

---

AUTHOR'S REPLY by Vedat Batu<sup>1</sup>, Martinus Th. van Genuchten<sup>2</sup>, and John C. Parker<sup>3</sup>

<sup>1</sup>Corresponding author: URS Corporation, 100 South Wacker Drive, Chicago, IL 60606; vedat\_batu@urscorp.com

<sup>2</sup>Department of Mechanical Engineering, COPPE/LTTC, Federal University of Rio de Janeiro, UFRJ, Rio de Janeiro, RJ 21945-970, Brazil.

<sup>3</sup>Department of Civil and Environmental Engineering, University of Tennessee at Knoxville, Knoxville, TN 37996.

---

We appreciate the comments by Gorokhovski (2012) and Neville (2012) about the papers by Batu (2010) since it gives us an opportunity to highlight some pervasive misconceptions about the use and misuse of first- and third-type boundary conditions in contaminant transport and degradation studies. As several of the issues raised by Gorokhovski (2012) and Neville (2012) were discussed in great detail in earlier papers by J. C. Parker and M. Th. van Genuchten (Parker and van Genuchten 1984; van Genuchten and Parker 1984), these two authors were invited by Vedat Batu to join him in this response. As Gorokhovski (2012) and Neville (2012) both commented on the same paper, we are responding here to both comments.

### **Response to the Comment by Gorokhovski (2012)**

Gorokhovski (2012) in his comments starts out by raising doubts about the practicality of evaluating degradation rates based on the differential equations describing steady-state solute transport, for either the resident or flux concentration (Equations 1 and 11, respectively), and states that “Much simpler is to evaluate it by measuring changes of the concentration in time in motionless pure solution or in saturated samples, if the interaction between the solution and the material of the samples does not depend on velocity of the flux as in the discussed paper.” We disagree. The use of a “motionless pure solution” is unrealistic since it does not represent actual physical or biogeochemical conditions in the field.

Gorokhovski (2012) next derived one-dimensional steady-state first-type and third-type solutions through his Equations G3 through G4, which were previously given by Batu (2010), as well as in various forms earlier by Gershon and Nir (1969), Bear (1979), and van Genuchten

---

© 2012, The Author(s)  
Ground Water © 2012, National Ground Water Association.  
doi: 10.1111/j.1745-6584.2012.01018.x

(1981), among others. The first-type source solution, as given by Equation 5 in Batu (2010), has been used since the mid 1990s (Buscheck and Alcantar 1995; Chapelle et al. 1995). The purpose of Batu (2010) was to present a method for estimating degradation rates using field-measured concentrations that satisfy mass balance constraints at the inlet, and address the issue of first-type versus third-type solution applicability. We do acknowledge that Gorokhovski's Equation G11 does provide a useful basis for estimating degradation rates from measured concentrations at two locations downgradient of the inlet location, independent of whether flux or resident concentrations are measured. This method was first proposed by Buscheck and Alcantar (1995). Equation G12 similarly holds for flux-averaged concentrations measured at the outlet of a finite medium, but not for resident concentrations.

We have no major problems with the remainder of his mathematical analyses between Equations G8 and G17, except for the statement under Equation G9 that if one assumes continuity in the resident concentration ( $C_r$ ) across the inlet boundary, then the derived equation for the flux concentration ( $C_f$ ) will describe the resident concentration as well. Unfortunately, it escapes us how two different mathematical equations can describe the exact same physical quantity. Gorokhovski (2012) also states below Equation G14 that "Mathematical considerations require continuity of  $C_r$  at  $x = 0$ ", but fails to elaborate exactly which mathematical considerations would lead to that requirement. He next agrees with the derivation of Equation G17, i.e.,

$$C_M = C_r(+0, t) - \frac{D}{U} \frac{\partial C_r(+0, t)}{\partial x} \quad (1)$$

which encapsulates the requirement of solute flux continuity by approaching the inlet boundary from both sides. But then Gorokhovski immediately questions the validity of solute flux continuity since, presumably, Parker and van Genuchten (1984) "by default" assumed that

$$\frac{\partial C_r(-0, t)}{\partial x} = \frac{\partial C_r(+0, t)}{\partial x} = 0 \quad (2)$$

This assumption was never stated, either directly or "by default," in Parker and van Genuchten (1984) or van Genuchten and Parker (1984). The left equality may be correct for the fore section or inlet system ( $x < 0$ ), but the right-hand equality of Equation 2 is plainly wrong. This is immediately evident from analytical solutions of the advection-dispersion equation with or without degradation. The spatial derivatives of these solutions (van Genuchten and Parker 1984) are always negative, approaching zero only at large times when degradation is absent. One may easily verify also that the slopes of the steady-state solutions with degradation (Equations G8 and G9) are always negative for any  $x \geq 0$ , and also do not become zero at large times because of the degradation term. These properties are clearly shown by the plots in Figures 1 and 3 of Batu (2010).

