  $k_{600}$  relationships reported here using Eq. 2. The newer set of dependencies is the product of experimentally determined diffusion coefficients compiled in an extensive review (Langø et al. 1996), temperature dependence of kinematic water viscosity modeled from absolute viscosity (Reid et al. 1987; Viswanath and Natarajan 1989; Daubert and Danner 1994), and temperature dependence of water density (Lide 2010).

### Stream Hydraulics

[11] In order to probe how modeled turbulent energy dissipation and  $k$  scaled with stream order for regions of the United States, we performed a hydraulic geometry analysis and coupled it with data from the National Hydrography Dataset (NHDPlus; see below). Understanding the hydraulic geometry of streams has long been an interest in hydrology (Horton 1945; Leopold and Mad-

dock 1953). Original work in this area demonstrated that width ( $W$ ), depth ( $D$ ), and velocity ( $V$ ) all scaled with discharge ( $Q$ ; Leopold and Maddock 1953) so that

$$W = aQ^b, \quad (4)$$

$$D = cQ^d, \quad (5)$$

$$V = eQ^f, \quad (6)$$

where the hydraulic geometry exponents ( $b$ ,  $d$ ,  $f$ ) and coefficients ( $a$ ,  $c$ ,  $e$ ) of stream width, depth, and velocity curves are constrained by the fact that discharge is equal to the product of width, depth, and velocity (Leopold and Maddock 1953), so that

$$b + d + f = 1, \quad (7)$$

$$a \times c \times e = 1. \quad (8)$$

For the data set here, we reevaluated the hydraulic geometry exponents and coefficients. For the analysis of the hydraulic exponents, we used the entire Melching and Flores (1999) data set and all available hydraulic measurements available in the appendix of the other studies. This led to a total of 1026 paired measurements of discharge, width, depth, and velocity.

### NHDPlus

[12] In order to obtain average discharge and slope by stream order for regions of the United States, we collated the National Hydrography Dataset Plus (NHDPlus), with the USGS water resources region major hydrologic unit codes (HUCs; <http://water.usgs.gov/GIS/huc.html>). The NHDPlus data set is developed from a 30-m digital elevation model. Included within the NHDPlus data are measured lengths of center stream lines for all streams and rivers throughout the contiguous 48 states, as well as information on the Strahler stream order (Strahler 1952), stream slope, and discharge associated with each stream line. The NHDPlus data set produces a modeled flow based on the work of Jobson (1997).

[13] For this work, each stream segment length was summed according to stream order to get the total length within an HUC. For each stream order within an HUC, modeled flow and slope were normalized to the length of each stream segment prior to cal-

**Table 1** Coefficients for calculation of kinematic water viscosity and Schmidt numbers for selected gases for 4–35 °C. Numbers in parenthesis in the last column are the temperature range over which the reported variation holds.

