Communication

Is the Hyporheic Zone Relevant beyond the Scientific Community?

Jörg Lewandowski [1,2,*], **Shai Arnon** [3], **Eddie Banks** [4], **Okke Batelaan** [4], **Andrea Betterle** [5,6], **Tabea Broecker** [7], **Claudia Coll** [8], **Jennifer D. Drummond** [9], **Jaime Gaona Garcia** [1,10,11], **Jason Galloway** [1,2], **Jesus Gomez-Velez** [12], **Robert C. Grabowski** [13], **Skuyler P. Herzog** [14], **Reinhard Hinkelmann** [7], **Anja Höhne** [1,15], **Juliane Hollender** [5], **Marcus A. Horn** [16,17], **Anna Jaeger** [1,2], **Stefan Krause** [9], **Adrian Löchner Prats** [18], **Chiara Magliozzi** [13,19], **Karin Meinikmann** [1,20], **Brian Babak Mojarrad** [21], **Birgit Maria Mueller** [1,22], **Ignacio Peralta-Maraver** [23], **Andrea L. Popp** [5,24], **Malte Posselt** [8], **Anke Putschew** [22], **Michael Radke** [25], **Muhammad Raza** [26,27], **Joakim Riml** [21], **Anne Robertson** [23], **Cyrus Rutere** [16], **Jonas L. Schaper** [1,22], **Mario Schirmer** [5], **Hanna Schulz** [1,2], **Margaret Shanafield** [4], **Tanu Singh** [9], **Adam S. Ward** [14], **Philipp Wolke** [1,28], **Anders Wörman** [21] and **Liwen Wu** [1,2]

[1] Department Ecohydrology, Leibniz-Institute of Freshwater Ecology and Inland Fisheries, 12587 Berlin, Germany; jgaona@obsebre.es (J.G.G.); jason.austin.galloway@student.hu-berlin.de (J.G.); anja.hoehne@posteo.de (A.H.); anna.jaeger@igb-berlin.de (A.J.); karin.meinikmann@julius-kuehn.de (K.M.); b.mueller@igb-berlin.de (B.M.M.); schaper@igb-berlin.de (J.L.S.); h.schulz@igb-berlin.de (H.S.); wolke@igb-berlin.de (P.W.); liwen.wu@igb-berlin.de (L.W.)

[2] Geography Department, Humboldt University of Berlin, 12489 Berlin, Germany

[3] Zuckerberg Institute for Water Research, The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Midreshet Ben-Gurion 84990, Israel; sarnon@bgu.ac.il

[4] National Centre for Groundwater Research and Training (NCGRT), College of Science & Engineering, Flinders University, Adelaide, SA 5001, Australia; eddie.banks@flinders.edu.au (E.B.); okke.batelaan@flinders.edu.au (O.B.); margaret.shanafield@flinders.edu.au (M.S.)

[5] Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland; andrea.betterle@eawag.ch (A.B.); juliane.hollender@eawag.ch (J.H.); andrea.popp@eawag.ch (A.L.P.); mario.schirmer@eawag.ch (M.S.)

[6] AAWA-Autorità di distretto idrografico delle Alpi Orientali, 38122 Trento, Italy

[7] Chair of Water Resources Management and Modeling of Hydrosystems, Technische Universität Berlin, 10623 Berlin, Germany; tabea.broecker@uwi.tu-berlin.de (T.B.); reinhard.hinkelmann@wahyd.tu-berlin.de (R.H.)

[8] Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, 11418 Stockholm, Sweden; claudia.coll@aces.su.se (C.C.); malte.posselt@aces.su.se (M.P.)

[9] School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK; j.drummond@bham.ac.uk (J.D.D.); s.krause@bham.ac.uk (S.K.); txs523@bham.ac.uk (T.S.)

[10] Biology, Chemistry and Pharmacy Department, Free University Berlin, 14195 Berlin, Germany

[11] Civil and Environmental Engineer Department, University of Trento, 38123 Trento, Italy

[12] Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, TN 37205, USA; jesus.gomezvelez@vanderbilt.edu

[13] School of Water, Energy and Environment, Cranfield University, Cranfield MK43 0AL, UK; r.c.grabowski@cranfield.ac.uk (R.C.G.); chiara.magliozzi@isti.cnr.it (C.M.)

[14] O'Neill School of Public and Environmental Affairs, Indiana University, Bloomington, IN 47405, USA; skuyherz@iu.edu (S.P.H.); adamward@indiana.edu (A.S.W.)

[15] School of Earth Sciences, University of Western Australia, Crawley, Western Australia 6009, Australia

[16] Department of Ecological Microbiology, University of Bayreuth, 95440 Bayreuth, Germany; marcus.horn@uni-bayreuth.de (M.A.H.); cyrusrnjeru@gmail.com (C.R.)

[17] Institute of Microbiology, Leibniz University of Hannover, 30419 Hannover, Germany

[18] Naturalea Conservació, SL, 08211 Castellar del Vallès, Spain; adrianlochner@naturalea.eu

[19] Istituto di Scienza e Tecnologie dell'Informazione (ISTI) National Research Council (CNR), Area della Ricerca CNR di Pisa, 56124 Pisa, Italy

[20] Julius Kühn-Institute, Institute for Ecological Chemistry, Plant Analysis and Stored Product Protection, 14195 Berlin, Germany

[21] Department of Sustainable Development, Environmental Science and Engineering, KTH Royal Institute of Technology, 10044 Stockholm, Sweden; mojarrad@kth.se (B.B.M.); riml@kth.se (J.R.); worman@kth.se (A.W.)

[22] Department of Environmental Science and Technology, Chair Water Quality Engineering, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany; anke.putschew@tu-berlin.de

[23] Department of Life Sciences, University of Roehampton, London SW15 4JD, UK; nacho.peralta@roehampton.ac.uk (I.P.-M.); a.robertson@roehampton.ac.uk (A.R.)

[24] Department of Environmental Systems Science, ETH Zurich, 8000 Zurich, Switzerland

[25] Institute for Hygiene and Environment, Free and Hanseatic City of Hamburg, 20539 Hamburg, Germany; michael.radke@hu.hamburg.de

[26] IWW Water Centre, 45476 Mülheim an der Ruhr, Germany; raza@geo.tu-darmstadt.de

[27] Institute of Applied Geosciences, Technische Universität Darmstadt, 64287 Darmstadt, Germany

[28] Department of Earth Science, Free University Berlin, 12249 Berlin, Germany

* Correspondence: lewe@igb-berlin.de; Tel.: +49-30-64181-668

Abstract: Rivers are important ecosystems under continuous anthropogenic stresses. The hyporheic zone is a ubiquitous, reactive interface between the main channel and its surrounding sediments along the river network. We elaborate on the main physical, biological, and biogeochemical drivers and processes within the hyporheic zone that have been studied by multiple scientific disciplines for almost half a century. These previous efforts have shown that the hyporheic zone is a modulator for most metabolic stream processes and serves as a refuge and habitat for a diverse range of aquatic organisms. It also exerts a major control on river water quality by increasing the contact time with reactive environments, which in turn results in retention and transformation of nutrients, trace organic compounds, fine suspended particles, and microplastics, among others. The paper showcases the critical importance of hyporheic zones, both from a scientific and an applied perspective, and their role in ecosystem services to answer the question of the manuscript title. It identifies major research gaps in our understanding of hyporheic processes. In conclusion, we highlight the potential of hyporheic restoration to efficiently manage and reactivate ecosystem functions and services in river corridors.

Keywords: hyporheic zone; hyporheic exchange flow; surface water–groundwater exchange; ecosystem services; nutrient turnover; refuge; hyporheos; removal of trace organic compounds; emerging pollutants; self-purification capacity

1. Introduction

The "hyporheic zone" (HZ) is a unique habitat that is located at the interface of surface water and groundwater within river corridors. While the term hyporheic zone is sometimes used as a synonym for the streambed, it is more accurately the zone in which surface water and groundwater mix. The HZ is an interfacial zone important to many key stream processes and organisms. Because of the large surface area of sediment grains within the streambed and the high activity of microbes living in the HZ, it plays a key role as a reactive zone, transforming pollutants and natural solutes, as well as providing a habitat for benthic communities [1].

The term hyporheic zone was originally proposed by Orghidan in 1955 in Romanian, who described this interface as a discrete streambed compartment hosting a distinctive community [2]. Today, HZ research encompasses fields such as ecology, hydrology, hydrogeology, microbiology, geomorphology, biogeochemistry, environmental engineering, and conservation [3]. Therefore, a general definition and delineation of the HZ covering all disciplines is extraordinarily challenging [4]. Definitions of the HZ differ between disciplines, and sometimes even within the same discipline [5,6]. In ecology, it is generally assumed that the HZ is located just below the surface layer of the

streambed (also known as the benthic zone) and that its thickness typically oscillates in the centimeter range. In hydrology, and especially in modelling studies, the HZ is defined as the zone that contains all the flowpaths that begin and end at the sediment–water interface, whereas in biogeochemistry, it is defined as a zone where surface water and groundwater mix and where at least a certain percentage (e.g., 10%) of surface water is present [5]. The depth to which the HZ extends can vary over time because fluctuations of surface water level, surface water flow velocity, groundwater table level, and water temperature impact subsurface flow paths. In contrast to the lower boundary, the upper boundary of the HZ is clearly determined by the sediment surface. A comprehensive discussion and comparison of these definitions can be found in Gooseff [5], Gomez-Velez et al. [7], and Ward [6]. Here, we use the definition that the HZ comprises (1) saturated, porous streambed sediments (2) with a characteristic hyporheic community, either with (3) flowpaths originating from and returning to surface water or (4) a mixture of groundwater and at least 10% of surface water, and (5) with hyporheic residence times on time scales relevant for the processes of interest [6]. The flow of water into, in, out, or across the HZ is termed hyporheic exchange flow, or equally hyporheic exchange flux, both abbreviated as HEF [8]. In our definition, HEF is a specific type of surface water–groundwater exchange, but the terms HEF and surface water–groundwater exchange are not interchangeable. While some authors have used HEF to describe the general exchange between surface water and groundwater [9,10], a HZ may not always exist. For example, in river sections with strong up- or downwelling flow, the HZ could be minimized or vanish, but there would still be fluxes within the saturated, porous streambed sediments [11]. Thus, surface water–groundwater exchange is a broad term describing exchange between the aquifer and river, while HEF is a specific exchange under the prerequisite that a HZ is present.

Since 1955, there has been a steady increase in HZ research and several key papers have been published. For example, Brunke and Gonser [12] reviewed the ecological significance of exchange processes between groundwater and rivers and discussed human impacts and alterations of natural exchange processes, such as reduced connectivity due to colmation by fine particle loads or organic and toxic contamination of surface water. Hancock [13] also reviewed human impacts on HZs and their ecosystem services and suggested that the HZ should be considered in river management. Boulton et al. [14] focused more on transport processes and biogeochemical turnover in the HZ itself. Their review includes the relevant mechanisms, the fate of major chemical compounds, and involved organisms. Fischer et al. [15] investigated hyporheic processes from a microbial perspective and highlighted the importance of the activity and composition of the microbial communities for biochemical reactions in the HZ. Due to its significance for carbon and nitrogen cycling, they called the HZ "the river's liver". Krause et al. [16] published a review of HZ functions and discussed how to advance HZ process understanding across disciplinary boundaries. This was further elaborated by Krause et al. [17], who discussed the high biogeochemical activity of the HZ. The review by Boano et al. [1], focusing on modelling water, heat, and dissolved and sediment transport processes, directed research towards the scale and magnitude of HZ fluxes [18], while Magliozzi et al. [11] summarized the five main drivers (i.e., hydrological, topographical, hydrogeological, ecological, and anthropogenic) at catchment, valley, and reach scales that control spatial and temporal HEF variations.

Ward [6] stated that our understanding of coupled, interacting hyporheic processes is still quite limited and that there is an urgent need for cross-site comparisons that consider hydrological, ecological, and biogeochemical processes. Recent research has deepened our understanding of the ecological importance of the HZ and the response of communities to hydrological extremes. For example, Stubbington [19] and Dole-Olivier [20] discuss HZ function as a potential refuge for benthic invertebrates, especially during floods, low flows, and drying events. Other authors have investigated interactions between ecology and chemical processes; for example, Peralta-Maraver et al. [21] focused on the hierarchical interplay of hydrology, community ecology, and fate of nutrients, as well as pollutants in the HZ. Methodological advances have increased the precision and resolution of measurements of HEF, which has been essential for biogeochemical research. For

example, Anderson [22], Rau et al. [23], and Ren et al. [24] reviewed the use of heat as a tracer to study HEF. Knapp et al. [25] outlined the application of the "smart" tracer system resazurin–resorufin to study HEF and biogeochemical turnover in the HZ, as described in more detail below. Kalbus et al. [26] and Brunner et al. [27] gave an overview of the manifold measurement and modelling techniques for HEF processes. Further research has investigated biogeochemical processing in the HZ. While earlier studies focused on nutrients [28,29] and mining-derived pollutants, such as metals [30], recent papers have begun to investigate emerging pollutants, such as microplastics [31], pesticides [32], organic stormwater contaminants [33], and pharmaceuticals [34,35]. Even though there has been so much HZ research published in recent decades, it is unclear whether the hyporheic zone is of any relevance beyond the scientific community. This will be addressed with the present manuscript.

Despite the advancements in our scientific understanding of the HZ, further work is needed to link hydrological, ecological, and biogeochemical processes to develop a conceptual framework of the HZ and its associated ecosystem services [36,37]. Such ecosystem services are defined as "the benefits people obtain from ecosystems" by the Millennium Ecosystem Assessment [38], which also categorizes the services according to four main aspects: provisioning (e.g., food), regulating (e.g., water quality), supporting (e.g., nutrient cycling), and cultural services (e.g., recreation). From the history of HZ research, it is clear that the HZ provides ecosystem services, for example by supporting fish spawning and by serving as a "bioreactor", improving water quality. Ecosystem services provided by HZs are one option to show the relevance of the HZ beyond the research community. The ecosystem services framework has been criticized as overly anthropocentric and reductionist in its consideration of nature in purely monetary terms. Despite these shortcomings, we use ecosystem services provided by the HZ to illustrate the relevance of the HZ in a broader context, but avoid any monetary quantification in this review.

The aims of the present paper are (i) to provide a brief overview of recent developments in HZ research, (ii) to identify major research and knowledge gaps, and (iii) to show the relevance of the HZ beyond research focusing on HZ processes. Therefore, we identify ecosystem services provided by HZs and discuss the HZ's impact on the adjacent compartments, as well as on entire ecosystems.

2. Hyporheic Zone Drivers and Processes

2.1. Physical Drivers of Hyporheic Exchange Flows

HEFs (Figure 1) are driven by pressure gradients created by local streambed topographic variations and modulated by subsurface sediment architecture, combined with large-scale geomorphological and hydrogeological characteristics of the river network and adjacent aquifer systems, which can critically impact the spatial variability of HEF patterns [9,39–41]. At the scale of the HZ, very small water level fluctuations drive changes in the hydraulic gradients across streambed bedform structures.

The hydrogeology (i.e., the location, hydraulic conductivity, recharge, and discharge zones of local to regional aquifers) governs the overall spatio-temporal fluxes of surface water–groundwater exchange, and therefore the general gaining or losing character of rivers and river sections [42]. As discussed in the introduction, the HZ is the zone where flowpaths originate from and return to surface water. This zone may be compressed or absent in gaining and losing sections of streams [8,43], because gaining and losing flows that do not originate from the stream or terminate in the stream, respectively, are considered surface water–groundwater exchange flows, but not HEFs. Of course, gain or loss flows can still be highly relevant from an ecohydrological perspective. The absolute gaining or losing of water from streams is a dynamic feature which can vary spatially and temporally. The fragmentation of coherent gaining or losing zones at the streambed interface strongly depends on the regional groundwater contribution [41]. In gaining streams, local regional groundwater systems discharge groundwater through the HZ into surface waters. This is common in humid climates, where rivers drain groundwater systems. However, in (semi-)arid climates,

losing rivers are predominant (i.e., groundwater pressures below streams are often lower than the stream water pressure, resulting in infiltration of stream water) [44].