One reason for the negative slope of the advection dispersion equation, even without degradation, is diffusion and dispersion away from the inlet location, especially at early times when the slope is very large (approaching infinity when  $t$  approaches zero). This is exactly the reason for the macroscopic discontinuity in the resident concentration. This discontinuity is further exacerbated by the fact that hydrodynamic dispersion effects (often relatively large) are lumped with diffusion (relatively small) into one overall dispersion coefficient. This is a shortcoming of the advection-dispersion equation since hydrodynamic dispersion should not affect the center of mass of a solute pulse, while diffusion does. An alternative approach would be to let the dispersion coefficient grow from purely diffusive at the boundary to diffusive-dispersive at a particular distance from the inlet. Unfortunately, this approach adds considerable complexity to the mathematical formulation of the advection-dispersion equation, and hence is rarely followed. For these reasons we merely require macroscopic solute flux continuity across the inlet and invoke a spatially independent overall dispersion coefficient in the solute transport equations.

Regarding the solute flux continuity (mass balance) property of the third-type source condition, Gorokhovski (2012) states: "Therefore, the suggestion to apply the third-type boundary condition instead of the first-type for simulating mass-transport problems is a not properly grounded and controversial hypothesis." Actually, both solutions are properly grounded if the first-type solution Equation G8 is viewed as the flux concentration, and the third-type solution given by Equation G9 as the resident concentration. Of course, if one can only measure the resident concentration, then only the solution given by Equation G9 for the resident concentration should be used. Likewise, Equation G12 should only be used for flux-averaged concentrations such as breakthrough (effluent) curves of finite columns and perhaps for fully screened wells in field situations.

The bottom line is that whatever boundary condition is used, mass should be conserved when solutes move across a boundary, so that no solutes are lost or created in that boundary. To demonstrate the latter, let us look closely at the first-type and third-type solute flux expressions at the inlet as given by Equations 9 and 21 of Batu (2010) and interpreted as representing resident concentrations. As can be seen from Equation 21, the third-type flux is simply the product of the source concentration and the Darcy velocity. On the other hand, Equation 9 for the first-type boundary condition indicates that the solute flux is not only equal to the product of these same quantities but also contains an additional term that is a function of several transport parameters, including the degradation rate. This situation is illustrated graphically in Figure 2, which shows that for third-type boundary conditions the ratio of incoming ( $-0$ ) and outgoing ( $+0$ ) boundary fluxes,  $F_X/F_M$ , is always equal to unity regardless of the dimensionless degradation parameter  $N$ , thus satisfying continuity in the solute flux. Figure 2 also shows that for first-type cases,  $F_X/F_M$  is no longer constant but always larger than

unity, which is violation of flux continuity across the inlet. Figure 4 of Batu (2010) shows the same situation using dimensional parameters. In the example of Figure 4, the solute flux  $F_M$  at the inlet is always 25 mg/day/m<sup>2</sup> for the third-type solution, regardless of the value of the degradation parameter. However, the first-type boundary condition leads to a solute flux which increases markedly with increasing degradation, in violation of required flux continuity across the inlet boundary.

Similarly as in many previous analyses of transient solute transport problems (Kreft and Zuber 1978; van Genuchten and Parker 1984; Parker and van Genuchten 1984; Batu and van Genuchten 1990, among others), we conclude that solutions based on a first-type boundary condition or source conditions during steady-state uniform groundwater flow conditions, if applied to resident concentrations, violate mass balance constraints across the inlet, and that the errors involved depend upon the values of the degradation, solute transport, and hydrogeologic parameters of the medium. By contrast, third-type source solutions such as given by Equation 18 of Batu (2010), always do satisfy mass balance constraints at the inlet. Current methods of determining degradation parameter values based on the first-type solution can significantly overestimate the degradation parameters depending upon the values of the flow and solute transport parameters. The comments by Gorokhovski (2012) do not change this.

## Response to the Comment by Neville (2012)

Neville (2012) similarly starts by restating the governing transport equation and analytical solutions for the first- and third-type boundary conditions, while dropping the subscript on the concentration. We have no problem with his analysis here provided that the two solutions are associated with the flux ( $C_f$ ) and resident ( $C_r$ ) concentrations, respectively. Unfortunately, it seems that his derivations pertain exclusively with resident concentrations, for which case the appropriateness of the first-type solution is at issue.