Kinematic viscosity of water ( $\text{cm}^2 \text{s}^{-1} = A + BT + CT^2 + DT^3, T = ^\circ\text{C}$ )						
	$A (\times 10^{-3})$	$B (\times 10^{-4})$	$C (\times 10^{-6})$	$D (\times 10^{-8})$		
	1.735	-5.023	8.598	6.805		
References <sup>a</sup>						
	8 <sup>b</sup> , 34 <sup>c</sup> , 39 <sup>b</sup> , 49 <sup>b</sup>					
Schmidt number = $A + BT + CT^2 + DT^3, T = ^\circ\text{C}$						
Gas	A	B	C	D		
References						
Comparison with Wanninkhof (1992)						
N <sub>2</sub>	1615	-92.15	2.349	-0.0240	2, 13–15, 20, 23–25, 29, 33, 42, 44, 52	±9.0% (4–35)
N <sub>2</sub>	1971	-131.45	4.139	-0.0521	Wanninkhof (1992) calculated from 29	±10.6% (10–25)
O <sub>2</sub>	1568	-86.04	2.142	-0.0216	2, 4–6, 9, 11, 12, 14, 15, 17–19, 21–25, 28, 30–32, 35, 44, 46, 50, 52,	±1.6% (4–35)
O <sub>2</sub>	1801	-120.10	3.782	-0.0476	51	-0.7% (10–25)
N <sub>2</sub> O	2105	-130.08	3.486	-0.0365	9, 12, 20, 21, 23, 25, 29, 47	-2.2% (4–35)
N <sub>2</sub> O	2056	-137.11	4.317	-0.0543	Wanninkhof (1992) calculated from 29	±1.4% (10–25)
NO	2001	-141.49	4.131	-0.0454	53	
CO <sub>2</sub>	1742	-91.24	2.208	-0.0219	5, 7, 9, 12, 14, 16, 20, 25, 26, 34, 36, 38, 40, 43, 44, 45, 47, 48, 50	±4.9% (4–35)
CO <sub>2</sub>	1911	-118.11	3.453	-0.0413	Wanninkhof (1992) calculated after 51	±3.0% (10–25)
CO	1869	-109.09	2.820	-0.0290	53	
H <sub>2</sub>	650	-32.32	0.754	-0.0074	1, 2, 9, 15, 19, 20, 24, 26–29, 41, 44, 46, 50, 52	
CH <sub>4</sub>	1824	-98.12	2.413	-0.0241	29, 54	±4.1% (4–35)
CH <sub>4</sub>	1898	-114.28	3.29	-0.0391	Wanninkhof (1992) calculated after 51	±2.6% (10–25)
C <sub>2</sub> H <sub>6</sub>	2080	-105.61	2.509	-0.0247	23, 54	
C <sub>3</sub> H <sub>8</sub>	2864	-154.14	3.791	-0.0379	54	
C <sub>4</sub> H <sub>10</sub>	3708	-203.97	5.084	-0.0512	54	
SF <sub>6</sub>	3255	-217.13	6.837	-0.0861	Wanninkhof (1992)	
He	368	-16.75	0.374	-0.0036	2, 3, 10, 16, 24, 29, 33, 42, 50, 52	±3.5% (4–35)
He	377	-19.15	0.501	-0.0057	Wanninkhof (1992) calculated from 29	±3.0% (10–25)
Ne	807	-40.71	0.964	-0.0095	3, 24, 29, 53	±9.4% (4–35)
Ne	764	-42.23	1.158	-0.0134	Wanninkhof (1992) calculated from 29	±8.9% (10–25)
Ar	1799	-106.96	2.797	-0.0289	2, 3, 12, 24, 34, 37, 42, 52	±6.8% (4–35)
Ar	1760	-117.37	3.696	-0.0465	Wanninkhof (1992) calculated after 51	±5.8% (10–25)
Kr	1880	-105.97	2.681	-0.0272	5, 29, 53	
Xe	3152	-185.32	4.812	-0.0496	3, 53, 55	
Rn	2939	-173.87	4.532	-0.0468	29	

<sup>a</sup>1, Alkazyan and Fedonova (1952)<sup>4</sup>; 2, Baird and Davidson (1962)<sup>1,3</sup>; 3, Boerboom and Kleyn (1969)<sup>4</sup>; 4, Bridcka and Wiesner (1947)<sup>4</sup>; 5, Carlson (1911)<sup>4</sup>; 6, Chiang and Toor (1959)<sup>4</sup>; 7, Clarke (1964)<sup>4</sup>; 8, Daubert and Damer (1994)<sup>4</sup>; 9, Davidson and Cullen (1957)<sup>4</sup>; 10, Davies et al. (1964)<sup>4</sup>; 11, Davis et al. (1967)<sup>4</sup>; 12, Duda and Vrentas (1968)<sup>4</sup>; 13, Eggleton et al. (1945)<sup>4</sup>; 14, Ferrell and Himmelblau (1967)<sup>4</sup>; 15, Gertz and Loeschke (1954)<sup>4</sup>; 16, Gertz and Loeschke (1956)<sup>4</sup>; 17, Grote (1967)<sup>4</sup>; 18, Grote and Thews (1962)<sup>4</sup>; 19, Gubbins and Walker (1965)<sup>4</sup>; 20, Hagenbach (1898)<sup>4</sup>; 21, Landolt et al. (1912)<sup>4</sup>; 22, Han and Bartels (1990)<sup>4</sup>; 23, Himmelblau (1964)<sup>4</sup>; 24, Houghton et al. (1962)<sup>4</sup>; 25, Hüfner (1897)<sup>4</sup>; 26, Hüfner (1898)<sup>4</sup>; 27, Ipatieff et al. (1933)<sup>4</sup>; 28, Ipatieff and Teodorovitch (1937)<sup>4</sup>; 29, Jähne et al. (1987)<sup>4</sup>; 30, Jordan et al. (1956)<sup>4</sup>; 31, Kolthoff and Miller (1941)<sup>4</sup>; 32, Kreuzer (1950)<sup>4</sup>; 33, Krieger et al. (1967)<sup>4</sup>; 34, Lide (2010)<sup>4</sup>; 35, Müller (1948)<sup>4</sup>; 36, Nijsing et al. (1959)<sup>4</sup>; 37, O'Brien and Hystop (1977)<sup>4</sup>; 38, Rehm et al. (1963)<sup>4</sup>; 39, Reid et al. (1987)<sup>4</sup>; 40, Ringbom (1938)<sup>4</sup>; 41, Rütschi (1967)<sup>4</sup>; 42, Smith et al. (1955)<sup>4</sup>; 43, Stefan (1878)<sup>4</sup>; 44, Tamman and Jessen (1929)<sup>4</sup>; 45, Tang and Himmelblau (1963)<sup>4</sup>; 46, Tham et al. (1970)<sup>4</sup>; 47, Thomas and Adams (1965)<sup>4</sup>; 48, Unver and Himmelblau (1964)<sup>4</sup>; 49, Viswanath and Natarajan (1989)<sup>4</sup>; 50, Vivian and King (1964)<sup>4</sup>; 51, Wilke and Chang (1955)<sup>4</sup>; 52, Wise and Houghton (1966)<sup>4</sup>; 53, Witherspoon and Saraf (1965)<sup>4</sup>; 54, Witherspoon and Saraf (1965)<sup>4</sup>; 55, Wolber et al. (1998).