HEFs can also be induced by hydrodynamic pressure gradients along the stream bed arising from the flowing surface water [45,46]. On a rugged streambed surface, the surface water flow field produces a heterogeneous pressure distribution acting on the exchange between surface and subsurface water. In this setting, the streambed morphology and the overlying flow field control the spatial patterns of pressure gradients and boundary shear stress along the surface–subsurface water interface. The pressure distribution on the streambed surface significantly differs between ripples and dunes. Therefore, determining the stream water level (reflecting the hydrostatic pressure), as well as the hydrodynamic pressure arising from inertia effects along the streambed surface, is crucial for HEF investigations.
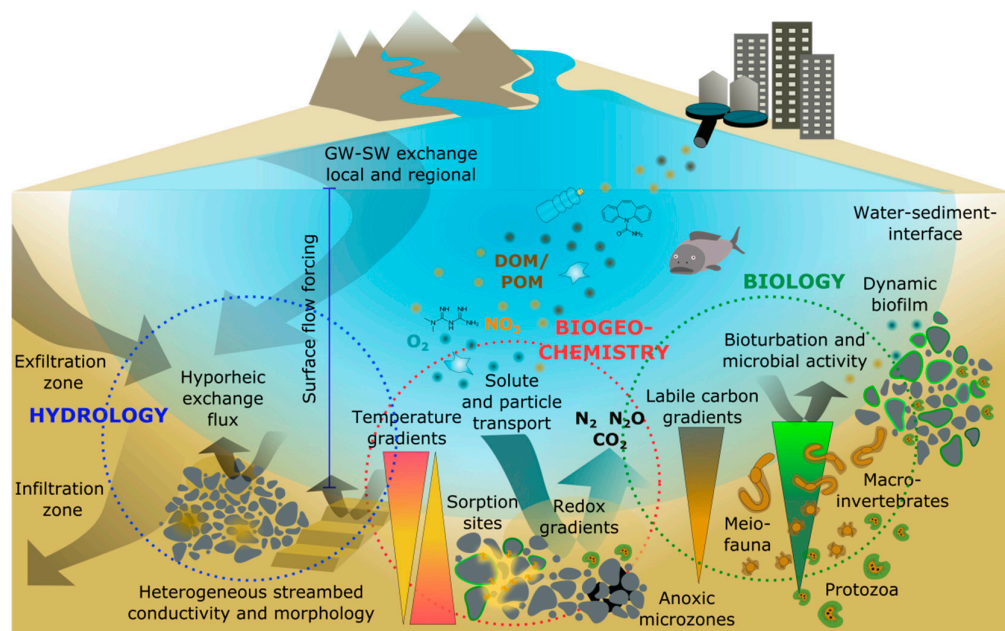

Figure 1. Conceptual model of the major hyporheic zone drivers and processes, as discussed in Section 2 of the present review. Dashed circles indicate the separation of disciplines in current hyporheic research, despite the high system complexity and manifold interconnections of hyporheic processes. GW-SW exchange is groundwater-surface water exchange; DOM and POM are dissolved or particulate organic matter, respectively.

At large scales, the stream water surface follows the streambed topography very closely, but as scales decrease the water surface tends to be smoother in comparison to the bed surface. This impedes direct use of the streambed topography to estimate the hydrostatic head, especially at small spatial scales, since very fine topographic features are often not reflected as similar features at the water surface. Recent investigations have suggested a scale (wavelength)-dependent ratio between stream water and bed surface fluctuations, thus providing a way to estimate the hydrostatic head distribution based on the streambed topography [40,41]. Pressure gradients might also be caused by flow of stream water over and around obstacles in the water body, such as woody debris [47–49]. Hydrodynamic pressure gradients and turbulent momentum transfer into the streambed sediments can control HEFs that are generally characterized by surficial flowpaths and short residence times. In particular, hyporheic exchange triggered by turbulent momentum transfer and by shear stresses at the sediment–water interface can be relevant, especially in the case of permeable sediments with large grain sizes [50,51]. This is due to the fact that increasing sediment permeability results in higher HEFs. Moreover, a larger grain size increases shear stress at the water–sediment interface and turbulence intensity of the boundary layer, which control the HEFs.

Other processes that can influence pressure gradients include the subtle differences in (hydrostatic) water levels across in-stream geomorphological features (e.g., HEF through a gravel island in the stream channel due to different water levels around the island). Another example is intra-meander groundwater flow, commonly triggered along tortuous rivers by longitudinal gradients of river stage [52]. Moreover, flow through streambed riffles is commonly driven by changing water levels along pool–riffle sequences of the stream. Besides pressure gradients, hydraulic conductivity of the sediment determines the intensity of HEFs, and the spatial heterogeneity of hydraulic conductivity might result in uneven distributions of HEF patterns [53–55]. In fact, according to the description of flow in saturated porous media (i.e., Darcy's law), HEFs tend to increase linearly with the hydraulic conductivity of the sediments, which, in turn, can span several orders of magnitude. As a result, given the short autocorrelation length of the hydraulic conductivity field in many environmental contexts, HEFs can display a lot of spatial heterogeneity, even at short scales [56,57].

Numerous well-known methods for measuring surface water–groundwater exchange exist [26,27,58]. Measurement techniques based on seepage meters, mini-piezometers, and thermal sensors have strongly improved our capacity to estimate HEFs. Vertical and longitudinal surveys of radon-222 (naturally occurring radioactive gas tracer with a half-life of 3.8 days) can also be used to quantify HEF along stream reaches [59,60]. Tracking surface water–groundwater interactions using temperature as a tracer is a particularly advantageous approach because it is easy to measure, the costs of temperature sensors are relatively low, and natural temperature differences at interfaces are common. Moreover, temperature depth profiles in the HZ are used to calculate HEFs [61–65]. Active heat pulse sensors have been developed to determine dynamic 3D flow fields in the near subsurface and quantify HEFs [66–68]. These overcome the limiting factors of streambed heat tracer studies, which use vertical, ambient temperature profiles and a 1D analytical solution of the heat diffusion–advection equation [22], ignoring horizontal flow components. Among the multiple thermal techniques, fiber-optic distributed temperature sensing (FO-DTS), pioneered by Selker et al. [69], Lowry et al. [70], and Tyler et al. [71], enables the spatio-temporal identification of the patterns of surface water–groundwater interactions. Subsequent research has showed the potential of this technique for estimating vertical exchanges by measuring thermal profiles with a higher depth resolution [72], or obtaining spatial flux patterns within the shallow streambed at relatively high resolution [73,74]. Combining FO-DTS with other techniques, such as thermal infrared reflectometry (TIR) [75] or geophysics [74,76,77] can provide insights into the impacts that the hydrogeological characteristics of the subsurface material can have on defining exchange patterns (i.e., to inform about the existence of different components of groundwater-surface water interactions, such as groundwater discharge, interflow, and local downwelling, depending on the hydrogeology) [74].

The physical drivers of HEF (channel slope, bedform geometry, flowpath length, sediment properties, and hydraulic head) and the transient hydraulic forcing control the residence times of water in the HZ, and thus, the development of potential hot spots for biogeochemical reactions [7,78,79]. For example, fine organic matter in the hyporheic zone reduces the hydraulic conductivity of the sediment, and thus increases hyporheic residence times. Consequently, there is a longer reaction time in the HZ and the redox pattern along flow paths will change. Under similar driving forces, HZs develop more easily under higher aspect ratios (the ratio between bedform height and width) and steeper channel slopes. This is important from an ecological perspective, as it is not only the amount of HEF but also the length and depth of the flowpaths in the HZ and the water residence time that play critical roles in modulating biogeochemical processes in the HZ [80].

On the reach scale, HEFs are often modelled using transient storage models [1]. This approach is subject to a variety of assumptions. For instance, when using transient storage models, it is commonly assumed that transient storage in the investigated river reach is primarily caused by HEFs [35,81]. This assumption only holds true if morphological features that cause surface water transient storage—such as pool–riffle sequences or side pools, where the flow velocity is orders of magnitudes lower than the advective surface water velocity—are largely absent in the investigated stream reach [82]. Furthermore, the most commonly used transient storage models predefine a

characteristic shape for the residence time distribution (RTD) in the HZ (i.e., parametric transient storage models). In the simplest case, the transient storage zone is described as a well-mixed compartment that mathematically transfers to an exponentially shaped RTD [83]. Further research has subsequently shown that in some streams, log-normal [84] and truncated power law [85] parameterization of residence times in the transient storage zone fit measured breakthrough curves more accurately, particularly in regard to longer residence times. However, assuming a characteristic shape of the RTD might be the biggest shortcoming of all parametric transient storage models, as the RTD, in fact, integrates over all stream processes, and thus, should directly be used to infer insights on physical, chemical, and biological processes [86–88]. Therefore, the flexibility of a shape-free or non-parametric deconvolution approach can also capture non-traditional features of measured BTCs, such as multiple peaks [88–90]. However, having higher flexibility consequently results in a higher degree of freedom, which makes the optimization procedure challenging when estimating hydrological model parameters [88]. Nevertheless, only the shape-free approach allows an accurate estimation of the hyporheic residence time, and likewise, its significance on water quality in riverine systems.

2.2. Hyporheic Assemblages and Biological Processes

The high surface area of the sedimentary matrix in the HZ is an important habitat for a wide range of organisms (Figure 1). A diverse assemblage of biofilms grow attached to sediment grains and cover the cavities of the pore space [91]. Furthermore, protists, meiofauna, and macroinvertebrates (see Table 1 for definition) occupy the interstitial spaces among sediment particles in the HZ, swimming in the pore space or digging into the sediment. Hyporheic assemblages (the "hyporheos") [92] play a critical role in the ecological functioning of the HZ. Hyporheic biofilms are mainly composed of diverse consortia of archaea and bacteria embedded in a matrix of extracellular polymeric substances, including polysaccharides [91]. Consequently, hyporheic biofilms present a high diversity of operational units [93] and metabolic capabilities [94], and are hot spots of enzymatic activity [95]. Hyporheic biofilms have the ability to degrade and even to consume a broad range of dissolved compounds (including nutrients, pollutants, and trace organic compounds) [91], supporting the water purifying capacity of the stream (as a hyporheic bioreactor, discussed below). Thus, hyporheic biofilms are considered crucial components of the global biogeochemical fluxes of carbon, nitrogen, and phosphorous [96]. Biofilms degrade large quantities of organic matter, releasing carbon dioxide to the atmosphere [1], and also denitrify nitrate, emitting nitrous oxide and nitrogen gas to the atmosphere [97]. The type, relative abundance, and distribution and interactions of microorganisms result in dynamic microbial communities inhabiting both nutrient-rich, reducing HZ sediments, as well as nutrient-poor, oxidizing HZ sediments [98]. Protists, meiofauna, and invertebrates inhabiting the streambed sediments also come into play, boosting biofilm activity by grazing and bioturbating the hyporheic sediments [21].

Table 1. Definition of different groups inhabiting the streambed. Note these are paraphyletic groups.

Group	Definition
Biofilms	Unicellular consortia of prokaryotes (archaea and bacteria), fungi, and algae (in the top sediment layers) embedded in a porous extracellular matrix.
Protozoa	Eukaryotic single cell free-living organisms such as flagellates, ciliates, and amoeba.
Meiofauna	Eumetazoa invertebrates whose body size generally ranges between 0.45 μm and 500 μm.
Macroinvertebrates	Eumetazoa invertebrates whose body size is generally greater than 500 μm.

The HZ is not only colonized by the hyporheos, but also by organisms from adjacent environments, such as stygobites from groundwater or excavating benthic biota [99]. In addition, the HZ may act as a refuge for benthic organisms escaping from a variety of perturbations and the pressures of biotic interactions [100] (Section 3.4). Therefore, categorically stating that the hyporheos

forms a discrete community (as an ecological entity) could be ambiguous and imprecise. Indeed, ecological communities, such as the hyporheos, are often inadequately described and quantified in ecological research [101]. However, Peralta-Maraver et al. [4] recently demonstrated that the hyporheos can be clearly distinguished from benthos as a discrete community with ecological integrity. Moreover, Peralta-Maraver et al. [4] also showed that the demarcation between both communities and the extension of their biotopes were quite dynamic as a result of the vertical hydrodynamic conditions and time. Vertical variability, direction, and magnitude of surface water–groundwater exchange, as well as heat and solute gradients, control the ecology in the HZ and in the benthic zone [14,102–107]. The concentration of solutes such as oxygen plays an important role in the ecology of the hyporheic zone (e.g., downwelling zones typically have higher concentrations of organic matter and oxygen, and possess a greater diversity and abundance of the hyporheos) [4]. These results reflect the ecotonal nature of the HZ [14] and also draw attention to the importance of ecological processes and services that the hyporheos sustains. To this end, hyporheic conditions favor the occurrence in the hyporheos of specific functional traits (e.g., body size and form) that reflect adaptation to the surrounding environment and that are dissimilar to those present in the benthos [108]. The consequences of trait diversification in the HZ extend beyond adaptive species shifts to exploit productive habitats, and suggest benefits to river restoration by enhancing functional interactions among different ecological niches [108].

Defining natural system boundaries is a critical aspect when assessing ecological processes and services [109,110]. Peralta-Maraver et al. [111] demonstrated that the streambed compartment and the biological features of the benthos and hyporheos drive the rate of coarse organic carbon (litter) decomposition, and thus play a crucial role in the wider functioning of the streambed ecosystem as a bioreactor. In the benthos, the biomass of metazoa was the primary predictor of decomposition, whereas in the hyporheic zone the protozoa were the strongest predictors [111]. Previous studies [112,113] showed that total mineralization of allochthonous organic carbon was actually higher in the benthic zone, while the HZ fulfils the role of an allochthonous organic carbon sink. The whole community of both compartments from biofilms to macroinvertebrates plays a vital and distinctive role in the ecological functioning of the hyporheic bioreactor. More importantly, the reduction in the supply of resources (e.g., oxygen) with depth and under upwelling conditions exerts a greater selective pressure on large body size classes [4]. As a result, streambed assemblages become more size-structured as environmental constraints increase, resulting in a reduction of the metabolic capacity of the hyporheic bioreactor [114].

2.3. Biogeochemical Processes

Most stream metabolic processes (including nutrient turnover, degradation of contaminants, removal of trace organic compounds, and other redox-related processes) occur not in the overlying water body but in the HZ (and the benthic zone), predominantly due to the presence of diverse microbial biofilms [25]. That is why they are called biogeochemical processes and not simply chemical or geochemical processes. Surface water that enters the HZ drives oxygen, nutrients, and other chemical compounds into the HZ, which in turn drives mineralization of organic matter along the flowpath through the HZ (Figure 1). Consequently, a redox zonation develops in the HZ. First, oxygen is consumed, and once oxygen is depleted nitrate is consumed, allowing for nitrate removal in the presence of non-limiting amounts of electron donors. This is followed by reduction and dissolution of iron(oxy)hydroxides. Subsequently, sulfate is reduced to sulfide and finally methane is produced. Archaea-driven methanogenesis is a widely spread anaerobic respiration mechanism in the HZ [115]. In a study by Jones et al. [116], methanogenesis accounted for all the respiration in anoxic sediments and up to 0.6% in oxic sediments. Paired with observations of denitrification in bulk-oxic sediments [80,117,118], these studies suggest that anoxic microzones with redox potentials below sulphate respiration occur, even in oxygenated sediments.