We first note our agreement with his statement that the first- and third-type solutions both are solutions of the transport equation and as such satisfy the mass balance (continuity) equation inherent in the solute transport formulation (Batu 2010, p. 566). However, the issue here is not the transport equation as such, but the inlet boundary condition imposed on the transport equation. The culprit is the first-type boundary condition, which does not satisfy continuity in the solute flux across the inlet, while the third-type boundary condition does (van Genuchten and Parker 1984, among others). As we mentioned in our response to Gorokhovski (2012), in the example of Figure 4 of Batu (2010), the incoming solute flux  $F_M$  at the inlet is always 25 mg/day/m<sup>2</sup> for the third-type solution, regardless of the value of the degradation parameter. This is not the case for the first-type boundary condition, thus demonstrating mass balance (solute flux continuity) problems at the inlet boundary.

Neville (2012) next states below his Equation 5 that the solute flux across the inlet for a third-type inlet boundary condition, his Equation 4, is based on the assumption that the dispersive mass flux from the fore-section into the porous medium is zero. This is correct; it implies that dispersion will occur only within the porous medium (i.e., for  $x \geq 0$ ), but not for  $x < 0$  (thereby assuming that any diffusion in the fore-section, if present, can be neglected). Let us restate the third-type inlet condition here using the notation of Batu (2010):

$$F_M \equiv \varphi_e U C_M = \left[ \varphi_e U C_r(x) - \varphi_e D_x \frac{\partial C_r(x)}{\partial x} \right]_{x=0^+} \quad (3)$$

where  $x = 0^+$  indicates evaluation at the inlet boundary just inside the profile. Equation 3 is the same as Equation 4 of Neville (2012) and consistent with Equation 2 in this reply with the exception that  $x = 0$  is approached from inside of the porous medium, which is shown mathematically as  $x = 0^+$  (van Genuchten and Parker 1984, Equation 3; Leij et al. 1991a, Equation 2; Leij et al. 1991b, Equation 6; Batu 2010, Equation 13, among others).

Neville (2012) next derives the total mass fluxes into the porous medium, leading to his Equations 9 and 10 for the third- and first-type boundary conditions, respectively. The difference between the two equations is indeed a reflection of the difference in the analytical solutions for the two boundary conditions.

Where we start deviating from Neville's analysis is his next assumption that it is possible to reconcile the first- and third-type boundary conditions by writing a more general form of the third-type condition "...by relaxing the assumption that the dispersive mass flux is zero," presumably for the third type condition. He then inexplicably adds a dispersive mass flux to the left-hand side of Equation 4 to obtain his Equation 11, which can be written as

$$\begin{aligned} & \left[ \varphi_e U C_M - \varphi_e D \frac{\partial C_r(x)}{\partial x} \right]_{x=0^-} \\ & = \left[ \varphi_e U C_r(x) - \varphi_e D \frac{\partial C_r(x)}{\partial x} \right]_{x=0^+} \end{aligned} \quad (4)$$

In the ensuing analysis, Neville (2012) assumes that the incoming dispersion mass flux (in the term on the left for  $x = 0^-$ ) is exactly the same as the dispersive mass flux inside the medium (at  $x = 0^+$ ) resulting from the first-type analytical solution. By doing so he reformulates the third-type boundary condition to become again a first-type condition through cancelation of the gradient terms on the left and right sides of Equation 4. The resulting problem is hence described immediately again by the first-type analytical solution as shown in Figure 3 of Batu (2010) and duplicated in Figure 1 of Neville (2012).

It is worth noting once more that the extra dispersive mass flux into the porous medium as advocated by Neville (2012) is not constant, but a function of the physical and chemical properties of the porous medium (notably the

dispersivity, the retardation factor and the degradation rate coefficient) as embodied in his Equation 8. Moreover, if the considered transport scenario had been a fully transient problem, the added flux would be a time-dependent term which at time  $t = 0$  would attain an infinite value.

Neville (2012) ends his comment by suggesting that applicability of the first- and third-type solutions “will depend on whether in a particular situation it is appropriate to assume that the dispersive mass flux is zero.” We maintain that in most or all cases the incoming dispersive flux indeed will be zero, which implies that only third-type inlet boundary conditions should be used.