<sup>b</sup>Source for absolute viscosity used in calculation of kinematic viscosity.

<sup>c</sup>Source for water density used in calculation of kinematic viscosity.

<sup>d</sup>Compiled by Lange et al. (1996).

culating averages for each. All spatial data manipulation and analysis were conducted within ArcGIS (Esri, USA). Aggregation and averaging across stream orders within HUCs were completed with ACCESS (Microsoft, USA).

## Results and Discussion

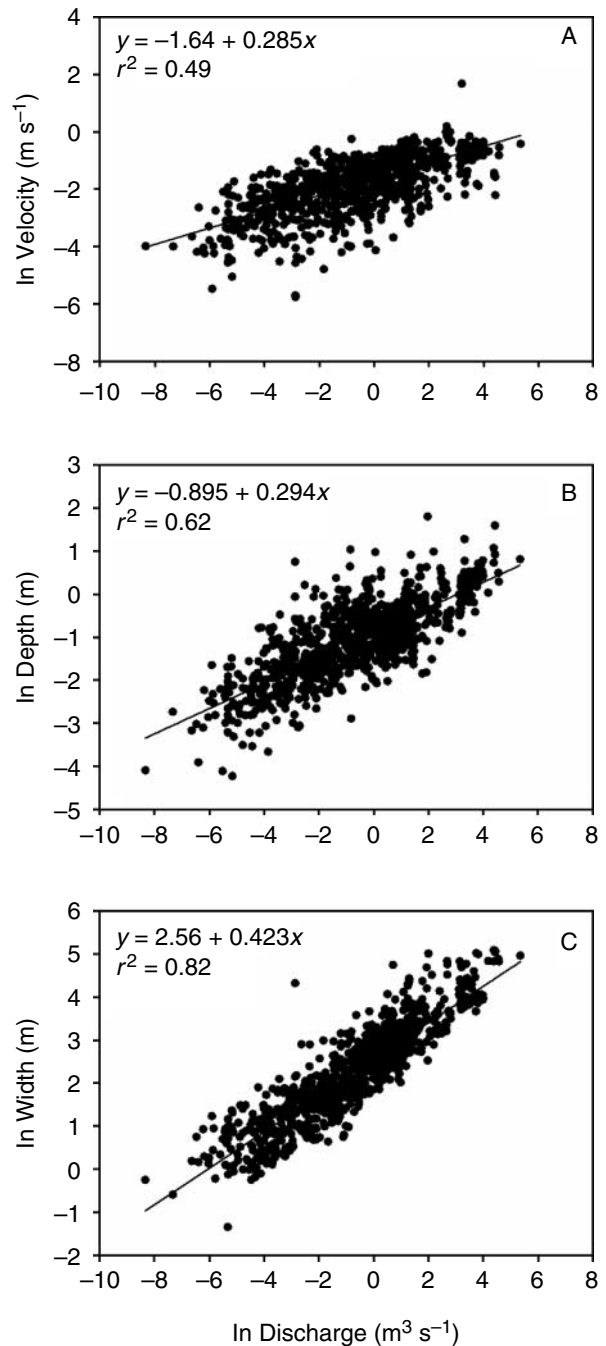
### Schmidt Numbers

[14] Where comparisons could be drawn, Schmidt numbers calculated from Wanninkhof (1992) were in close agreement with those calculated using the more comprehensive compilation of diffusion coefficients for all gasses except  $N_2$  and Ne (Table 1). For oxygen, average agreement was within  $\pm 1.6\%$  over a temperature range of 4–35 °C and within  $\pm 0.7\%$  over a temperature range of 10–25 °C. Differences in Schmidt number calculated using the 2 sets of coefficients are a negligible source of error relative to uncertainties in direct measurement of tracer gas transfer velocities when converting  $k_{O_2}$  values to  $k_{600}$  values, as was done in this study.