As discussed, bacterial (and archea) consortia mainly dominate hyporheic biofilms. This results in the coexistence of diverse operational taxonomic units and metabolic capabilities [91], such as chemolithotropy, where bacteria obtain energy from the oxidation of sulfide, sulfur, metal,

ammonium, or nitrite, among others, to fuel their metabolism. For example, nitrification, in which ammonium is converted by bacteria into nitrate, is a chemolithotrophic process occurring in the HZ. Nitrification has a major impact on the predominant form and abundance of nitrogen found in different parts of the HZ [119]. Moreover, even in cases of low nitrifier abundance and productivity, nitrification can significantly impact oxygen dynamics, accounting for up to 50% of the biological oxygen demand in the HZ [98]. In anoxic zones, denitrification is an important process where anaerobic respiration using nitrate occurs. The nitrate may be supplied by infiltrating water, but in most cases coupled nitrification–denitrification reactions occur as water enters anoxic microzones within the aerobic HZ [120]. The contribution of denitrification to total organic matter decomposition in streambed sediments has been reported to account for up to 50% of total carbon mineralization [121], although denitrification rates can vary dramatically between sites and even at different locations within a single stream cross-section due to sediment composition heterogeneity [81]. Denitrification rates are higher under higher availability of nitrate and dissolved organic carbon (DOC), higher hyporheic exchange rates determining substrate transport and oxygen concentrations, greater abundance of denitrifying microbes, the occurrence of anoxic microzones, as well as higher surface area of granular material [81]. Bacteria also use Fe^{2+} and Mn^{2+}, H_2, or reduced sulfur compounds as electron donors under anoxic conditions [98]. HZs receiving reduced groundwater are, therefore, predictably colonized by iron-oxidizing bacteria, since Fe^{2+} is a major groundwater constituent. In most natural waters, Mn^{2+} occurs in low concentrations and manganese oxidizers are present in low abundance. Moreover, since iron and manganese oxidation yield low energy and their oxidation is predominantly performed by heterotrophic bacteria, these ions do not contribute considerably to hyporheic productivity, except under extremely low organic matter concentrations and high metal concentrations [98].

Redox gradients in HZs can be quite steep at millimeter or even submillimeter scales, and are primarily controlled by microbial activity. Other chemical compounds are released or degraded depending on the redox zonation. For example, the pharmaceutical gabapentin is degraded under oxic and suboxic redox conditions (i.e., when nitrate is still present) but is stable under anoxic conditions [122]. In contrast, phosphate is released under anoxic conditions because it is bound to iron(oxy)hydroxides that are dissolved under reducing conditions [123]. The reactivity of the HZ is highly sensitive to the interactions with groundwater, since surface water and groundwater can differ considerably in temperature and chemical composition [124,125].

The reactivity of the HZ can be determined by measuring the turnover of individual electron donors and acceptors, such as organic carbon compounds, nitrate, oxygen, or iron redox species. Alternatively, Haggerty et al. [126,127] proposed the resazurin–resorufin system to approximate the microbial reactivity of transient storage zones. It uses the reactive tracer resazurin and its transformation product resorufin to determine metabolic activity of surface and subsurface storage zones [25]. Such a system provides a good estimate of microbial activity in a rather short period of time relative to measurements of turnover rates of individual electron donors and acceptors.

3. Relevance of the Hyporheic Zone

Due to physical, biological, and biogeochemical characteristics and processes, the HZ plays a crucial role in nutrient turnover, removal of TrOCs, and particle retention in streams (Figure 2). Furthermore, hyporheic sediments constitute an important habitat and refuge for aquatic organisms, as well as a reservoir of biodiversity. Often these functions are called ecosystem services. The classic definition of ecosystem services is based on a rather anthropocentric view of ecosystems as resources for society; we, however, also want to emphasize the use of these services for the ecosystem itself and for organisms depending on the ecosystem. Furthermore, the concept of ecosystem service has been introduced to make the services monetarily quantifiable and comparable in our economic world. In the present manuscript, we look at and discuss the conceptual benefits of ecosystem services without attempting any monetary quantification. Thus, we look at the major ecosystem services provided by the HZ to answer the question of whether the HZ is relevant beyond the scientific community. Generally, interactions between groundwater and surface water play a

fundamental role in the functioning of riverine and riparian ecosystems, and therefore underpin numerous ecosystem services. In the context of sustainable river basin management, it is crucial to understand and quantify HZ processes to understand the benefits they confer, and to restore functions and services where necessary [128]. Here, we highlight the role of the HZ in regulating and supporting ecosystem services.

3.1. Nutrient Turnover

HZs are characterized by steep redox gradients, intense microbial diversity, and high turnover rates (Figure 1). Therefore, they are sometimes considered (hydrodynamically driven) bioreactors [21,129]. Physico-chemical controlled sorption on the large surface area of the sediment matrix removes various compounds from the pore water. Sorption reactions and filtration of particles might be followed by degradation or desorption. HZs are often hot spots of phosphorus (P), nitrogen (N), and carbon (C) turnover [80,117,119].
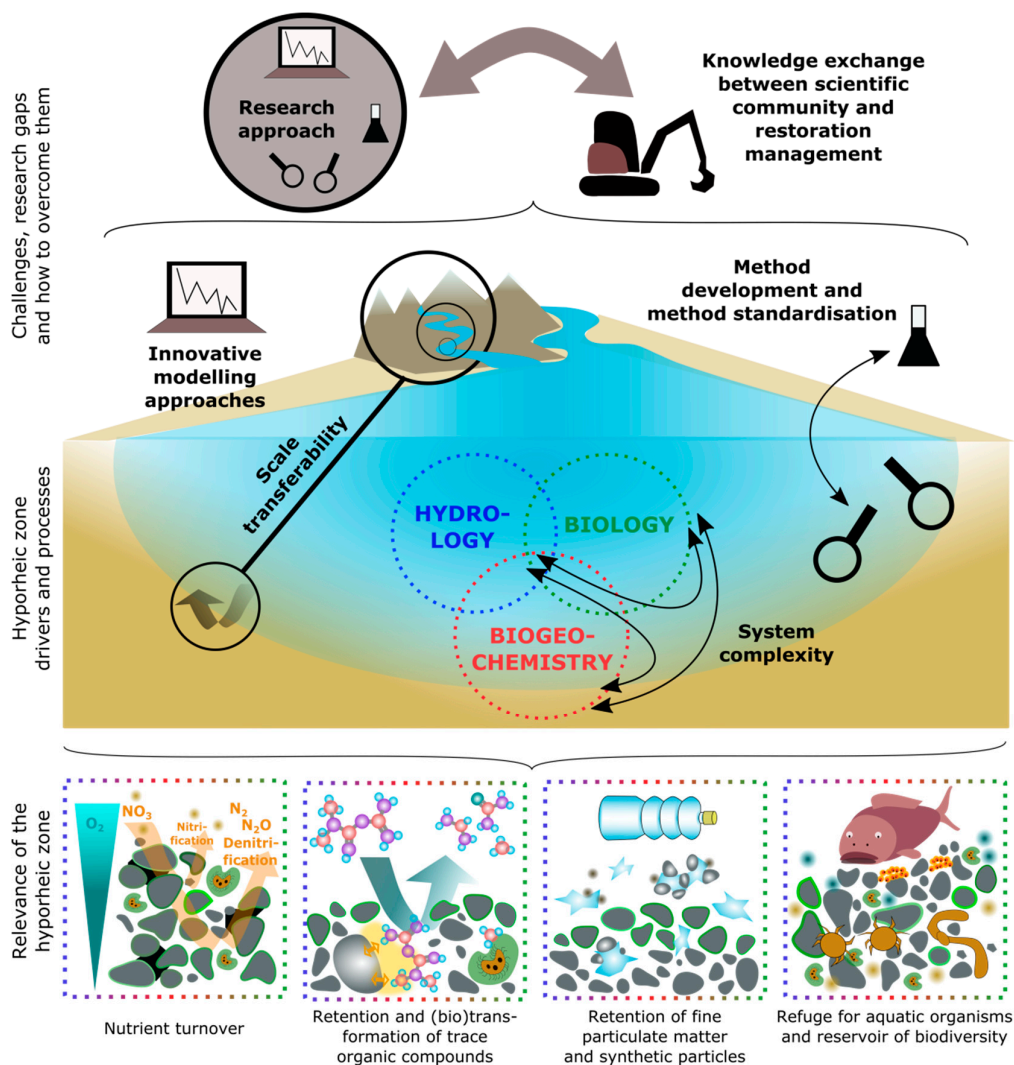

Figure 2. Graphic illustration of the relevance of the hyporheic zone based on different ecosystem services (lower row of panels in the figure; discussed in Section 3), major hyporheic research disciplines (central panel in the figure; see details in Figure 1, also discussed in Section 2), and challenges and research gaps of HZ research (shown as bold black in the figure; discussed in Section 4).

In other words, the HZ is both a sink and a source of nutrients. Phosphate and ammonium in the pore water in the HZ might originate from the mineralization of organic matter. Additionally, phosphate might be released by reductive dissolution of iron-bound phosphorus or weathering of bedrock [123]. Phosphate can only be released if it was previously uptaken, sorbed, or imported into the HZ as particulate matter, either due to gravity or filtration by HEFs [123]. Lapworth and Goody [130] found for a chalk stream that colloidal and particulate matter regulating bioavailable forms of P might also be formed in the HZ, perhaps through co-precipitation with $CaCO_3$. Depending on the biogeochemical milieu and the sediment composition, HZs might be sinks for dissolved phosphate. For example, Butturini and Sabater [131] measured the nutrient retention efficiency in the HZ of a sandy Mediterranean stream, finding an uptake length of 3.3 cm for ammonium and 37 cm for phosphate.

Denitrification and nitrification are mainly driven by nitrate, dissolved organic carbon, and oxygen concentrations, which is why the HZ has a high potential to regulate the fate of nitrate in streams. While inorganic nitrogen can be removed in the HZ by various processes, such as sorption or assimilation, the microbial process of denitrification is the major removal mechanism. At the same time, formation of nitrate by oxidation of ammonium (nitrification) can counteract the effect of denitrification. Nitrification particularly occurs in the surficial sections of the benthic biofilm [132]. Zarnetske et al. [80] investigated, in a gravel-bar-inducing HEF, the transition of nitrification to denitrification for a range of residence times. While short residence times at the head of the gravel bar caused net nitrification, longer residence times of more than 6.9 h, in this case, led to net denitrification, particularly at its tail. Formation of N_2 across all residence times showed that denitrification likely occurred in oxygen-reduced microsites, even where nitrification was the predominant process. The study demonstrated that whether the HZ is a net sink or a net source of nitrate depends to a large extent on the distribution of residence times. In addition, the quality of dissolved organic carbon influences denitrification [117]. Addition of acetate led to an increased denitrification rate in the HZ, showing that the nitrate removal process is limited by transport of labile dissolved organic carbon to the HZ.

Current river management measures focus not only on restoring flora and fauna but also aim to improve N removal by increasing hyporheic connectivity and optimizing hyporheic residence times [133]. To maximize the reaction yield, hyporheic water must interact with reactive sediments and biofilms for a period comparable with the relevant reaction timescale(s). Damköhler numbers can provide a quantitative estimate of the effectiveness of reactions in the HZ [81,134]. For first order approximations of attenuation rates, the hyporheic Damköhler number (Da_{HZ}) is the product of the hydraulic retention time and the reaction rate coefficient. A Da_{HZ} of 1 means that the amount of water treated by the HZ and the completeness of such treatment are balanced. In contrast, very small Da_{HZ} are indicative of reaction limitation, in which hyporheic retention times are much shorter compared to reaction timescales, so attenuation reactions do not have time to proceed effectively. In the opposite case of transport limitation ($Da_{HZ} \gg 1$), attenuation reactions run to completion relatively early along a flowpath, meaning the remaining retention time is not beneficial in terms of water quality. The small HEF in the case of transport limitation implies that only a limited percentage of the stream water is affected by the biogeochemical reactions in the HZ.

Although the capacity to reduce nitrate loads by hyporheic restoration in individual stream reaches might be small [135,136], the cumulative nitrate removal capacity over longer reaches or stream networks can be significant under favorable environmental conditions. Morén et al. [137] showed in a nationwide simulation that small agricultural streams have high potential to reduce the terrestrial N load in Sweden, and thus, highlighted that hyporheic restoration can be seen as one action strategy of several in a spatially differentiated remediation plan [138] working towards the goals of the water framework directive. Harvey et al. [133] recently introduced the reaction significance factor and showed that intermediate levels of hyporheic connectivity, rather than the highest or lowest levels, are the most efficient ones in removing nitrogen from river networks. Moreover, it has been shown that the hydrological regime of a stream can substantially affect the reach-scale turnover of nutrients [139]. Streamflow dynamics and river morphology jointly control

river stage and flow velocity, and in turn, the extent of HEFs. As a consequence, temporal variability of river flow conditions mediated by landscape, geomorphological, and climatic features at the catchment scale is of paramount importance for the temporal dynamics of biogeochemical reaction yields.

3.2. Retention and (Bio)transformation of Trace Organic Compounds

Trace organic compounds (TrOCs) of anthropogenic origin occur in very low concentrations (µg L^{-1} to ng L^{-1}) in freshwaters, but might exhibit ecotoxicological effects, such as endocrine disruption, oxidative stress, growth inhibition, or altered behavior, even in the ng L^{-1} range [140–143]. For the HZ, especially polar, and thus highly mobile and persistent or pseudo-persistent (continuous release in the environment) TrOCs, are of relevance. Examples include industrial chemicals, pesticides, washing and cleaning agents, personal care products, pharmaceuticals, artificial sweeteners, and substances leaching from facade or surface sealing. TrOCs typically enter surface waters via wastewater treatment plant effluents, since wastewater is most commonly only purified in treatment plants with respect to organic matter, phosphorus, and nitrogen [144], while many TrOCs are not, or only partially, degraded in wastewater treatment plants [145]. Furthermore, urban drainage, combined sewer overflow [146], or leaking water from sewer systems [147], onsite wastewater treatment systems [148], and landfills [149] reach the aquatic environment without undergoing human-induced purification processes. This means that a significant amount of TrOCs are discharged into rivers and streams [150]. In cities with partially closed water cycles or with water supply wells downstream of TrOC sources, TrOCs might end up in drinking water supply systems [151].

Biotransformation, sorption, dispersion, photolysis, and volatilization influence the fate and attenuation of TrOCs in aquatic systems [152] (Figure 2). All these processes are affected by the physico-chemical properties of the compounds (i.e., octanol water partitioning coefficient log Kow, functional groups, ionization), as well as by physical and biological parameters of the river and the sediment (i.e., river flow rate, hydraulic conductivity, turbidity, dissolved oxygen concentration, pH, temperature, the structure of microbial communities, the hydraulic regime, and the extent of hyporheic exchange in the river) [153]. Several studies on bank filtration for drinking water production strongly indicate that natural attenuation of TrOCs is most pronounced in the first few meters of infiltration (i.e., within the highly reactive HZ) [12,154–158], making this zone very important in contributing to this ecosystem service.

As described for nutrient retention, hyporheic connectivity, water, and solute residence times are relevant for TrOC removal as well. The specific biogeochemistry, especially redox conditions and carbon availability, along a flowpath plays a major role in the turnover efficiency and reactivity of TrOCs in the HZ. TrOC reactivity (i.e., the rate of chemical transformation of a given TrOC) along a hyporheic flowpath was found to be a function of the ambient redox conditions, the availability of biodegradable organic carbon, and the structure and diversity of the microbial community. Burke et al. [159] examined the fate of ten TrOCs in sediment cores taken from a bank filtration site under varying redox conditions caused by different temperatures. Although they observed compound-specific behavior, especially related to redox sensitivity of compounds, they generally showed that reactivity was highest under warm/oxic conditions, lower in cold/oxic conditions, and lowest in warm manganese-reducing conditions. Moreover, Schaper et al. [122] found that several TrOCs are preferentially transformed under oxic and suboxic conditions. Schaper et al. [160] investigated attenuation of 28 TrOCs along a hyporheic flowpath in an urban lowland river in situ. They observed differences in turnover rates and differences in retardation coefficients caused by reversible sorption between consecutive sections of the flowpath (0–10, 10–30, and 30–40 cm). Most compounds showed highest transformation in the first 10 cm of the flowpath, although the oxic zone reached down to 30 cm. They attributed the spatial difference in transformation within the same redox zone to the higher availability of biodegradable dissolved organic matter in the first 10 cm, which led to higher microbial activity in the shallow HZ. Not only the activity, but also the diversity and composition of TrOC-transforming bacteria communities can affect the reaction rate coefficients.