## Some Concluding Thoughts

Discussions about the applicability of first- and third-type inlet boundary conditions are certainly not new, as are applicable boundary conditions for transport across the exit boundary of a finite medium. Much of the initial discussion was in the chemical engineering and heat transport literature. Langmuir (1908) may well have been the first to advocate a third or flux-type condition, followed by Damköhler (1937) and later especially Danckwerts (1953) whose classic paper motivated many to refer to the third-type inlet boundary condition as the “Danckwerts boundary condition.” Many other papers in especially chemical engineering contributed to the discussion at the time from various perspectives (e.g., Wehner and Wilhelm 1956; Pearson 1958, and references therein), and later the classic paper by Kreft and Zuber (1978). An interesting account of the discussions in the 1950s and 1960s was made by Amundson (1986) as part of his inaugural P.V. Danckwerts memorial lecture presented at the Royal Society on May 12, 1986. We dare to quote a piece from the paper by Neal Amundson (1986) related to the 1953 paper by Peter V. Danckwerts (“P.V.D.”), which is still very relevant to this day (using our notation):

“In this same paper, the boundary conditions at the fore and aft ends of a packed tubular reactor are ‘derived’. I put derived in quote since it is apparent that P.V.D. did not really believe that his idea was a very deep one. His reasoning goes essentially as follows. At the front end

$$UC_M = UC - D_x \left. \frac{\partial C}{\partial x} \right|_{x=0^+}, \quad x = 0 \quad (5)$$

Since this merely says that the flux into the front must be equal to the flux leaving at  $x = 0^+$ , clearly satisfactorily provided there is no diffusion in the  $x$  upstream direction at  $x = 0, \dots$ ” Amundson (1986) went on to justify also why Danckwerts used a zero gradient ( $\partial C/\partial x$ ) at the exit of a finite column (not the main focus of the comments and reply here). Amundson concluded that “It is not possible to estimate how many papers have been written justifying or invalidating these boundary conditions under various situations.”

The boundary conditions were initially also an issue in the soil, hydrologic and hydrogeologic sciences. While Brenner (1962) was likely to derive the first-type

complete solutions for finite systems subject to third-type inlet condition, to our knowledge, the first third-type solution for a semi-infinite medium was obtained by Lindstrom et al. (1967). Since the 1970s two- and three-dimensional third-type solutions have been published extensively, including discussions of volume and flux-averaged concentrations (van Genuchten and Parker 1984; Parker and van Genuchten 1984), extensions to layered, multi-dimensional and/or nonequilibrium transport systems (Batu and van Genuchten 1990; Leij et al. 1991a; Toride et al. 1993), and more recent applications and discussions (Peters and Smith 2001; Chen et al. 2011; Burnell et al. 2012). While we thought, like Danckwerts (1953), that the issue was relatively transparent and had been solved convincingly, the topic unfortunately seems to remain controversial with some.

In conclusion, we remain solidly behind the statements in Batu (2010) that third-type solutions should be used in transport studies that focus on resident concentrations since they guarantee solute flux continuity across inlet boundaries. On the other hand, first-type boundary conditions satisfy mass balance criteria only if the modeled concentrations are meant to represent flux concentrations; they do not satisfy mass balance constraints for resident concentrations.

## References

- Amundson, N.R. 1986. P.V. Danckwerts—His research career and its significance. *Chemical Engineering Science* 41, no. 8:1947–1955.
- Batu, V. 2010. Estimation of degradation rates by satisfying mass balance at the inlet. *Ground Water*, 48, no. 4: 560–568.
- Batu, V., and M.Th. van Genuchten. 1990. First- and third-type boundary conditions in two dimensional solute transport modeling. *Water Resources Research* 26, no. 2: 339–350.
- Bear, J. 1979. *Hydraulics of Groundwater*. New York: McGraw-Hill Inc.
- Brenner, H. 1962. The diffusion model of longitudinal mixing in beds of finite length. Numerical values. *Chemical Engineering Science* 17: 229–243.
- Burnell, D.K., J.W. Mercer, and L.S. Sims. 2012. Reply. *Ground Water*, 50, no. 5: 665–668.
- Buscheck, T.E., and C.M. Alcantar. 1995. Regression methods and analytical solutions to demonstrate intrinsic bioremediation. In *Intrinsic Bioremediation*, ed. R.E. Hinchee, J.T. Wilson, and D.C. Downey, 109–116. Columbus, Ohio: Battelle Press.
- Chapelle, H.C., P.M. Bradley, D.R. Lovley, and D.A. Vroblesky. 1995. Measuring rates of biodegradation in a contaminated aquifer using field and laboratory methods. *Ground Water*, 34, no. 4: 691–698.
- Chen, J.-S., Y.-H. Liu, C.-P. Liang, C.-W. Liu, and C.-W. Lin. 2011. Exact analytical solutions for two-dimensional advection-dispersion equation in cylindrical coordinates subject to third-type inlet boundary condition. *Advances in Water Resources* 34: 365–375.
- Damköhler, G. 1937. Einflüsse der Strömung, Diffusion und des Wärmeüberganges auf die Leistung von Reaktionsöfen: III. Zur Frage der maximalen Übertemperatur in einem rohrförmigen Kontaktofen bei exothermen Reaktionen, *Z. Elektrochem*, 43–1, 8–13.
- Danckwerts, P.V. 1953. Continuous flow systems; Distribution of residence times. *Chemical Engineering Science* 2: 1–13.