### Stream Hydraulics

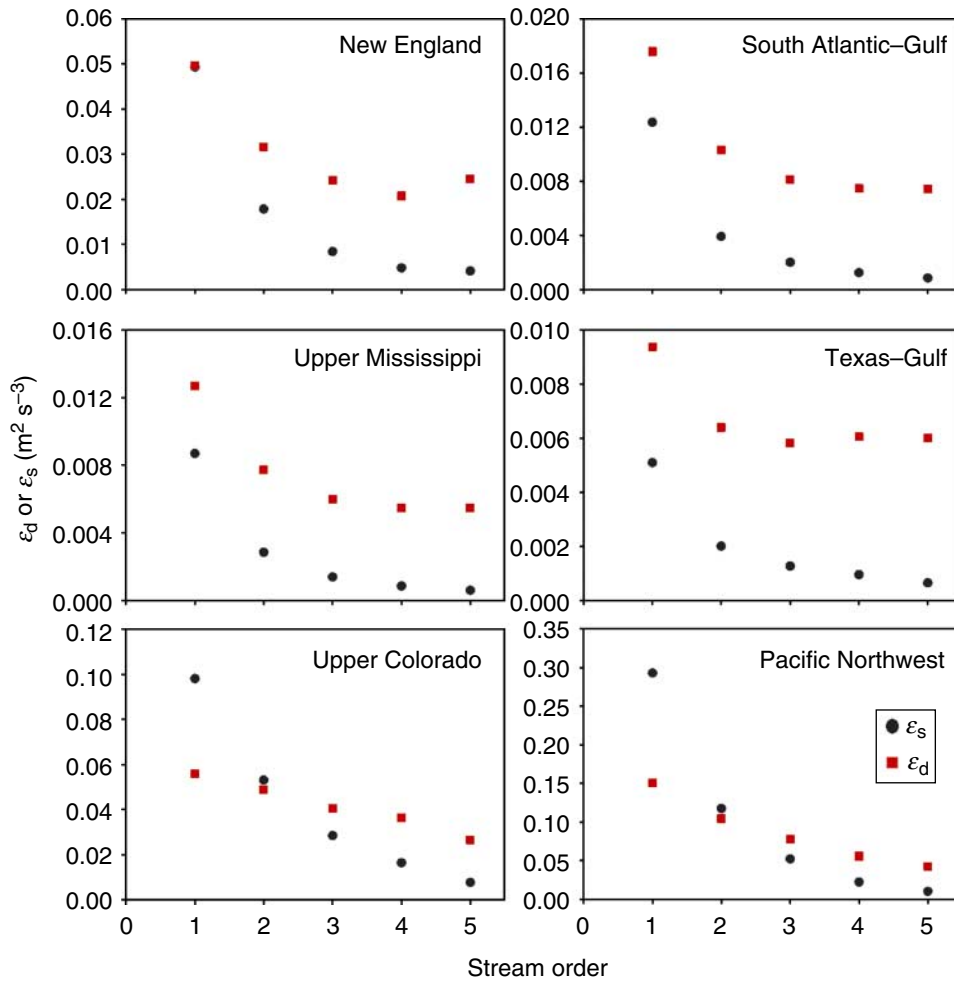
[15] The hydraulic relationships reported here are from the largest data set to date, provide statistically significant results, and are different than some published values that relied on data from gauging stations. The relationships between discharge and depth, width, and velocity had  $r^2$  values of 0.62, 0.82, and 0.49, respectively (Fig. 1). The weaker relationship for velocity is likely due to the comparatively difficult nature of this measurement. The hydraulic exponents ( $b$ ,  $d$ , and  $f$ ; Eqs. 4–6) were  $0.29 \pm 0.0072$  (mean  $\pm$  SE),  $0.42 \pm 0.0063$ , and  $0.29 \pm 0.0091$  for depth, width, and velocity, respectively. These values sum to 1.0, which is consistent with Eq. 7. For the coefficients ( $a$ ,  $c$ , and  $e$ ; Eqs. 4–6) we obtained values of 0.4, 12.88, and 0.19 for depth, width, and velocity, respectively. The product of these values is 0.98, which is consistent with Eq. 8.

[16] Leopold and Maddock (1953) reported corresponding exponents (average exponents in “a downstream direction”) of 0.4, 0.5, and 0.1 for depth, width, and velocity, respectively. The difference between these 2 sets of values may originate from Leopold and Maddock’s choice of sites, since they used USGS gauging stations for their analysis. Gauging stations are not



**Fig. 1** Hydraulic geometry relationships for streams and rivers of this study. Presented are the relationships between discharge and velocity (A), depth (B), and width (C).

necessarily representative of typical natural stream hydraulics because they are chosen for specific morphologic characteristics that provide the most accurate discharge estimate, which was noted by Leopold and



**Fig. 2** Turbulent dissipation rates predicted from stream hydraulics for stream orders from different U.S. Geological Survey hydrologic units (<http://water.usgs.gov/GIS/huc.html>): turbulent dissipation from bed friction ( $\epsilon_s$ ) and depth-scale form drag ( $\epsilon_d$ ).