In a mesocosm study investigating TrOC half-lives in recirculating flumes, three different levels of sediment bacterial diversity were compared. Higher bacterial diversity significantly increased degradation of both the artificial sweetener acesulfame and the anti-epileptic drug carbamazepine [161]. In addition, the microscopic trophic interactions between bacterial biofilms and microscopic grazers (i.e., flagellates and ciliates) in the pore space can also determine the performance of the HZ during processing of TrOCs. Moderate levels of grazing might even have a positive effect on bacterial activity due to the selective consumption of less active bacteria [162], via the predator effect on bacteria dispersal in the medium (as a consequence of swimming around and grazing). Grazing on biofilms may result in better exposure of TrOCs to potential degraders [163], predation-induced recycling of nutrients (microbial loop) [162], and the increase of the absorption surface [21]. Nevertheless, this hypothesis has not been tested yet.

In contrast to most TrOCs that are either best degraded under oxic or suboxic conditions or which are degraded independent of the redox potential, very few persistent compounds and transformation products are preferentially degraded under anoxic conditions in saturated sediments. El-Athman et al. [164–166] showed that the very persistent triiodinated benzoic acid unit of the iodinated X-ray contrast media can be deiodinated in reducing environments using cobalamines (e.g., vitamin B12 as an electron shuttle). Under aerobic conditions, the apparent removal via transformation of iodinated X-ray contrast media is just based on side chain alterations, but not on deiodination. It is expected that alternating redox conditions may enhance the degree of transformation; for example, by opening the aromatic structure of the triiodo benzoic acid derivatives, which might be possible after removal of the relatively large iodine atoms under reduced conditions followed by a further transformation under aerobic conditions.

Many TrOCs, such as pharmaceuticals from urban drainage, but also phosphorus in runoff from agriculture or heavy metals, can be removed in the HZ through physico-chemical controlled adsorption on the large inner surfaces of the sediments, often followed by other transforming or degrading reactions. The degree of retention of solutes subject to reversible sorption is directly proportional to HEFs and the solute residence time in the HZ, but also depends on the equilibrium partition coefficient of the sorption reaction [34,167]. Sorption of TrOCs is also impacted by biogeochemical conditions in the HZ. For example, pH and organic matter in the HZ affect the sorption of charged and ionizable pharmaceuticals [168]. Pharmaceutical compounds with specific functional groups, such as ibuprofen and sulfamethoxazole, have the capability to transform into anionic species with increasing pH, while becoming neutral at lower pH [169]; thus, sorption rates increase at lower pH and high organic matter content. Similar mechanisms arise by adsorption of solutes on colloidal particles that are transported in flowing water, subjected to HEF, and subsequently clogged in the pores of the sediment matrix of the HZ [170,171].

Often, biodegradation of TrOCs does not result in complete mineralization, but in a myriad set of different transformation products (TPs). It has been demonstrated that some TPs are more toxic [172] and more stable [173,174] than their parent compounds. Usually, much less ecotoxicological data exist about TPs than their parent compounds. For example, in a bench-scaled flume experiment designed to study hyporheic processes [175], TPs were detected, which were only formed in the sediment but released to the water, hinting at secondary contamination with TPs [176]. In particular, valsartan acid, a rather stable TP of the common blood pressure medication valsartan, forms in situ in the HZ [160,177] and significantly increases its concentrations in the surface water of wastewater receiving streams [178].

3.3. Retention of Fine Particulate Matter and Synthetic Particles

Fine particles in the stream water column are problematic if they occur in high concentrations or are carrying sorbed contaminants [179]. Hyporheic filtration can reduce the concentration of fine particles despite low settling velocities [180,181]. Therefore, the HZ and HEF are highly relevant for particle removal [182]. Increased sediment loads that often result from agricultural run-off, particularly fine sediments <2 mm in size, can lead to colmation (clogging) in the benthic zone and HZ. This results in reduced hydraulic connectivity and concomitant changes in the hyporheos [183–

185]. The functional traits of hyporheos also change along a colmation gradient [184,186]. The ecosystem services delivered by the HZ also diminish under colmation (e.g., survival of salmonid eggs and embryos is much lower under colmated conditions) [187,188]. While colmation has a negative impact on the biological community in the HZ, the removal of particulate matter by filtration is positive from the perspective of surface water quality [180] (Figure 2).

Previous research on deposition and retention of fine suspended particles in streams focused on clay and organic matter particles [182,189]. The impacts of microplastics and nanomaterials in streams are still unclear. While research on marine microplastics is advancing rapidly, there is still a lack of data and knowledge on microplastic abundance and fate in freshwater systems. Few studies have been conducted in rivers, with most of them focusing on larger systems and urban environments [190,191]. The observed microplastic abundances in riverine water, as well as hyporheic sediment samples, were generally high, and sometimes an order of magnitude above levels reported for marine environments [192].

The major sources of microplastics in rivers are sludge from wastewater treatment plants (WWTP) that is spread over agriculture fields and illegally dumped plastic [193]. WWTP effluents contain fewer particles than sludge, but due to their continuous input into the environment they can be a significant source to streams [194,195]. Road runoff and stormwater runoff from urban areas also source microplastics [196]. Since most rivers in central Europe receive WWTP effluent, road, and stormwater runoff, it can be assumed that most, if not all, rivers and their HZs are contaminated by microplastics.

Laboratory experiments indicate that heteroaggregates with suspended solids can be formed, which is supported by modelling approaches [197,198]. Aggregation, fouling, and particle size distribution appear to affect sedimentation behavior. Several authors highlight the uneven distribution of sampled microplastics in water and sediment along river corridors [191,192,198,199]. Hotspots with considerable concentrations were commonly found in the HZ. This result coincides with a recent experimental study showing that microplastics are transported similarly to naturally occurring allochthonous particles [200], which are known to develop hotspots in river corridors. Finally, deposit feeders seem to affect microplastic transport into the HZ [201] and flood events can partially remobilize microplastics retained in river sediments [202].

3.4. Refuge for Aquatic Organisms and Reservoir of Biodiversity

The HZ is considered a refuge for aquatic organisms, especially during adverse environmental conditions, such as floods, droughts, and heat waves [19,20,203] (Figure 2). Disturbances are generally reduced in the HZ compared to the benthic zone due to its capacity for retaining water during drying periods and its greater stability during floods [99]. In addition, the HZ is a refuge for invertebrates and fish during their early stages of development due to the reduced predator pressure [92]. For example, the HZ is critical in salmonid life histories; salmonids bury their eggs in the HZ of gravel bed streams, and the developing embryos remain there until emerging as free-swimming fish some months later [204].The use of the HZ as a refuge is not exclusive to invertebrates or fish. Biofilms, composed of consortia of bacterial strains, use hyporheic sediments as a refuge during dry events, surviving in the deeper wetted sections and recolonising the sediment matrix when interstitial pore spaces become re-filled with water [205]. This is especially relevant to the role of streambed biofilms on the functioning of the hyporheic bioreactor during pollutant breakdown and nutrient cycling.

Still, the importance of the HZ as a refuge is debated and some studies contradict this idea [99]. Nevertheless, the importance of the HZ as a refuge becomes evident in intermittent systems [21]. These systems are common all around the world, sustaining and supporting diverse communities that are well adapted to persist in the HZ during dry conditions [206]. Streambed communities in Mediterranean streams and rivers are the typical example of well-adapted organisms to natural intermittency that make use of the HZ as a refuge [207].

4. Challenges, Research Gaps, and How to Overcome Them

Despite a great amount of HZ research during the past two decades, there are still major research gaps (Figure 2) that need to be addressed to progress our understanding of HZ processes and functioning. Further research closing the gaps is necessary to improve our understanding of HZs, to protect HZs and ecosystem services provided by them, and finally to conduct adequate and efficient management measures to restore ecosystem functions and ecosystem services.

4.1. System Complexity

Our knowledge about coupled physical, chemical, and biological processes is still limited [6]. Until now, most studies have focused on 1–3 hyporheic processes, which limits our ability to characterize and understand interactions [6]. Individual studies address, for example, the hyporheos, HEFs, hyporheic biogeochemistry, the fate of pharmaceuticals in streambeds, the geomorphology of streams, subsurface hydrogeology, microplastic abundance in streams, or ecological effects of river management measures and damming. Therefore, the water–sediment interface is also an interface of different scientific disciplines. Each discipline has its own methods, definitions, rules, and standards, and often methods vary even between different research groups. In addition, most research groups work only on specific catchments, making it difficult to synthesize the results and translate them to a bigger picture. Thus, there is a need for large studies bringing together different disciplines and research groups to simultaneously investigate various hypotheses. Examples of such efforts are the joint experiments of the project HypoTRAIN [161] and the field campaigns of the project, "Where Rivers, Groundwater, and Disciplines Meet: A Hyporheic Research Network", funded by the Leverhulme Trust [49,208].

Simplifications are common and necessary in HZ research because of the complexity of this system and the involved processes. Nevertheless, much care is required to assure that common simplifications do not result in a systematic bias. For example, bedforms occurring in many streams are dynamic features that form, change shape, migrate, and erode by the force of flowing water. As long as there is sufficient flow velocity in the overlying water body, these bedforms migrate downstream. However, nearly all flume studies have investigated stagnant bedforms and their impacts on HEF. The researchers only rarely considered bed movement, even though the relevance of bed movement for hyporheic exchange has been long recognized [45,46], and can lead, for example, to overestimation of nitrate removal [209]. Another example of simplification of complexity is the representation of redox potentials in HZs. There is little empirical evidence on the spatio-temporal extent of the redox zones, how these zones change in response to dynamic hydrologic conditions, and their impacts on nutrients. Furthermore, in many streams the oxygen concentration of the surface water varies dramatically between day and night due to photosynthesis during daytime and respiration of organic matter during nighttime, as already shown in 1956 by Odum [210], as well as in studies by Mulholland et al. [211], Roberts et al. [212], and Rajwa-Kuligiewicz et al. [213]. However, impacts of fluctuating surface water oxygen concentrations on the extent of the oxic zone in the streambed have rarely been studied (although one example is Brandt et al. [214]). Fieldwork is typically only conducted during the day, potentially missing important diurnal variations in processes.

4.2. Scale Transferability

Most field investigations have scale limitations, meaning they are either very localized point measurements in heterogeneous HZs or lack sufficient resolution to draw conclusions about local conditions. Tracer tests remain the primary method for exploring HZ residence times and even nutrient cycling. However, they typically only give a spatially averaged indication of HZ residence times and other characteristics. An improved process understanding is usually difficult or impossible based on large scale investigations. Few studies combine tracer tests with high resolution sampling within the study area. For example, Zarnetske et al. [117] conducted a $\delta^{15}NO_3$ and chloride tracer test in a stream in Oregon, United States, in which they sampled detailed solute and nutrient concentrations at many locations within a gravel bar. Schaper et al. [35] combined plot- and

reach-scale investigations to identify the relevance of hyporheic removal of TrOCs for their removal in the whole stream.

Furthermore, temporal dynamics are often insufficiently studied because common methods are often labor- and cost-intensive, resulting in one-time investigations. In addition, it is necessary to know spatial and random variability to ensure that observed differences are indeed due to time variance and not due to spatial or random differences. Thus, we need improvements in sensing and modelling of space–time variability of processes in the HZ. Yet, it has not been satisfactorily assessed how temporal dynamics affect ecological processes in the benthic zone and the HZ. Temporal dynamics (from daily- to seasonal-scale) affect hydrological exchange between the benthic zone and the HZ [26,215] and the organization of the streambed biota [216,217]. Hence, it is reasonable to expect that the location of the boundary between benthos and hyporheos is time-dependent. Peralta-Maraver et al. [4] discussed, in their one-month study, that the line of demarcation between benthos and hyporheos tended to be relatively persistent, although their study was not replicated through time. On the one hand, future surveys might assess the integrity of benthos and hyporheos at a daily scale by increasing the frequency of sampling times. Recalling the daily variation of the surface water level, a reasonable strategy would be repeating sample collection during the maximum and minimum water stage level. On the other hand, assessing the seasonal variation in the boundary between both communities implies repeating the same protocols during different seasons.

As described above (2.1), hydrostatic and hydrodynamic heads along uneven streambeds have long been known as drivers of hyporheic flow [1,27,45] that pose a hydromechanical (transport) limitation on nutrient biogeochemistry [39,218,219] and impact the regional groundwater discharge patterns [41]. However, there is still uncertainty connected to the importance of these drivers over a wide range of temporal and spatial scales [220,221]. A comprehensive description of the spatio-temporal variability of physical and biogeochemical exchange processes at the surface water–groundwater interface is, thus, necessary to upscale and understand the ecosystem services provided by hyporheic processes along river networks.

4.3. Research Approach

Researchers focus typically either on field investigations, mesocosm studies, batch scale experiments, or modelling. Each type of study has its advantages: Field investigations represent reality best but spatial and temporal variation of manifold environmental factors, for example the complexity of the streambed hinders individual process understanding, manipulation experiments, and generalizability. Batch-scale experiments are further from reality but are easy to conduct, allow manipulation and control of all environmental factors, and therefore are useful for investigating individual processes. Flume studies are in between field investigations and batch experiments. Some environmental factors (e.g., discharge, temperature, sunlight, precipitation) can be controlled, they are closer to reality than batch experiments, and allow the study of coupled processes, however the effort is much higher. Modelling is used to estimate non-measurable process variables, such as turnover rates and process interactions, and is usually based on measured data. Combining several types of studies at the same site and from multidisciplinary perspectives reduces the shortcomings of single methods, and thus, adds invaluable insight into processes in the HZ [161]. Boano et al. [1] suggested that detailed measurements within the HZ improve our understanding of solute transport and residence times using tracer studies. However, the logistical and economic efforts to gather in situ measurements within the HZ are relatively high, and also the implementation of such data in the model approaches themselves is challenging [222]. Therefore, novel numerical models that include both complex transport and reaction models but also appropriately conceptualize the HZ are needed to interpret those in situ measurements.

4.4. Method Development and Method Standardization

As mentioned above (4.1), methods differ between disciplines, but also between different research groups of the same scientific discipline. For a comparison of results obtained at different

sites, it is necessary to measure the same basic parameters with comparable methods. For that purpose, a general method standardization and harmonization is an essential prerequisite. Thus, there is a need for research projects focusing on method development, on clearly defined protocols, as well as on intercomparison studies. In this context, it is very important to develop simple and cheap methods and easy to follow protocols so that they can be applied reliably and with manageable effort by scientists with different disciplinary backgrounds. Standardization of metadata and system characterization will allow comparison of different study sites and result in a big step forward in HZ research.

Furthermore, there is an urgent need for novel and innovative methods to improve process understanding. For example, it is particularly important to develop methods of flowpath identification to be able to sample along those flowpaths. Only when flowpath geometries are known is it possible to study biogeochemical processing of water parcels moving through the HZ [66].

Generally, microbial respiration and activity measurements are restricted to a daily temporal resolution or to methods involving the extraction of sediment cores, which makes in situ investigations on a temporal scale difficult. There is a need for in situ measurements that can assess microbial activities on a sub-daily scale to cover sub-daily fluctuations of environmental conditions and their effect on the microbial biota in hyporheic sediments. Similarly, new microbiology tools, such as high-throughput sequencing can help to characterize microbial communities in the HZ, and in particular, identify microorganisms that cannot be cultured. Further development of these methods may help to elucidate the complex microbiological interactions that regulate TrOC and nutrient turnover.

Novel methods such as highly dynamic sampling of pore water [223], time-integrated passive sampling techniques [177], and isotopic techniques are under development and will allow better insights into hyporheic processes. Peter et al. [33] injected visible dye into shallow HZ sediments in a known downwelling location and pinpointed the area where the labeled flowpath re-emerged to the stream. Piezometers and seepage meters were installed at these locations and used to collect paired influent–effluent samples and determine the water treatment occurring along the flowpath.