- Gershon, N.D., and A. Nir. 1969. Effect of boundary conditions of models on tracer distribution in flow through porous mediums. *Water Resources Research* 5, no. 4: 830–840.
- Gorokhovski, V. 2012. Technical commentary on ‘Estimation of degradation rates by satisfying mass balance at the inlet’ by Vedat Batu. *Ground Water* 48, no. 4: 560–568.
- Kreft, A., and A. Zuber. 1978. On the physical meaning of the dispersion equation and its solution for different initial and boundary conditions. *Chemical Engineering Science* 33: 1471–1480.
- Langmuir, I. 1908. The velocity of reactions in gases moving through heated vessels and effect of convection and diffusion. *Journal of the American Chemical Society* 43: 2457–2462.
- Leij, F.J., T.H. Skaggs, and M.Th. van Genuchten. 1991a. Analytical solutions for solute transport in three-dimensional semi-infinite porous medium. *Water Resources Research* 27, no. 10: 2719–2733.
- Leij, F.J., J.H. Dane, and M.Th. van Genuchten. 1991b. Mathematical analysis of one-dimensional solute transport in a layered soil profile. *Soil Science Society of America Journal* 58: 944–953.
- Lindstrom, F.T., R. Haque, V.H. Freed, and L. Boersma. 1967. Theory on the movement of some herbicides in soils: Linear diffusion and convection of chemicals in soils. *Environmental Science & Technology* 1: 561–565.
- Neville, C.J. 2012. Discussion of ‘Estimation of degradation rates by satisfying mass balance at the inlet’ by Vedat Batu.” *Ground Water* 48, no. 4: 560–568.
- Parker, J.C., and M.Th. van Genuchten. 1984. Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport. *Water Resources Research* 20, no. 7: 866–872.
- Pearson, J.R.A. 1958. A note on the “Danckwerts” boundary conditions for continuous flow reactors. *Chemical Engineering Science* 10: 281–284.
- Peters, G.P., and D.W. Smith. 2001. Numerical study of boundary conditions for solute transport through a porous medium. *International Journal for Numerical and Analytical Methods in Geomechanics*, 25: 629–650.
- Toride, N., F.J. Leij, and M.Th. van Genuchten. 1993. Flux-averaged concentrations for transport in soils having nonuniform initial solute distributions. *Soil Science Society of America Journal* 57: 1406–1409.
- van Genuchten, M.Th. 1981. Analytical solutions for chemical transport with simultaneous adsorption, zero-order production and first-order decay. *Journal of Hydrology* 49: 213–233.
- van Genuchten, M.Th., and J.C. Parker. 1984. Boundary conditions for displacement experiments through short laboratory soil columns. *Soil Science Society of America Journal* 48: 703–714.
- Wehner, J.F., and R.H. Wilhelm. 1956. Boundary conditions of flow reactor. *Chemical Engineering Science* 6: 89–93.



## Invest in your future by investing in an NGWA membership.

A \$120.00\* NGWA membership is one of the best investments you can make for yourself, your company, and your future—and one that pays for itself many times over.

As an NGWA scientist/engineer member, you receive:

### SAVINGS

- Complimentary subscriptions to NGWA's award-winning peer-reviewed journals:
 

<i>Groundwater</i> ®	<b>\$538.00</b>
<i>Groundwater Monitoring &amp; Remediation</i> ®	<b>\$267.00</b>
- Reduced registration fees on educational offerings—including the annual NGWA Summit, a savings alone of \$150.00 **\$150.00**
- Discounted prices on bookstore purchases such as *Groundwater Economics*—a savings of \$27.00 **\$27.00**
- Special pricing on job postings and resume reviews on our online NGWA Career Center—a savings of \$100.00 **\$100.00**
- And the list goes on!

**TOTAL SAVINGS ON JUST THESE ITEMS!**  
**\$1,082.00**

\*The \$120.00 yearly fee is for an individual NGWA scientist/engineer membership; the company rate is \$375.00, which includes three employee memberships; additional employees can be added for only \$95.00 each. International rates are slightly higher.



800 551.7379  
www.NGWA.org/Membership  
614 898.7791