Maddock and others (Park 1977). Another recent compilation of stream hydraulics by Harman et al. (2008) that avoided gauging stations reported exponents of 0.43, 0.38, and 0.23 for depth, width, and velocity, respectively, for streams and rivers of Australia. Thus, we believe our estimates are representative, and because they have the largest number of observations and are for the United States, we utilized exponents and coefficients derived from this data set (Fig. 1) for the hydraulic scaling performed below.

### Gas Transfer Velocity

[17] Most equations in the literature, including those in Melching and Flores (1999), O'Connor and Dobbins

(1958), Lau (1972), and Parkhurst and Pomeroy (1972), use slope ( $S$ ) and velocity to predict the reaeration coefficient. The idea that slope and velocity are major terms determining stream energy dissipation, or turbulence, and therefore important to gas exchange, goes back to some of the original work on stream aeration (Streeter and Phelps 1925) that was elaborated on by Tsvoglou and Neal (1976) and Moog and Jirka (1999).

[18] Work on large rivers and estuaries has demonstrated that surface turbulence and the gas transfer velocity scales with turbulent dissipation (Zappa et al. 2007). In streams, Tsvoglou and Neal (1976) outlined a model for the dissipation rate,  $\epsilon_d$ , based on stream power per unit weight of water, so that

$$\epsilon_d \approx gSV \tag{9}$$

where  $g$  is the acceleration due to gravity. They found that  $\epsilon_d$  varied linearly with  $k_2$ . Moog and Jirka (1999) formulated a macro-rough near-surface energy dissipation rate,  $\epsilon_m$ , that distinguished bed friction (i.e., stream bed roughness) from depth-scale form drag (i.e., the general cross-sectional shape of a stream). The dissipation rate due to bed friction ( $\epsilon_s$ ; for smooth or small-roughness flows) scales as

$$\epsilon_s \approx u_*^3/D, \tag{10}$$

where  $u_*$  is the friction velocity ( $[g \times R_h \times S]^{0.5}$ ), and  $R_h$  is the hydraulic radius ( $R_h = DW/[W + 2D]$ ).

**Table 2** Fitted equations for predicting the  $k_{600}$  ( $\text{m d}^{-1}$ ) based on stream velocity ( $V$ , in  $\text{m s}^{-1}$ ), slope ( $S$ ; unitless), depth ( $D$ , in meters), discharge ( $Q$ , in  $\text{m}^3 \text{s}^{-1}$ ), and the Froude number ( $Fr = V/(gD)^{0.5}$ ). Also displayed are the standard deviations ( $\pm 1$  SD) for the equation parameters,  $r^2$ , slope ( $\pm \text{SE}$ ), and  $y$ -intercept ( $\pm \text{SE}$  for regressions of the equation output vs. actual values; Fig. 3). All  $p$ -values for the regressions are 0.0001.

Model equation	$r^2$	Slope	$y$ -Intercept
1. $k_{600} = (VS)^{0.89 \pm 0.020} \times D^{0.54 \pm 0.030} \times 5037 \pm 604$	0.72	$0.92 \pm 0.024$	$0.98 \pm 0.17$
2. $k_{600} = 5937 \pm 606 \times (1 - 2.54 \pm 0.223 \times Fr^2) \times (VS)^{0.89 \pm 0.017} \times D^{0.58 \pm 0.027}$	0.76	$0.94 \pm 0.022$	$0.76 \pm 0.16$
3. $k_{600} = 1162 \pm 192 \times S^{0.77 \pm 0.028} V^{0.85 \pm 0.045}$	0.54	$0.91 \pm 0.036$	$0.91 \pm 0.24$
4. $k_{600} = (VS)^{0.76 \pm 0.027} \times 951.5 \pm 144$	0.53	$0.82 \pm 0.037$	$0.92 \pm 0.24$
5. $k_{600} = VS \times 2841 \pm 107 + 2.02 \pm 0.209$	0.55	$1.0 \pm 0.038$	$-4.8 \times 10^{-3} \pm 0.26$
6. $k_{600} = 929 \pm 141 \times (VS)^{0.75 \pm 0.027} \times Q^{0.011 \pm 0.016}$	0.53	$0.92 \pm 0.036$	$0.81 \pm 0.24$
7. $k_{600} = 4725 \pm 445 \times (VS)^{0.86 \pm 0.016} \times Q^{-0.14 \pm 0.012} \times D^{0.66 \pm 0.029}$	0.76	$0.95 \pm 0.023$	$0.57 \pm 0.17$