4.5. Innovative Modelling Approaches

Integration of theoretical advances into modelling studies is urgently required. Although the understanding of HZ processes has improved over the past decades, most numerical models still use different model concepts for groundwater and turbulent open channel flow, assuming hydrostatic pressure distributions, and couple these models [124,224–232]. Until now, only a few fully integrated surface water–groundwater flow models exist, such as HydroGeoSphere [233] or the solver porousInter by Oxtoby et al. [234]. For the porousInter solver, an extended version of the Navier–Stokes equation is applied for surface water and groundwater, including porosities as well as an additional drag term for the application within the sediment and different turbulence models [235,236]. Similar to the transformation from separate investigations to an integral consideration of processes within groundwater and surface water, we expect a change towards more integral numerical approaches for a better resolution of processes at the stream and aquifer interface. As such approaches require a very high spatial and temporal resolution, upscaling methods must be developed to come from small scales to the river reach scale. Commercial numerical software (such as Comsol Multiphysics®) are nowadays attempting to explicitly couple different physics within and across modelling domains. In surface water–groundwater interactions, the possibility of coupling, for example, thermodynamic and turbulent or laminar flows could open promising avenues to reveal the effect of feedback processes in the overall functioning of the HZ.

Classic modelling of the fate and transport of TrOC in rivers often struggles to capture the spatial and temporal variability in river conditions. Most models do not consider the specific processes in the HZ, especially at larger scales [237–239]. Similarly to hydraulic modelling, these approaches also have high data demands regarding spatial and temporal resolution. In situ monitoring data and characterization of partitioning and degradation rates are not available for the

great majority of case studies. The degradation rates, in particular, are obtained from laboratory experiments or in silico (as a function of structure); the extrapolation to river conditions carries large uncertainties [240]. Recent modelling of TrOC in the Rhine River basin showed that degradation rates in small- and medium-sized streams, where the HZ is usually most important, are being underestimated [237].

The relevance of the HZ for nutrient turnover, removal of trace organic compounds, and pollutant dynamics in streams can be assessed by quantifying the relative contribution of hyporheic removal to in-stream (i.e., reach-scale removal of a reactive compound). The relative contribution is not only a function of the hyporheic reactivity (i.e., the turnover rate or reaction rate of a given compound in the HZ), but also of the physical exchange characteristics. The relative hyporheic contribution has been assessed by simultaneously quantifying hyporheic reactivity and the reach-scale relative removal of a reactive compound, as well as the characteristics of the HEF on the reach-scale, for instance via transient storage models [81,122].

For many compounds, such as pharmaceuticals and nitrate, hyporheic reactivity is, furthermore, dependent on redox conditions in the HZ. To properly assess the relative contribution of the HZ to overall in-stream removal of these compounds, it could, therefore, be more appropriate to not only quantify the overall residence time in the HZ but also to disentangle reach-scale exposure times to different redox conditions in streambed sediments [241]. The hyporheic turnover length (i.e., the distance that is required for streamflow to be entirely exchanged with the HZ) increases with river discharge [18]. Also, in higher-order streams, lateral hyporheic flowpaths (e.g., through meander bends) along which redox conditions are likely to become anoxic, gaining importance relative to short, vertical flowpaths [9]. It is, thus, reasonable to assume that the relative contribution of the HZ to in-stream compound removal decreases with river discharge, particularly for compounds that are preferably removed in oxic and suboxic sections of the HZ.

First, future research should aim to develop a more versatile model approach to account for complex stream transport processes, inform about the actual RTD, and consider that compound reactivity along a hyporheic flowpath varies as a function of depth and residence time in the transient storage zone. Natural tracers, such as radon-222 [59,60,242], could be combined with conservative tracer tests to reduce uncertainties inherent in the quantification of HEFs. In addition, smart tracers, such as the resazurin–resorufin system [25], could be used to disentangle hyporheic and surface water contributions to transient storage, and may provide the means to quantify reach-scale exposure times to oxic redox conditions in the HZ. Secondly, in order to inform river management and hyporheic restoration efforts, future studies should aim to experimentally investigate the relative contribution of the HZ to overall in-stream removal of reactive compounds in various lotic systems and river networks that differ with respect to their hydrological conditions.

4.6. Knowledge Exchange Between the Scientific Community and Restoration Practitioners

River restoration typically focuses on the preservation or creation of habitats that have been lost by human alteration to rivers and floodplains to increase ecological diversity, biomass, presence of target species, or flood retention potential. HEF and streambed biogeochemical processes are rarely considered, other than in the context of the restoration of spawning grounds for salmonids. However, there is considerable potential to use catchment, river habitat, and flow restoration techniques to improve HEF and adjust residence times by acting on the physical drivers of HEF or hydrogeological factors influencing HEF (e.g., hydraulic conductivity, channel bedforms, hydraulic head; see Section 2.1), for instance through nature-based solutions, such as large, woody debris, to promote habitat structure and nutrient spiraling [47].

At river-basin-scale, improved land management practices can reduce fine sediment generation and delivery to the river (e.g., cover crops, buffer strips), which deposits on, and ingresses into, the riverbed, clogging coarse bed sediments [182,243]. In-channel measures can be used to narrow the channel, increase river flow velocities, and induce scour (e.g., willow spilling, flow deflectors, and natural riparian vegetation growth) to flush fine sediment from the riverbed, which increases hydraulic conductivity and promotes the formation of bedforms [244].

Many stream restoration practices can reliably improve hyporheic connectivity, but do not explicitly control hyporheic residence times, with overall water quality improvements depending on whether transport timescales align with reaction rates of interest [135,245,246]. However, most restoration interventions are not targeting the development of optimal flowpath lengths or biogeochemical conditions to yield specific biogeochemical reactions of interest [247]. The efficiency of river restoration structures can likely be improved by attending to design variables that can alter HZ functioning. Example variables include controlling hydraulic gradients (e.g., the height of a step [218]), manipulating hydraulic conductivities (e.g., with sediment coarsening [248]), changing flowpath geometries (e.g., with baffle walls [54,249] or hyporheic caps and increased HZ depth [33]), or shielding a structure from groundwater upwelling or downwelling (e.g., with a liner). Future research should focus on tailoring river restoration practices to deliver specific regulating ecosystem services, while also recognizing that in-channel structures alone are not able to overcome catchment-scale degradation of these services [250]. Additionally, despite extensive research demonstrating potential effects of restoration measures on river hydrodynamics, little is known about their effects on the hyporheos. Experimental studies on large wood, commonly used in restoration design, and structure-induced HEF [251] have confirmed that there is both a taxonomic and functional effect on the local benthos and hyporheos [108,252].

Despite the potential for restoration to impact HEF, there is little evidence as yet of an improvement in river water quality with restoration [253]. There are several reasons for this: (i) the objective of most restoration projects has been habitat creation not water quality; (ii) there are numerous factors influencing water quality in rivers (e.g., diffuse pollution from urban and rural environments or treated wastewater); and (iii) water quality and ecological monitoring is infrequently conducted at the appropriate scale and sufficient duration prior to and after restoration. However, new research should support river managers and restoration practitioners in incorporating HEF in their restoration goals. For example, Magliozzi et al. [254] developed a framework to integrate existing environmental data to prioritize catchments, sub-catchments, and river reaches for HEF restoration.

Thus, as river restoration aims to address physical habitat degradation to improve biodiversity (i.e., species and ecosystem diversity), targeting biological responses of hyporheos communities would be a logical direction for a holistic approach to river functioning. These results suggest that there is an increasing emphasis on addressing the HZ into site-specific restoration design to optimize ecohydrological understanding of aquatic ecosystems and explore new methods to target retention of local priority pollutants. Finally, while hyporheic structures have primarily been considered in river restoration, there is potential to utilize HZ treatment processes in stormwater, wastewater, and agricultural contexts. For example, engineered HZ could be used in artificial or heavily modified channels, such as stormwater drainages, canals, channels that convey treated wastewater to receiving water bodies, and in irrigation return flow ditches. However, more research is needed to show whether hyporheic processing is an efficient water quality management technique and to integrate it with existing management.

5. Conclusions

Coming back to the title of the present manuscript, we conclude: Yes, the HZ can be highly relevant beyond the scientific community. Several important ecosystem services (e.g., nutrient turnover, TrOC transformation, filtering of fine particles, refuge for aquatic organisms, and reservoir of biodiversity) provided by streams are based on HZ processes and are relevant at the catchment level. Thus, HZ research can support sustainable management practices of water resources. Nevertheless, it is also clear that the restoration of hyporheic functions is only one piece in a comprehensive river management system. For example, there is a need to reduce nutrient emissions to aquifers and surface water bodies. A well-functioning HZ can help to improve water quality by a further reduction of remaining nutrient loads, but it cannot be the sole management measure compensating for high nutrient emissions. Similarly, emissions of TrOCs, such as pharmaceuticals, need to be reduced in the first place by developing easily degradable pharmaceuticals, responsible

use, reduced release of the compounds, and the implementation of advanced treatment steps in wastewater treatment plants. Subsequently, the HZ may reduce the remaining TrOC loads. In this way, future exposure of aquatic organisms and humans to TrOCs and their potentially adverse effects can be avoided. For example, the widespread use of antibiotics for both human and animal treatment is attracting rising attention because of the undesirable consequences that an increased bacterial resistance of pathogens can have on life. The massive release of antibiotics in surface water bodies will likely increase the attention on self-purification processes of river networks and on the potential for HZs to reduce contaminant loads in the forthcoming years.

It is clear that even though our knowledge of the HZ has improved over the last 70 years, there are still more open questions than answers. HZ research is extraordinarily challenging because this interface is also a place where different disciplines meet. In addition, temporal fluctuations of the overlying water body and spatial variability of the underlying aquifer render HZ research extremely challenging for process understanding and upscaling. There is a need for novel methods and method standardization, joint investigations, studies that avoid systematic simplifications, and data-model integration. Furthermore, interdisciplinary approaches combining expertise obtained through large-scale field surveys with carefully designed experiments are needed to acquire a fully mechanistic understanding of the ecosystem services provided by the HZ and predict its functioning given the upcoming global change. Specifically, based on the state of the science, as described in detail in the present paper, focused research on HEF processes is still needed:

- to understand geomorphic-climatic controls that underlie spatial patterns of streamflow dynamics to quantify hydrologically critical drivers of HEF across different scales [255,256]. A proper description of the spatial variability of hydrological processes would help clarify how the ecosystem services provided by HEFs can be extended and upscaled to entire river networks.
- to enlighten the role of HEF, hyporheic sediments, and processes in cycling of microplastics, as HEF has the potential to retain large amounts of microplastics.
- to develop methods of incorporating stream restoration structures into site-specific designs that optimize retention of local priority pollutants.
- to clarify the relative contribution of the HZ to overall in-stream removal of reactive compounds in various stream systems differing with respect to their hydrological characteristics.

Author Contributions: Conceptualization, J.L., O.B., T.B., S.P.H., R.H., J.H., S.K., K.M. and B.M.M.; figures, A.J. and C.C.; writing—original draft preparation, J.L., S.A., E.B., O.B., A.B., C.C., J.D.D., J.G.G., S.P.H., A.H., J.H., A.J., A.L.P., C.M., K.M., B.B.M., B.M.M., I.P.-M., A.P., M.P., A.L.P., J.R., A.R., C.R., J.L.S., M.S., H.S., M.S., T.S., A.S.W., P.W., A.W. and L.W.; writing—review and editing, J.L., S.A., E.B., O.B., A.B., T.B., C.C., J.D.D., J.G., J.G.-V., R.C.G., S.P.H., R.H., A.H., J.H., M.A.H., A.J., C.M., B.B.M., B.M.M., I.P.-M., A.L.P., M.P., M.R. (Michael Radke), M.R. (Muhammad Raza), J.R., A.R., C.R., J.L.S., M.S. and A.W.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the writing of the manuscript, or in the decision to publish this manuscript.

References

1. Boano, F.; Harvey, J.W.; Marion, A.; Packman, A.I.; Revelli, R.; Ridolfi, L.; Wörman, A. Hyporheic flow and transport processes: Mechanisms, models, and biogeochemical implications. *Rev. Geophys.* **2014**, *52*, 603–679, doi:10.1002/2012RG000417.
2. Orghidan, T. A new habitat of subsurface waters: The hyporheic biotope. *Fundam. Appl. Limnol. Arch. Hydrobiol.* **2010**, *176*, 291–302, doi:10.1127/1863-9135/2010/0176-0291.

3. Dahm, C.N.; Valett, H.M.; Baxter, C.V.; Woessner, W.W. Hyporheic zones. In: *Methods in Stream Ecology*, 2nd ed.; Hauer, F.R., Lamberti, G., Eds.; Academic Press: San Diego, CA, USA, 2007; pp. 119–236.

4. Peralta-Maraver, I.; Galloway, J.; Posselt, M.; Arnon, S.; Reiss, J.; Lewandowski, J.; Robertson, A.L. Environmental filtering and community delineation in the streambed ecotone. *Sci. Rep.* **2018**, *8*, 15871, doi:10.1038/s41598-018-34206-z.

5. Gooseff, M.N. Defining hyporheic zones–advancing our conceptual and operational definitions of where stream water and groundwater meet. *Geogr. Compass* **2010**, *4*, 945–955, doi:10.1111/j.1749-8198.2010.00364.x.

6. Ward, A.S. The evolution and state of interdisciplinary hyporheic research. *Wiley Interdiscip. Rev. Water* **2016**, *3*, 83–103, doi:10.1002/wat2.1120.

7. Gomez-Velez, J.D.; Wilson, J.L.; Cardenas, M.B.; Harvey, J.W. Flow and residence times of dynamic river bank storage and sinuosity-driven hyporheic exchange. *Water Resour. Res.* **2017**, *53*, 8572–8595, doi:10.1002/2017WR021362.

8. Fox, A.; Boano, F.; Arnon, S. Impact of losing and gaining streamflow conditions on hyporheic exchange fluxes induced by dune-shaped bed forms. *Water Resour. Res.* **2014**, *50*, 1895–1907, doi:10.1002/2013WR014668.

9. Gomez-Velez, J.D.; Harvey, J.; Cardenas, M.B.; Kiel, B. Denitrification in the Mississippi River network controlled by flow through river bedforms. *Nat. Geosci.* **2015**, *8*, 941–945, doi:10.1038/NGEO2567.

10. Boulton, A.J.; Hancock, P. J. Rivers as groundwater-dependent ecosystems: A review of degrees of dependency, riverine processes and management implications. *Aust. J. Bot.* **2006**, *54*, 133–144, doi:10.1071/BT05074.

11. Magliozzi, C.; Grabowski, R.C.; Packman, A.I.; Krause, S. Toward a conceptual framework of hyporheic exchange across spatial scales. *Hydrol. Earth Syst. Sci.* **2018**, *22*, 6163–6185, doi:10.5194/hess-22-6163-2018.

12. Brunke, M.; Gonser, T. The ecological significance of exchange processes between rivers and groundwater. *Freshw. Biol.* **1997**, *37*, 1–33, doi:10.1046/j.1365-2427.1997.00143.x.

13. Hancock, P.J. Human impacts on the stream-groundwater exchange zone. *Environ. Manag.* **2002**, *29*, 763–781, doi:10.1007/s00267-001-0064-5.

14. Boulton, A.J.; Findlay, S.; Marmonier, P.; Stanley, E.H.; Valett, H.M. The functional significance of the hyporheic zone in streams and rivers. *Annu. Rev. Ecol. Evol. Syst.* **1998**, *29*, 59–81, doi:10.1146/annurev.ecolsys.29.1.59.

15. Fischer, H.; Kloep, F.; Wilzcek, S.; Pusch, M.T. A river's liver–microbial processes within the hyporheic zone of a large lowland river. *Biogeochemistry* **2005**, *76*, 349–371, doi:10.1007/s10533-005-6896-y.

16. Krause, S.; Hannah, D.M.; Fleckenstein, J.H.; Heppell, C.M.; Kaeser, D.; Pickup, R.; Pinay, G.; Robertson, A.L.; Wood, P.J. Inter-disciplinary perspectives on processes in the hyporheic zone. *Ecohydrology* **2011**, *4*, 481–499, doi:10.1002/eco.176.

17. Krause, S.; Lewandowski, J.; Grimm, N.B.; Hannah, D.M.; Pinay, G.; McDonald, K.; Marti, E.; Argerich, A.; Pfister, L.; Klaus, J.; et al. Ecohydrological interfaces as hot spots of ecosystem processes. *Water Resour. Res.* **2017**, *53*, 6359–6376, doi:10.1002/2016WR019516.

18. Cranswick, R.H.; Cook, P.G. Scales and magnitude of hyporheic, river-aquifer and bank storage exchange fluxes. *Hydrol. Process.* **2015**, *29*, 3084–3097, doi:10.1002/hyp.10421.

19. Stubbington, R. The hyporheic zone as an invertebrate refuge: A review of variability in space, time, taxa and behavior. *Mar. Freshw. Res.* **2012**, *63*, 293–311, doi:10.1071/MF11196.

20. Dole-Olivier, M.J. The hyporheic refuge hypothesis reconsidered: A review of hydrological aspects. *Mar. Freshw. Res.* **2011**, *62*, 1281–1302, doi:10.1071/MF11084.

21. Peralta-Maraver, I.; Reiss, J.; Robertson, A.L. Interplay of hydrology, community ecology and pollutant attenuation in the hyporheic zone. *Sci. Total Environ.* **2018**, *610*, 267–275, doi:10.1016/j.scitotenv.2017.08.036.

22. Anderson, M.P. Heat as a ground water tracer. *Ground Water* **2005**, *43*, 951–968, doi:10.1111/j.1745-6584.2005.00052.x.

23. Rau, G.C.; Andersen, M.S.; McCallum, A.M.; Roshan, H.; Acworth, R.I. Heat as a tracer to quantify water flow in near-surface sediments. *Earth Sci. Rev.* **2014**, *129*, 40–58, doi:10.1016/j.earscirev.2013.10.015.

24. Ren, J.; Cheng, J.Q.; Yang, J.; Zhou, Y.J. A review on using heat as a tool for studying groundwater-surface water interactions. *Environ. Earth Sci.* **2018**, *77*, 756, doi:10.1007/s12665-018-7959-4.

25. Knapp, J.L.A.; González-Pinzón, R.; Haggerty, R. The resazurin-resorufin system: Insights from a decade of "Smart" tracer development for hydrologic applications. *Water Resour. Res.* **2018**, *54*, 6877–6889, doi:10.1029/2018WR023103.

26. Kalbus, E.; Reinstorf, F.; Schirmer, M. Measuring methods for groundwater–surface water interactions: A review. *Hydrol. Earth Syst. Sci.* **2006**, *10*, 873–887, doi:10.5194/hess-10-873-2006.

27. Brunner, P.; Therrien, R.; Renard, P.; Simmons, C.T.; Franssen, H.J.H. Advances in understanding river-groundwater interactions. *Rev. Geophys.* **2017**, *55*, 818–854, doi:10.1002/2017RG000556.

28. Hill, A.R. Nitrate removal in stream riparian zones. *J. Environ. Qual.* **1996**, *25*, 743–755, doi:10.2134/jeq1996.00472425002500040014x.

29. Birgand, F.; Skaggs, R.W.; Chescheir, G.M.; Gilliam, J.W. Nitrogen removal in streams of agricultural catchments -A literature review. *Crit. Rev. Environ. Sci. Technol.* **2007**, *37*, 381–487, doi:10.1080/10643380600966426.

30. Gandy, C.J.; Smith, J.W.N.; Jarvis, A.P. Attenuation of mining-derived pollutants in the hyporheic zone: A review. *Sci. Total Environ.* **2007**, *273*, 435–446, doi:10.1016/j.scitotenv.2006.11.004.

31. Klein, S.; Worch, E.; Knepper, T.P. Occurrence and spatial distribution of microplastics in river shore sediments of the Rhine-Main area in Germany. *Environ. Sci. Technol.* **2015**, *49*, 6070–6076, doi:10.1021/acs.est.5b00492.

32. Boutron, O.; Margoum, C.; Chovelon, J.-M.; Guillemain, C.; Gouy, V. Effect of the submergence, the bed form geometry, and the speed of the surface water flow on the mitigation of pesticides in agricultural ditches. *Water Resour. Res.* **2011**, *47*, 1–13, doi:10.1029/2011WR010378.

33. Peter, K.T.; Herzog, S.; Tian, Z.Y.; Wu, C.; McCray, J.E.; Lynch, K.; Kolodziej, E.P. Evaluating emerging organic contaminant removal in an engineered hyporheic zone using high resolution mass spectrometry. *Water Res.* **2019**, *150*, 140–152, doi:10.1016/j.watres.2018.11.050.

34. Riml, J.; Wörman, A.; Kunkel, U.; Radke, M. Evaluating the fate of six common pharmaceuticals using a reactive transport model: Insights from a stream tracer test. *Sci. Total Environ.* **2013**, *458-460*, 344–354, doi:10.1016/j.scitotenv.2013.03.077.

35. Schaper, J.L.; Posselt, M.; McCallum, J.L.; Banks, E.W.; Hoehne, A.; Meinikmann, K.; Shanafield, M.A.; Batelaan, O.; Lewandowski, J. Hyporheic exchange controls fate of trace organic compounds in an urban stream. *Environ. Sci. Technol.* **2018**, *52*, 12285−12294, doi:10.1021/acs.est.8b03117.

36. Conant, B.; Robinson, C.E.; Hinton, M.J.; Russell, H.A. A framework for conceptualizing groundwater-surface water interactions and identifying potential impacts on water quality, water quantity, and ecosystems. *J. Hydrol.* **2019**, *574*, 609–627, doi:10.1016/j.jhydrol.2019.04.050.

37. Ward, A.S.; Packman, A.I. Advancing our predictive understanding of river corridor exchange. *Wiley Interdiscip. Rev. Water* **2018**, *6*, e1327, doi:10.1002/wat2.1327.

38. Millennium Ecosystem Assessment. *Ecosystems and Human Well-Being: Synthesis*; Island Press: Washington, DC, USA, 2005; p. 160.

39. Gomez-Velez, J.D.; Harvey, J.W. A hydrogeomorphic river network model predicts where and why hyporheic exchange is important in large basins. *Geophys. Res. Lett.* **2014**, *41*, 6403–6412, doi:10.1002/2014GL061099.

40. Caruso, A.; Ridolfi, L.; Boano, F. Impact of watershed topography on hyporheic exchange. *Adv. Water Resour.* **2016**, *94*, 400–411, doi:10.1016/j.advwatres.2016.06.005.

41. Mojarrad, B.B.; Riml, J.; Wörman, A.; Laudon, H. Fragmentation of the hyporheic zone due to regional groundwater circulation. *Water Resour. Res.* **2019**, *55*, 1242–1262, doi:10.1029/2018WR024609.

42. Kurth, A.-M.; Dawes, N.; Selker, J.; Schirmer, M. Autonomous distributed temperature sensing for long-term heated applications in remote areas. *Geosci. Instrum. Meth.* **2013**, *2*, 71–77, doi:10.5194/gi-2-71-2013.

43. Boano, F.; Revelli, R.; Ridolfi, L. Quantifying the impact of groundwater discharge on the surface-subsurface exchange. *Hydrol. Process.* **2009**, *23*, 2108–2116, doi:10.1002/hyp.7278.

44. Shanafield, M.; Cook, P.G. Transmission losses, infiltration and groundwater recharge through ephemeral and intermittent streambeds: A review of applied methods. *J. Hydrol.* **2014**, *511*, 518–529, doi:10.1016/j.jhydrol.2014.01.068.

45. Elliott, A.H.; Brooks, N.H. Transfer of nonsorbing solutes to a streambed with bed forms: Theory. *Water Resour. Res.* **1997a**, *33*, 123–136, doi:10.1029/96WR02784.

46. Elliott, A.H.; Brooks, N.H. Transfer of nonsorbing solutes to a streambed with bed forms: Laboratory experiments. *Water Resour. Res.* **1997**, *33*, 137–151, doi:10.1029/96WR02783.

47. Krause, S.; Klaar, M.; Hannah, D.; Mant, J.; Bridgeman, J.; Trimmer, M.; Manning-Jones, S. The potential of large woody debris to alter biogeochemical processes and ecosystem services in lowland rivers. *Wiley Interdiscip. Rev. Water* **2014**, *1*, 263–275, doi:10.1002/wat2.1019.

48. Dixon, S.J.; Sear, D.A. The influence of geomorphology on large wood dynamics in a low gradient headwater stream. *Water Resour. Res.* **2014**, *50*, 9194–9210, doi:10.1002/2014WR015947.

49. Blaen, P.J.; Kurz, M.J.; Drummond, J.D.; Knapp, J.L.A.; Mendoza-Lera, C.; Schmadel, N.M.; Klaar, M.J.; Jäger, A.; Folegot, S.; Lee-Cullin, J.; et al. Woody debris is related to reach-scale hotspots of lowland stream ecosystem respiration under baseflow conditions. *Ecohydrology* **2018**, e1952, doi:10.1002/eco.1952.

50. Packman, A.; Salehin, M.; Zaramella, M. Hyporheic exchange with gravel beds: Basic hydrodynamic interactions and bedform-induced advective flows. *J. Hydraul. Eng.* **2004**, *130*, 1647–656, doi:10.1061/(ASCE)0733-9429(2004)130:7(647).

51. Roche, K.R.; Blois, G.; Best, J.L.; Christensen, K.T.; Aubeneau, A.F.; Packman, A.I. Turbulence links momentum and solute exchange in coarse-grained streambeds. *Water Resour. Res.* **2018**, *54*, 3225–3242, doi:10.1029/2017WR021992.

52. Wroblicky, G.; Campana, M.; Valett, H.; Dahm, C. Seasonal variation in surface-subsurface water exchange and lateral hyporheic area of two stream-aquifer systems. *Water Resour. Res.* **1998**, *34*, 317–328, doi:10.1029/97WR03285.

53. Salehin, M.; Packman, A.I.; Paradis, M. Hyporheic exchange with heterogeneous streambeds: Laboratory experiments and modelling. *Water Resour. Res.* **2004**, *40*, W11504, doi:10.1029/2003WR002567.

54. Vaux, W.G. Intragravel flow and interchange of water in a streambed. *Fish. Bull. NOAA* **1968**, *66*, 479–489.

55. Pryshlak, T.T.; Sawyer, A.H.; Stonedahl, S.H.; Soltanian, M.R. Multiscale hyporheic exchange through strongly heterogeneous sediments. *Water Resour. Res.* **2015**, *51*, 9127–9140, doi:10.1002/2015WR017293.

56. Kalbus, E.; Schmidt, C.; Molson, J.W.; Reinstorf, F.; Schirmer, M. Influence of aquifer and streambed heterogeneity on the distribution of groundwater discharge. *Hydrol. Earth Syst. Sci.* **2009**, *13*, 69–77, doi:10.5194/hess-13-69-2009.

57. Raghavendra Naganna, S.; Chandra Deka, P. Variability of streambed hydraulic conductivity in an intermittent stream reach regulated by vented dams: A case study. *J. Hydrol.* **2018**, *562*, 477–491, doi:10.1016/j.jhydrol.2018.05.006.

58. Schirmer, M.; Leschik, S.; Musolff, A. Current research in urban hydrogeology—A review. *Adv. Water Resour.* **2013**, *51*, 280–291, doi:10.1016/j.advwatres.2012.06.015.

59. Bourke, S.A.; Cook, P.G.; Shanafield, M.; Dogramaci, S.; Clark, J.F. Characterisation of hyporheic exchange in a losing stream using radon-222. *J. Hydrol.* **2014**, *519*, 94–105, doi:10.1016/j.jhydrol.2014.06.057.

60. Cranswick, R.H.; Cook, P.G.; Lamontagne, S. Hyporheic zone exchange fluxes and residence times inferred from riverbed temperature and radon data. *J. Hydrol.* **2014**, *519*, 1870–1881, doi:10.1016/j.jhydrol.2014.09.059.

61. Schmidt, C.; Bayer-Raich, M.; Schirmer, M. Characterization of spatial heterogeneity of groundwater-stream water interactions using multiple depth streambed temperature measurements at the reach scale. *Hydrol. Earth Syst. Sci.* **2006**, *10*, 849–859, doi:10.5194/hess-10-849-2006.

62. Gordon, R.P.; Lautz, L.K.; Briggs, M.A.; McKenzie, J.M. Automated calculation of vertical pore-water flux from field temperature time series using the VFLUX method and computer program. *J. Hydrol.* **2012**, *420*, 142–158, doi:10.1016/j.jhydrol.2011.11.053.

63. Mojarrad, B.B.; Betterle, A.; Singh, T.; Olid, C.; Wörman, A. The effect of stream discharge on hyporheic exchange. *Water* **2019**, *11*, 1436, doi:10.3390/w11071436.

64. Vandersteen, G.; Schneidewind, U.; Anibas, C.; Schmidt, C.; Seuntjens, P.; Batelaan, O. Determining groundwater-surface water exchange from temperature-time series: Combining a local polynomial method with a maximum likelihood estimator. *Water Resour. Res.* **2015**, *51*, 922–939, doi:10.1002/2014WR015994.

65. Schneidewind, U.; van Berkel, M.; Anibas, C.; Vandersteen, G.; Schmidt, C.; Joris, I.; Seuntjens, P.; Batelaan, O.; Zwart, H.J. LPMLE3: A novel 1-D approach to study water flow in streambeds using heat as a tracer. *Water Resour. Res.* **2016**, *52*, 6596–6610, doi:10.1002/2015WR017453.

66. Lewandowski, J.; Angermann, L.; Nützmann, G.; Fleckenstein, J.H. A heat pulse technique for the determination of small-scale flow directions and flow velocities in the streambed of sand-bed streams. *Hydrol. Process.* **2011**, *25*, 3244–3255, doi:10.1002/hyp.8062.

67. Angermann, L.; Krause, S.; Lewandowski, J. Application of heat pulse injections for investigating shallow hyporheic flow in a lowland river. *Water Resour. Res.* **2012**, *48*, W00P02, doi:10.1029/2012WR012564.

68. Banks, E.W.; Shanafield, M.A.; Noorduijn, S.; McCallum, J.; Lewandowski, J.; Batelaan, O. Active heat pulse sensing of 3D-flow fields in streambeds. *Hydrol. Earth Syst. Sci.* **2018**, *22*, 1917–1929, doi:10.5194/hess-22-1917-2018.

69. Selker, J.; Van de Giesen, N.; Westhoff, M.; Luxemburg, W.; Parlange, M.B. Fiber optics opens window on stream dynamics. *Geophys. Res. Lett.* **2006**, *33*, L24401, doi:10.1029/2006GL027979.

70. Lowry, C.S.; Walker, J.F.; Hunt, R.J.; Anderson, M.P. Identifying spatial variability of groundwater discharge in a wetland stream using a distributed temperature sensor. *Water Resour. Res.* **2007**, *43*, W10408, doi:10.1029/2007WR006145.

71. Tyler, S.W.; Selker, J.S.; Hausner, M.B.; Hatch, C.E.; Torgersen, T.; Thodal, C.E.; Schladow, S.G. Environmental temperature sensing using Raman spectra DTS fiber-optic methods. *Water Resour. Res.* **2009**, *45*, W00D23, doi:10.1029/2008WR007052.

72. Vogt, T.; Schneider, P.; Hahn-Woernle, L.; Cirpka, O.A. Estimation of seepage rates in a losing stream by means of fiber-optic high-resolution vertical temperature profiling. *J. Hydrol.* **2010**, *380*, 154–164, doi:10.1016/j.jhydrol.2009.10.033.