According to this model, the dissipation rate, or turbulence, will vary depending on the extremes of pure bed friction ( $\varphi = 0$ ) and pure depth-scale form drag ( $\varphi = 1$ ) according to

$$\varepsilon_m = (1 - \varphi)\varepsilon_s + \varphi\varepsilon_d. \quad (11)$$

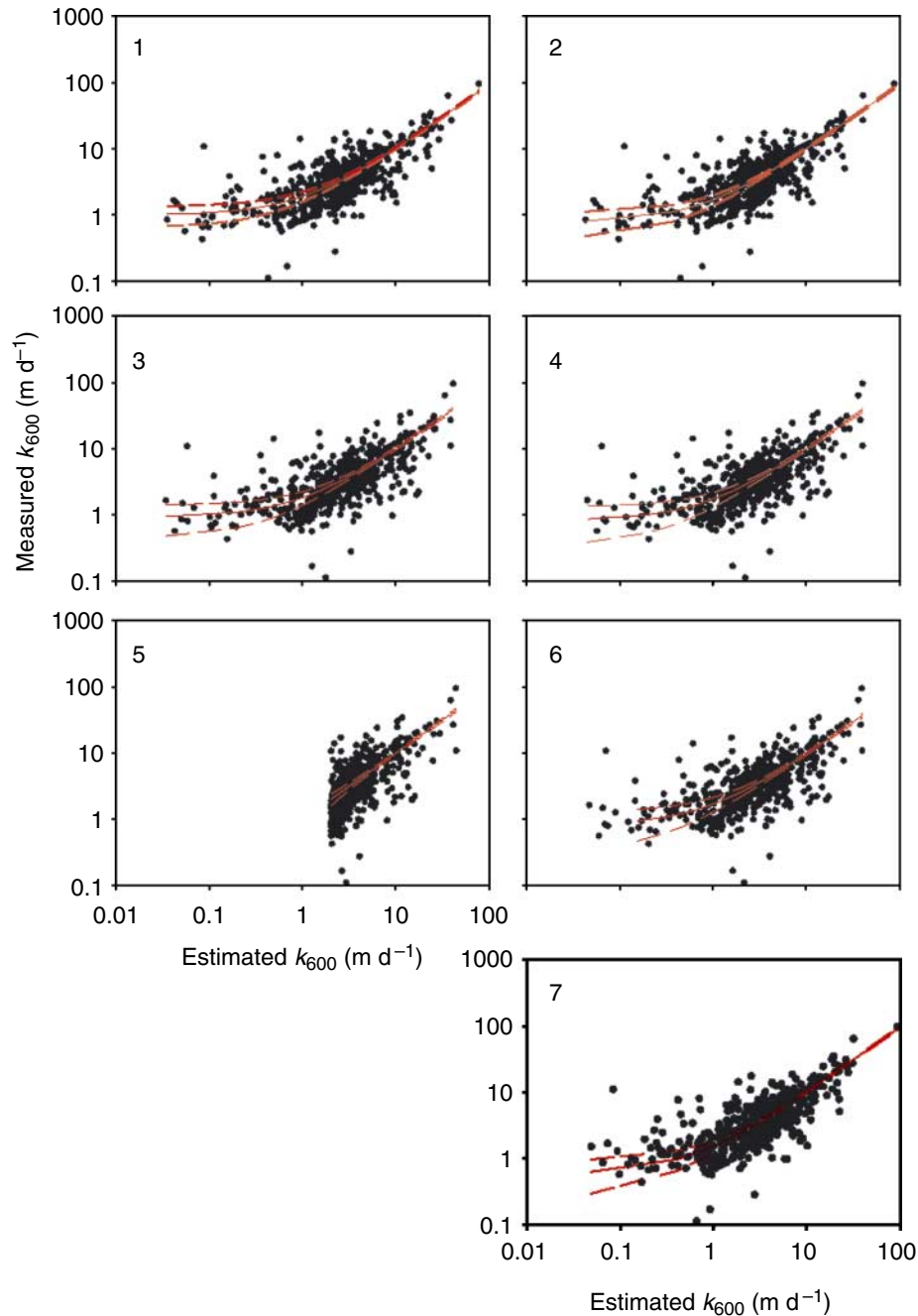
[19] We performed a simple exercise to explore how  $\varepsilon_d$  and  $\varepsilon_s$  vary for average streams across the United States by combining NHDPlus data with results from our stream hydraulic analysis for major U.S. hydrologic regions (see Methods). We found that, except for first-order streams,  $\varepsilon_d$  is generally predicted to be higher than  $\varepsilon_s$  (Fig. 2). Therefore, unless  $\varphi$  is large, the impact of  $\varepsilon_s$  on dissipation and the gas transfer velocity will be limited to low-order streams. Furthermore, both  $\varepsilon_d$  and  $\varepsilon_s$  decrease as stream order increases for all regions presented (Fig. 2). Thus, this simple exercise, based on conceptual theory, argues for a major role for  $S$  and  $V$  and for a general decrease in the gas transfer velocity with an increase in stream order.