73. Shanafield, M.; McCallum, J.L.; Cook, P.G.; Noorduijn, S. Using basic metrics to analyze high-resolution temperature data in the subsurface. *Hydrogeol. J.* **2017**, *25*, 1501–1508, doi:10.1007/s10040-017-1578-0.

74. Gaona, J.; Meinikmann, K.; Lewandowski, J. Identification of groundwater exfiltration, interflow discharge, and hyporheic exchange flows by fibre optic distributed temperature sensing supported by electromagnetic induction geophysics. *Hydrol. Process.* **2019**, *33*, 1390–1402, doi:10.1002/hyp.13408.

75. Hare, D.K.; Briggs, M.A.; Rosenberry, D.O.; Boutt, D.F.; Lane, J.W. A comparison of thermal infrared to fiber-optic distributed temperature sensing for evaluation of groundwater discharge to surface water. *J. Hydrol.* **2015**, *530*, 153–166, doi:10.1016/j.jhydrol.2015.09.059.

76. Ward, A.S.; Gooseff, M.N.; Singha, K. Imaging hyporheic zone solute transport using electrical resistivity. *Hydrol. Process.* **2010**, *24*, 948–953, doi:10.1002/hyp.7672.

77. McLachlan, P.J.; Chambers, J.E.; Uhlemann, S.S.; Binley, A. Geophysical characterisation of the groundwater-surface water interface. *Adv. Water Resour.* **2017**, *109*, 302–319, doi:10.1016/j.advwatres.2017.09.016.

78. Wu, L.; Singh, T.; Gomez-Velez, J.; Nützmann, G.; Wörman, A.; Krause, S.; Lewandowski, J. Impact of dynamically changing discharge on hyporheic exchange processes under gaining and losing groundwater conditions. *Water Resour. Res.* **2018**, *54*, 10076–10093, doi:10.1029/2018WR023185.

79. Singh, T.; Wu, L.; Gomez-Velez, J.D.; Lewandowski, J.; Hannah, D.M.; Krause, S. Dynamic hyporheic zones: Exploring the role of peak flow events on bedform-induced hyporheic exchange. *Water Resour. Res.* **2019**, *55*, 218–235, doi:10.1029/2018WR022993.

80. Zarnetske, J.P.; Haggerty, R.; Wondzell, S.M.; Baker, M.A. Dynamics of nitrate production and removal as a function of residence time in the hyporheic zone. *J. Geophys. Res.* **2011**, *116*, G01025, doi:10.1029/2010JG001356.

81. Harvey, J.W.; Bohlke, J.K.; Voytek, M.A.; Scott, D.; Tobias, C.R. Hyporheic zone denitrification: Controls on effective reaction depth and contribution to whole-stream mass balance. *Water Resour. Res.* **2013**, *49*, 6298–6316, doi:10.1002/wrcr.20492.

82. Johnson, Z.C.; Warwick, J.J.; Schumer, R. Factors affecting hyporheic and surface transient storage in a western U.S. river. *J. Hydrol.* **2014**, *510*, 325–339, doi:10.1016/j.jhydrol.2013.12.037.

83. Bencala, K.E.; Walters, R.A. Simulation of solute transport in a mountain pool-and-riffle stream: A transient storage model. *Water Resour. Res.* **1983**, *19*, 718–724, doi:10.1029/WR019i003p00718.

84. Wörman, A.; Packman, A.I.; Johansson, H.; Jonsson, K. Effect of flow-induced exchange in hyporheic zones on longitudinal transport of solutes in streams and rivers. *Water Resour. Res.* **2002**, *38*, 2-1–2-15, doi:10.1029/2001WR000769.

85. Gooseff, M.N.; Wondzell, S.M.; Haggerty, R.; Anderson, J. Comparing transient storage modeling and residence time distribution (RTD) analysis in geomorphically varied reaches in the Lookout Creek basin, Oregon, USA. *Adv. Water Resour.* **2003**, *26*, 925–937 doi:10.1016/S0309-1708(03)00105-2.

86. Jury, W.A. Simulation of solute transport using a transfer function model. *Water Resour. Res.* **1982**, *18*, 363–368, doi:10.1029/WR018i002p00363.

87. Sardin, M.; Schweich, D.; Leu, F.J.; Van Genuchten, M.T. Modeling the nonequilibrium transport of linearly interacting solutes in porous media: A review. *Water Resour. Res.* **1991**, *27*, 2287–2307, doi:10.1029/91WR01034.

88. Knapp, J.L.A.; Cirpka, O.A. Determination of hyporheic travel time distributions and other parameters from concurrent conservative and reactive tracer tests by local-in-global optimization. *Water Resour. Res.* **2017**, *53*, 4984–5001, doi:10.1002/2017WR020734.

89. Liao, Z.; Cirpka, O.A. Shape-free inference of hyporheic traveltime distributions from synthetic conservative and "smart" tracer tests in streams. *Water Resour. Res.* **2011**, *47*, W07510, doi:10.1029/2010WR009927.

90. Liao, Z.; Lemke, D.; Osenbrück, K.; Cirpka, O.A. Modeling and inverting reactive stream tracers undergoing two-site sorption and decay in the hyporheic zone. *Water Resour. Res.* **2013**, *49*, 3406–3422, doi:10.1002/wrcr.20276.

91. Battin, T.J.; Besemer, K.; Bengtsson, M.M.; Romani, A.M.; Packmann, A.I. The ecology and biogeochemistry of stream biofilms. *Nat. Rev. Microbiol.* **2016**, *14*, 251–263, doi:10.1038/nrmicro.2016.15.

92. Williams, D.D.; Hynes, H.B.N. The occurrence of benthos deep in the substratum of a stream. *Freshw. Biol.* **1974**, *4*, 233–256, doi:10.1111/j.1365-2427.1974.tb00094.x.

93. Zeglin, H.L. Stream microbial diversity responds to environmental changes: Review and synthesis of existing research. *Front. Microbiol.* **2015**, *6*, 454, doi:10.3389/fmicb.2015.00454.

94. Singer, G.; Besemer, K.; Schmitt-Kopplin, P.; Hödl, I.; Battin, T.J. Physical heterogeneity increases biofilm resource use and its molecular diversity in stream mesocosms. *PLoS ONE* **2010**, *5*, e9988, doi:10.1371/journal.pone.0009988.

95. Romaní, A.M.; Fund, K.; Artigas, J.; Schwartz, T.; Sabater, S.; Obst, U. Relevance of polymeric matrix enzymes during biofilm formation. *Microb. Ecol.* **2008**, *56*, 427–436, doi:10.1007/s00248-007-9361-8.

96. Battin, T.J.; Kaplan, L.A.; Findlay, S.; Hopkinson, C.S.; Marti, E.; Packman, A.I.; Newbold, J.D.; Sabater, F. Biophysical controls on organic carbon fluxes in fluvial networks. *Nat. Geosci.* **2008**, *1*, 95–100, doi:10.1038/ngeo101.

97. Mulholland, P.J.; Helton, A.M.; Poole, G.C.; Hall, R.O.; Hamilton, S.K.; Peterson, B.J.; Tank, J.L.; Ashkenas, L.R.; Cooper, L.W.; Dahm, C.N.; et al. Stream denitrification across biomes and its response to anthropogenic nitrate loading. *Nature* **2008**, *452*, 202–205, doi:10.1038/nature06686.

98. Storey, R.G.; Fulthorpe, R.R.; Williams, D.D. Perspectives and predictions on the microbial ecology of the hyporheic zone. *Freshw. Biol.* **1999**, *41*, 119–130, doi:10.2307/1467687.

99. Robertson, A.L.; Wood, P.J. Ecology of the hyporheic zone: Origins, current knowledge and future directions. *Fundam. Appl. Limnol Arch. Hydrobiol.* **2010**, *176*, 279–289, doi:10.1127/1863-9135/2010/0176-0279.

100. Wood, P.J.; Boulton, A.J.; Little, S.; Stubbington, R. Is the hyporheic zone a refugium for aquatic macroinvertebrates during severe low flow conditions? *Fundam. Appl. Limnol./Arch. Hydrobiol.* **2010**, *176*, 377–390, doi:10.1127/1863-9135/2010/0176-037.

101. Eichhorn, M. *Natural Systems: The Organisation of Life*; John Wiley and Sons: Chichester, UK, 2016; p. 359.

102. Dole-Olivier, M.J. Surface water-groundwater exchanges in three dimensions on a backwater of the Rhône River. *Freshw. Biol.* **1998**, *40*, 93–109, doi:10.1046/j.1365-2427.1998.00335.x.

103. Fraser, B.G.; Williams, D.D. Seasonal boundary dynamics of a groundwater/surface-water ecotone. *Ecology* **1998**, *79*, 2019–2031, doi:10.1890/0012-9658(1998)079[2019:SBDOAG]2.0.CO;2.

104. Miyake, Y.; Nakano, S. Effects of substratum stability on diversity of stream invertebrates during baseflow at two spatial scales. *Freshw. Biol.* **2002**, *47*, 219–230, doi:10.1046/j.1365-2427.2002.00798.x.

105. Sliva, L.; Williams, D.D. Responses of hyporheic meiofauna to habitat manipulation. *Hydrobiologia* **2005**, *548*, 217–232, doi:10.1007/s10750-005-5445-y.

106. Davy-Bowker, J.; Sweeting, W.; Wright, N.; Clarke, R.T.; Arnott, S. The distribution of benthic and hyporheic macroinvertebrates from the heads and tails of riffles. *Hydrobiologia* **2006**, *563*, 109–123, doi:10.1007/s10750-005-1482-9.

107. Andrushchyshyn, O.P.; Wilson, K.P.; Williams, D.D. Ciliate communities in shallow groundwater: Seasonal and spatial characteristics. *Freshw. Biol.* **2007**, *52*, 1745–1761, doi:10.1111/j.1365-2427.2007.01806.x.

108. Magliozzi, C.; Usseglio-Polatera, P.; Meyer, A.; Grabowski, R.C. Functional traits of hyporheic and benthic invertebrates reveal importance of wood-driven geomorphological processes in rivers. *Funct. Ecol.* **2019**, *33*, 1758–1770, doi:10.1111/1365-2435.13381.

109. Smock, L.A.; Gladden, J.E.; Riekenberg, J.L.; Smith, L.C.; Black, C.R. Lotic macroinvertebrate production in three dimensions: Channel surface, hyporheic, and floodplain environments. *Ecology* **1992**, *73*, 875–886, doi:10.2307/1940165.

110. Post, D.M.; Doyle, M.W.; Sabo, J.L.; Finlay, J.C. The problem of boundaries in defining ecosystems: A potential landmine for uniting geomorphology and ecology. *Geomorphology* **2007**, *89*, 111–126, doi:10.1016/j.geomorph.2006.07.014.

111. Peralta-Maraver, I.; Perkins, D.M.; Thompson, M.S.; Fussmann, K.; Reiss, J.; Robertson, A.L. Comparing biotic drivers of litter breakdown across streams compartments. *J. Anim. Ecol.* **2019**, *88*, 1146–1157, doi:10.1111/1365-2656.13000.

112. Smith, J.J.; Lake, P.S. The breakdown of buried and surface–placed leaf litter in an upland stream. *Hydrobiologia* **1993**, *271*, 141–148, doi:10.1007/BF00005411.

113. Cornut, J.; Elger, A.; Lambrigot, D.; Marmonier, P.; Chauvet, E. Early stages of leaf decomposition are mediated by aquatic fungi in the hyporheic zone of woodland streams. *Freshw. Biol.* **2010**, *55*, 2541–2556, doi:10.1111/j.1365-2427.2010.02483.x.

114. Peralta-Maraver, I.; Robertson, A.L.; Perkins, D.M. Depth and vertical hydrodynamics constrain the size structure of a lowland streambed community. *Biol. Lett.* **2019**, *15*, 20190317, doi:10.1098/rsbl.2019.0317.

115. Stumm, W.; Morgan, J.J. Redox conditions in natural waters. In: *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed.; Schnoor, J.L., Zehnder, A., Eds.; Wiley: New York, NY, USA, 1996; pp. 464–489, doi:10.5860/choice.33-6312.

116. Jones, J.B.; Holmes, R.M.; Fisher, S.G.; Grimm, N.B.; Greene, D.M. Methanogenesis in Arizona, USA dryland streams. *Biogeochemistry* **1995**, *31*, 155–173, doi:10.1007/BF00004047.

117. Zarnetske, J.P.; Haggerty, R.; Wondzell, S.M.; Baker, M.A. Labile dissolved organic carbon supply limits hyporheic denitrification. *J. Geophys. Res.* **2011**, *116*, G04036, doi:10.1029/2011JG001730.

118. Briggs, M.A.; Day-Lewis, F.D.; Zarnetske, J.P.; Harvey, J.W. A physical explanation for the development of redox microzones in hyporheic flow. *Geophys. Res. Lett.* **2015**, *42*, 4402–4410, doi:10.1002/2015GL064200.

119. Triska, F.J.; Duff, J.H.; Avanzino, R.J. The role of water exchange between a stream channel and its hyporheic zone in nitrogen cycling at the terrestrial-aquatic interface. *Hydrobiologia* **1993**, *251*, 167–184, doi:10.1007/BF00007177.

120. Triska, F.J.; Duff, J.H.; Avanzino, R.J. Patterns of hydrological exchange and nutrient transformation in the hyporheic zone of a gravel-bottom stream: Examining terrestrial-aquatic linkages. *Freshw. Biol.* **1993**, *29*, 259–274, doi:10.1111/j.1365-2427.1993b.tb00762.x.

121. Christensen, P.B.; Nielsen, L.P.; Sørensen, J.; Revsbech, N.P. Denitrification in nitrate-rich streams: Diurnal and seasonal variation related to benthic oxygen metabolism. *Limnol. Oceanogr.* **1990**, *35*, 640–651, doi:10.4319/lo.1990.35.3.0640.

122. Schaper, J.L.; Seher, W.; Nützmann, G.; Putschew, A.; Jekel, M.; Lewandowski, J. The fate of polar trace organic compounds in the hyporheic zone. *Water Res.* **2018**, *140*, 158–166, doi:10.1016/j.watres.2018.04.040.

123. Lewandowski, J.; Nützmann, G. Nutrient retention and release in a floodplain's aquifer and in the hyporheic zone of a lowland river. *Ecol. Eng.* **2010**, *36*, 1156–1166, doi:10.1016/j.ecoleng.2010.01.005.

124. Trauth, N.; Schmidt, C.; Vieweg, M.; Maier, U.; Fleckenstein, J.H. Hyporheic transport and biogeochemical reactions in pool-riffle systems under varying ambient groundwater flow conditions. *J. Geophys. Res. Biogeosci.* **2014**, *119*, 910–928, doi:10.1002/2013JG002586.

125. De Falco, N.; Boano, F.; Bogler, A.; Bar-Zeev, E.; Arnon, S. Influence of stream-subsurface exchange flux and bacterial biofilms on oxygen consumption under nutrient-rich conditions. *J. Geophys. Res. Biogeosci.* **2018**, *123*, 2021–2034, doi:10.1029/2017JG004372.

126. Haggerty, R.; Argerich, A.; Marti, E. Development of a "smart" tracer for the assessment of microbiological activity and sediment-water interaction in natural waters: The resazurin-resorufin system. *Water Resour. Res.* **2008**, *44*, W00D01, doi:10.1029/2007WR006670.

127. Haggerty, R.; Marti, E.; Argerich, A.; von Schiller, D.; Grimm, N.B. Resazurin as a "smart" tracer for quantifying metabolically active transient storage in stream ecosystems. *J. Geophys. Res. Biogeosci.* **2009**, *114*, G03014, doi:10.1029/2008JG000942.

128. Schirmer, M.; Luster, J.; Linde, N.; Perona, P.; Mitchell, E.A.D.; Barry, D.A.; Hollender, J.; Cirpka, O.A.; Schneider, P.; Vogt, T.; et al. Morphological, hydrological, biogeochemical and ecological changes and challenges in river restoration–The Thur River case study. *Hydrol. Earth Syst. Sci.* **2014**, *18*, 1–14, doi:10.5194/hess-18-2449-2014.