[20] We revisited many of the equations in the literature and found those that include slope and velocity were the best at predicting the gas transfer velocity (Table 2, Fig. 3), which is also consistent with a dominant role for  $\varepsilon_d$  (Eq. 9). The values and uncertainties for coefficients were determined by fitting  $k_{600}$  to the models in Table 2 using a Levenberg–Marquardt optimization algorithm (Press et al. 1992). The residuals are constant and random about zero. We found that 3 general types of models did an adequate job of predicting  $k$ . The first set utilized a velocity, slope, and depth term (models 1 and 2, Table 2). The second set all used only slope and velocity (models 3–5). The final 2

models used velocity and slope with discharge (model 6) and discharge and depth (model 7). The strongest correlations came from models that included a depth term.

[21] Contrary to our expectations, when we combined the models in Table 2 with the morphological data produced from the NHDPlus data set and hydraulic scaling laws, we found that for most hydrologic regions, the models with a depth term predict an increase in the gas transfer velocity with increasing stream order (Fig. 4). This finding is inconsistent with the conceptual theory of turbulent dissipation (Fig. 2). Thus, although the correlation coefficients are greater if a depth term is included, the inconsistency of these models with theory and the high reported  $k$  values for average streams suggest that they should be used only with caution.

[22] It appears that although the data set for direct measurements of the gas transfer velocity is growing, either it has not properly constrained the hydraulics of stream networks, or general theory needs revision. It should be noted, however, that most of the measurements collated here were made on relatively small systems (median depth, 0.28 m) and during low flow (median discharge,  $0.54 \text{ m}^3 \text{ s}^{-1}$ ). This may partially account for why these models break down when attempting to scale to the hydraulics of higher-order streams. Thus, although models 1 and 2 in Table 2 may not be applicable when trying to scale to larger-order streams, due to the higher  $r^2$ , models 1 and 2 are arguably more accurate for determining a gas transfer velocity for first-order systems. Certainly this highlights the need for systematic measurements of the gas transfer velocity, particularly in larger streams and those with high velocities and slopes.



**Fig. 3** The relationship between predicted and actual gas transfer velocities for the 7 models presented in Table 2. The graph numbers indicate the model equation number from Table 2. Dotted lines are 95% confidence bands.

[23] Future work should also try to constrain  $\varphi$  (Eq. 11). Some of the variation in our ability to predict  $k$  may be partially explained by the need to determine the relative importance of bed friction and form drag when measuring  $k$  in the field. This may explain why some

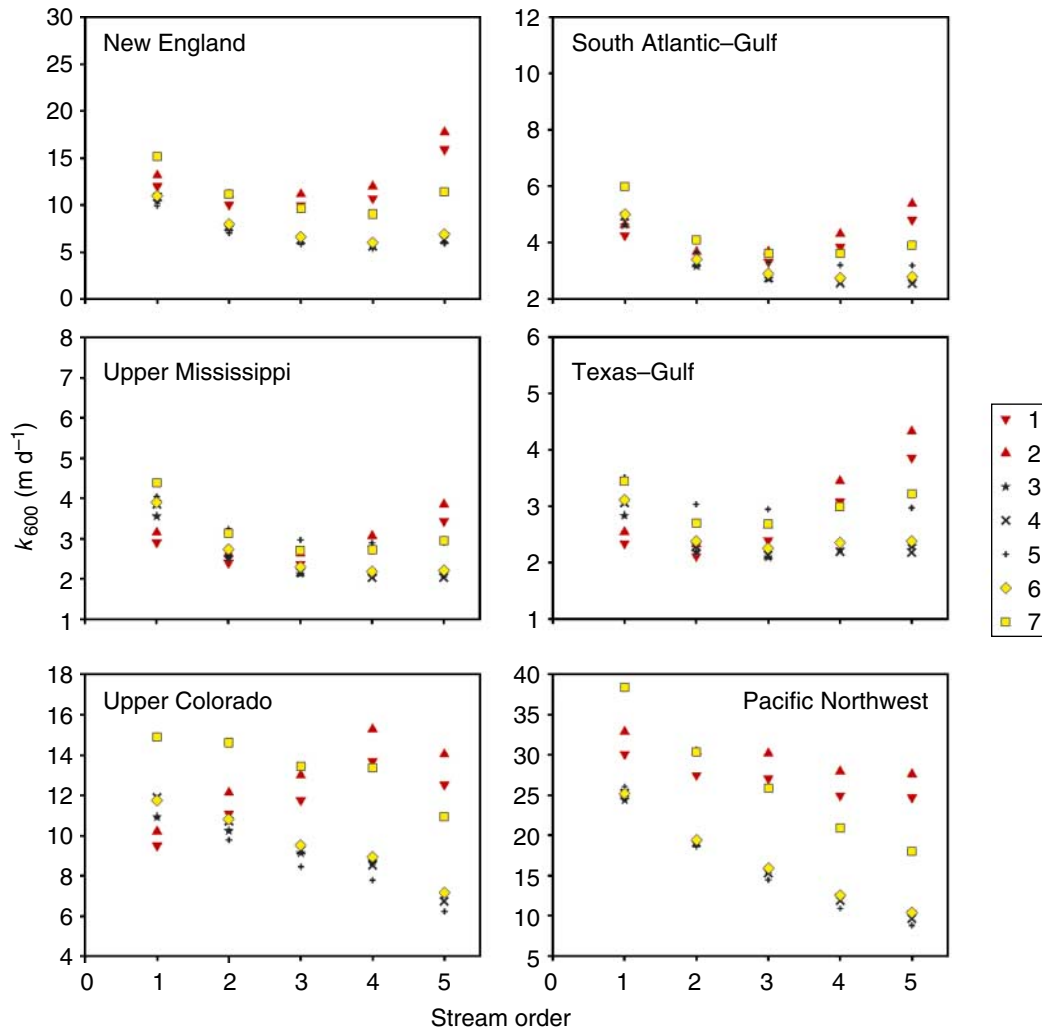
scale fluxes across broad regions where direct measurements are not possible or for studies where a high precision estimate is not needed, we advocate predicting the Schmidt number,  $k_{600}$ , based on slope and velocity. These models generally explain slightly more than half

studies find greater variation in  $k$  in smaller streams and rivers (Alin et al. 2011). That is, models that predict  $k$  based on stream hydraulics may be improved by including a term that approximates  $\varphi$ . In fact, some studies have utilized a proxy for bottom roughness in an attempt to improve prediction of gas transfer (Bicudo and Giorgetti 1991), while Melching and Flores (1999) were able to improve predictive capability by separating pool and riffle systems from channel controls (streams with uniform prismatic morphology). Finally, an additive effect of wind and stream flow (Chu and Jirka 2003) and a switching to wind dominance in large rivers (Alin et al. 2011) have been documented in the literature, as has the potential for lower  $k$  values due to biological or chemical films (Kothandaraman 1971). These factors, in addition to measurement error, may also be contributing to the variation we observed.

### Significance to Aquatic Environments

[24] Choosing a gas transfer velocity,  $k$ , to estimate gas exchange is important to stream studies. When attempting to





**Fig. 4** The gas transfer velocity ( $k_{600}$ ) estimated from stream hydraulics using the 7 different model equations provided in Table 2 for the same USGS hydrologic units presented in Fig. 2.

of the variance in  $k_{600}$  (Table 2) and are consistent with general theory. Stream hydraulics demonstrates that as one moves up in stream order, the slope of a watershed decreases while velocity increases in a predictable manner (Leopold and Maddock 1953). Therefore, the gas transfer velocity will change both across and within watershed networks in a manner that can be predicted by simple stream hydraulics (Fig. 4), and this effort offers a framework to calculate these changes.

[25] Slope and velocity are also easily made measurements, and therefore, this relationship is valuable to stream researchers. The use of slope and velocity to estimate  $k$  for a stream or river reach, however, should

be pursued with caution. The best use of this equation is for scaling gas evasion over large spatial scales or for determining the relative importance of gas exchange in bulk biogeochemical budgets. A recent attempt to understand the importance of air–water gas exchange of  $\text{CO}_2$  globally, for instance, could not incorporate small streams because of a lack of scaling laws to estimate the gas transfer velocity across a range of stream types (Cole et al. 2007). Researchers who need accurate estimates of gas exchange for process-based studies such as metabolism or denitrification, particularly systems with a high slope or velocity, still need to pursue direct measurements. A new study, for instance, reported errors of

100% when predicting reaeration rates from generalized equations (Wallin et al. 2011). When doing so, researchers should attempt to measure proxies that can be used to constrain the relative importance of bottom roughness and channel morphology to improve our ability to predict the gas transfer velocity.

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