129. Lewandowski, J.; Putschew, A.; Schwesig, D.; Neumann, C.; Radke, M. Fate of organic micropollutants in the hyporheic zone of a eutrophic lowland stream: Results of a preliminary field study. *Sci. Total Environ.* **2011**, *409*, 1824–1835, doi:10.1016/j.scitotenv.2011.01.028.

130. Lapworth, D.J.; Gooddy, D.C.; Jarvie, H.P. Understanding phosphorus mobility and bioavailability in the hyporheic zone of a chalk stream. *Water Air Soil Pollut.* **2010**, *218*, 213–226, doi:10.1007/s11270-010-0636-1.

131. Butturini, A.; Sabater, F. Importance of transient storage zones for ammonium and phosphate retention in a sandy-bottom Mediterranean stream. *Freshw. Biol.* **1999**, *41*, 593–603, doi:10.1046/j.1365-2427.1999.00406.x.

132. Arnon, S.; Yanuka, K.; Nejidat, A. Impact of overlying water velocity on ammonium uptake by benthic biofilms. *Hydrol. Process.* **2013**, *27*, 570–578, doi:10.1002/hyp.9239.

133. Harvey, J.J.; Gomez-Velez, J.; Schmadel, N.; Scott, D.; Boyer, E.; Alexander, R.; Eng, K.; Golden, H.; Kettner, A.; Konrad, C.; et al. How Hydrologic connectivity regulates water quality in river corridors. *J. Am. Water Resour. Assoc.* **2019**, *55*, 369–381, doi:10.1111/1752-1688.12691.

134. Ocampo, C.J.; Oldham, C.E.; Sivapalan, M. Nitrate attenuation in agricultural catchments: Shifting balances between transport and reaction. *Water Resour. Res.* **2006**, *42*, W01408, doi:10.1029/2004WR003773.

135. Gordon, R.P.; Lautz, L.K.; Daniluk, T.L. Spatial patterns of hyporheic exchange and biogeochemical cycling around cross-vane restoration structures: Implications for stream restoration design. *Water Resour. Res.* **2013**, *49*, 2040–2055, doi:10.1002/wrcr.20185.

136. Hester, E.T.; Hammond, B.; Scott, D.T. Effects of inset floodplains and hyporheic exchange induced by in-stream structures on nitrate removal in a headwater stream. *Ecol. Eng.* **2016**, *97*, 452–464, doi:10.1016/j.ecoleng.2016.10.036.

137. Morén, I.; Riml, J.; Wörman, A. *In-Stream Water Management Strategies for Reducing Nutrient Loads to the Baltic Sea*; BONUS Soils2Sea Deliverable 4.4; KTH Royal Institute of Technology: Stockholm, Sweden, March 2018. Available online: www.Soils2Sea.eu (accessed on 23 October 2019).

138. Refsgaard, J.C.; Chubarenko, B.; Donnely, C.; de Jonge, H.; Olesen, J.E.; Steljes, N.; Wachniew, P.; Wörman, A. Spatially differentiated regulation measures-can it save the Baltic Sea from excessive N-loads? *Ambio* **2019**, doi:10.1007/s13280-019-01195-w.

139. Botter, G.; Basu, N.B.; Zanardo, S.; Rao, P.S.C.; Rinaldo, A. Stochastic modeling of nutrient losses in streams: Interactions of climatic, hydrologic and biogeochemical controls. *Water Resour. Res.* **2010**, *46*, W08509, doi:10.1029/2009WR008758.

140. Kidd, K.A.; Blanchfield, P.J.; Mills, K.H.; Palace, V.P.; Evans, R.E.; Lazorchak, J.M.; Flick, R.W. Collapse of a fish population after exposure to a synthetic estrogen. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 8897–8901, doi:10.1073/pnas.0609568104.

141. Galus, M.; Rangarajan, S.; Lai, A.; Shaya, L.; Balshine, S.; Wilson, J.Y. Effects of chronic, parental pharmaceutical exposure on zebrafish (*Danio rerio*) offspring. *Aquat. Toxicol.* **2014** *151*, 124–134, doi:10.1016/j.aquatox.2014.01.016.

142. Cruz-Rojas, C.; SanJuan-Reyes, N.; Fuentes-Benites, M.P.A.G.; Dublan-García, O.; Galar-Martínez, M.; Islas-Flores, H.; Gómez-Oliván, L.M. Acesulfame potassium: Its ecotoxicity measured through oxidative stress biomarkers in common carp (Cyprinus carpio). *Sci. Total Environ.* **2019**, *647*, 772–784, doi:10.1016/j.scitotenv.2018.08.034.

143. Kubec, J.; Hossain, S.; Grabicová, K.; Randák, T.; Kouba, A.; Grabic, R.; Roje, S.; Buřič, M. Oxazepam alters the behavior of crayfish at diluted concentrations, venlafaxine does not. *Water* **2019**, *11*, 196, doi:10.3390/w11020196.

144. Luo, Y.; Guo, W.; Ngo, H.H.; Nghiem, L.D.; Hai, F.I.; Zhang, J.; Liang, S.; Wang, X.C. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* **2014**, *473-474*, 619–641, doi:10.1016/j.scitotenv.2013.12.065.

145. Melvin, S.; Leusch, F. Removal of trace organic contaminants from domestic wastewater: A meta-analysis comparison of sewage treatment technologies. *Environ. Int.* **2016**, *92-93*, 183–188, doi:10.1016/j.envint.2016.03.031.

146. Phillips, P.; Chalmers, A.; Gray, J.; Kolpin, D.; Foreman, W.; Wall, G. Combined Sewer Overflows: An Environmental Source of Hormones and Wastewater Micropollutants. *Environ. Sci. Technol.* **2012**, *46*, 563–579, doi:10.1021/es3001294.

147. Roehrdanz, P.R.; Feraud, M.; Lee, D.G.; Means, J.C.; Snyder, S.A.; Holden, P.A. Spatial models of sewer pipe leakage predict the occurrence of wastewater indicators in shallow urban groundwater. *Environ. Sci. Technol.* **2017**, *51*, 1213–1223, doi:10.1021/acs.est.6b05015.

148. Schaider, L.A.; Ackerman, J.M.; Rudel, R.A. Septic systems as sources of organic wastewater compounds in domestic drinking water wells in a shallow sand and gravel aquifer. *Sci. Total Environ.* **2016**, *547*, 470–481, doi:10.1016/j.scitotenv.2015.12.081.

149. Eggen, T.; Moeder, M.; Arukwe, A. Municipal landfill leachates: A significant source for new and emerging pollutants. *Sci. Total Environ.* **2010**, *408*, 5147–5157, doi:10.1016/j.scitotenv.2010.07.049.

150. Masoner, J.R.; Kolpin, D.W.; Cozzarelli, I.M.; Barber, L.B.; Burden, D.S.; Foreman, W.T.; Forshay, K.J.; Furlong, E.T.; Groves, J.F.; Hladik, M.L.; et al. Urban stormwater: An overlooked pathway of extensive mixed contaminants to surface and groundwaters in the United States. *Environ. Sci. Technol.* **2019**, *53*, 10070–10081, doi:10.1021/acs.est.9b02867.

151. Jekel, M.; Ruhl, A.S.; Meinel, F.; Zietzschmann, F.; Lima, S.P.; Baur, N.; Wenzel, M.; Gnirß, R.; Sperlich, A.; Dünnbier, U.; et al. Anthropogenic organic micro-pollutants and pathogens in the urban water cycle: Assessment, barriers and risk communication (ASKURIS). *Environ. Sci. Eur.* **2013**, *25*, 1–8, doi:10.1186/2190-4715-25-20.

152. Schwarzenbach, R.P.; Escher, B.I.; Fenner, K.; Hofstetter, T.B.; Johnson, C.A.; Von Gunten, U.; Wehrli, B. The challenge of micropollutants in aquatic systems. *Science* **2006**, *313*, 1072–1077, doi:10.1126/science.1127291.

153. Boulton, A.J.; Datry, T.; Kasahara, T.; Mutz, M.; Stanford, J.A. Ecology and management of the hyporheic zone: Stream-groundwater interactions of running waters and their floodplains. *Freshw. Sci.* **2010**, *29*, 26–40, doi:10.1899/08-017.1.

154. Heberer, T.; Massmann, G.; Fanck, B.; Taute, T.; Dunnbier, U. Behaviour and redox sensitivity of antimicrobial residues during bank filtration. *Chemosphere* **2008**, *73*, 451–460, doi:10.1016/j.chemosphere.2008.06.056.

155. Huntscha, S.; Singer, H.P.; McArdell, C.S.; Frank, C.E.; Hollender, J. Multiresidue analysis of 88 polar organic micropollutants in ground, surface and wastewater using online mixed-bed multilayer solid-phase extraction coupled to high performance liquid chromatography-tandem mass spectrometry. *J. Chromatogr. A* **2012**, *1268*, 74–83, doi:10.1016/j.chroma.2012.10.032.

156. Lawrence, J.E.; Skold, M.E.; Hussain, F.A.; Silverman, D.R.; Resh, V.H.; Sedlak, D.L.; Luthy, R.G.; McCray, J.E. Hyporheic zone in urban streams: A review and opportunities for enhancing water quality and improving aquatic habitat by active management. *Environ. Eng. Sci.* **2013**, *30*, 480–501, doi:10.1089/ees.2012.0235.

157. Regnery, J.; Barringer, J.; Wing, A.D.; Hoppe-Jones, C.; Teerlink, J.; Drewes, J.E. Start-up performance of a full-scale riverbank filtration site regarding removal of DOC, nutrients, and trace organic chemicals. *Chemosphere* **2015**, *127*, 136–142, doi:10.1016/j.chemosphere.2014.12.076.

158. Hollender, J.; Rothardt, J.; Radny, D.; Loos, M.; Epting, J.; Huggenberger, P.; Borer, P.; Singer, H. Target and Non-target Screening of micropollutants at riverbank filtration sites with short residence times using LC-HRMS/MS, *Water Res.* X **2018**, *1*, 100007, doi:10.1016/j.wroa.2018.100007.

159. Burke, V.; Greskowiak, J.; Asmuß, T.; Bremermann, R.; Taute, T.; Massmann, G. Temperature dependent redox zonation and attenuation of wastewater-derived organic micropollutants in the hyporheic zone. *Sci. Total Environ.* **2014**, *482-483*, 53–61, doi:10.1016/j.scitotenv.2014.02.098.

160. Schaper, J.L.; Posselt, M.; Bouchez, C.; Jaeger, A.; Nützmann, G.; Putschew, A.; Singer, G.; Lewandowski, J. Fate of trace organic compounds in the hyporheic zone: Influence of retardation, the benthic bio-layer and organic carbon. *Environ. Sci. Technol.* **2019**, *53*, 4224–4234, doi:10.1021/acs.est.8b06231.

161. Jaeger, A.; Coll, C.; Posselt, M.; Rutere, C.; Mechelke, J.; Betterle, A.; Raza, M.; Meinikmann, K.; Mehrtens, A.; Portmann, A.; et al Using recirculating flumes and a response surface model to investigate the role of hyporheic exchange and bacterial diversity on micropollutant half lives. *Environ. Sci. Process. Impacts* **2019** accepted, doi:10.1039/C9EM00327D.

162. Shapiro, O.H.; Kushmaro, A.; Brenner, A. Bacteriophage predation regulates microbial abundance and diversity in a full-scale bioreactor treating industrial wastewater. *ISME J.* **2010**, *4*, 327–336, doi:10.1038/ismej.2009.118.

163. Otto, S.; Harms, H.; Wick, L.Y. Effects of predation and dispersal on bacterial abundance and contaminant biodegradation. *FEMS Microbiol. Ecol.* **2017**, *93*, fiw241, doi:10.1093/femsec/fiw241.

164. El-Athman, F.; Adrian, L.; Jekel, M.; Putschew, A. Deiodination in the presence of *Dehalococcoides mccartyi* strain CBDB1: Comparison of the native enzyme and co-factor vitamin B$_{12}$. *Environ. Sci. Pollut. Res.* **2019**, doi:10.1007/s11356-019-06505-z.

165. El-Athman, F.; Jekel, M.; Putschew, A. Reaction kinetics of corrinoid-mediated deiodination of iodinated X-ray contrast media and other iodinated organic compounds. *Chemosphere* **2019**, *234*, 971–977, doi:10.1016/j.chemosphere.2019.06.135.

166. El-Athman, F.; Adrian, L.; Jekel, M.; Putschew, A. Abiotic reductive deiodination of iodinated organic compounds and X-ray contrast media catalyzed by free corrinoids. *Chemosphere* **2019**, *221*, 212–218, doi:10.1016/j.chemosphere.2019.01.003.

167. Jonsson, K.; Johansson, H.; Wörman, A. Sorption behaviour and long-term retention of reactive solutes in the hyporheic zone of streams. *J. Environ. Eng.* **2004**, *130*, 573–584, doi:10.1061/(ASCE)0733-9372(2004)130:5(573).

168. Hebig, K.H.; Groza, L.G.; Sabourin, M.J.; Scheytt, T.J.; Ptacek, C.J. Transport behavior of the pharmaceutical compounds carbamazepine, sulfamethoxazole, gemfibrozil, ibuprofen, and naproxen, and the lifestyle drug caffeine, in saturated laboratory columns. *Sci. Total Environ.* **2017**, *590*, 708–719, doi:10.1016/j.scitotenv.2017.03.031.

169. Nghiem, L.D.; Hawkes, S. Effects of membrane fouling on the nanofiltration of trace organic contaminants. *Desalination* **2009**, *236*, 273–281, doi:10.1016/j.desal.2007.10.077.

170. Packman, A.I.; Brooks, N.H.; Morgan, J.J. A physicochemical model for colloid exchange between a stream and a sand streambed with bed forms. *Water Resour. Res.* **2000**, *36*, 2351–2361, doi:10.1029/2000WR900059.

171. Packman, A.I.; Brooks, N.H.; Morgan, J.J. Kaolinite exchange between a stream and streambed: Laboratory experiments and validation of a colloid transport model. *Water Resour. Res.* **2000**, *36*, 2363–2372, doi:10.1029/2000WR900058.

172. Celiz, M.D.; Tso, J.; Aga, D.S. Pharmaceutical metabolites in the environment: Analytical challenges and ecological risks. *Environ. Toxicol. Chem.* **2009**, *28*, 2473–2484. doi:10.1897/09-173.1#.

173. Henning, N.; Kunkel, U.; Wick, A.; Ternes, T.A. Biotransformation of gabapentin in surface water matrices under different redox conditions and the occurrence of one major TP in the aquatic environment. *Water Res.* **2018**, *137*, 290–300, doi:10.1016/j.watres.2018.01.027.

174. Nödler, K.; Hillebrand, O.; Idzik, K.; Strathmann, M.; Schiperski, F.; Zirlewagen, J.; Licha, T. Occurrence and fate of the angiotensin II receptor antagonist transformation product valsartan acid in the water cycle—A comparative study with selected β-blockers and the persistent anthropogenic wastewater indicators carbamazepine and acesulfame. *Water Res.* **2013**, *47*, 6650–6659, doi:10.1016/j.watres.2013.08.034.

175. Li, Z.; Sobek, A.; Radke, M. Flume experiments to investigate the environmental fate of pharmaceuticals and their transformation products in streams. *Environ. Sci. Technol.* **2015**, *49*, 6009–6017, doi:10.1021/acs.est.5b00273.

176. Writer, J.H.; Antweiler, R.C.; Ferrer, I.; Ryan, J.N.; Thurman, E.M. In-stream attenuation of neuro-active pharmaceuticals and their metabolites. *Environ. Sci. Technol.* **2013**, *47*, 9781–9790, doi:10.1021/es402158t.

177. Mechelke, J.; Vermeirssen, E.L.M.; Hollender, J. Passive sampling of organic contaminants across the water-sediment interface of an urban stream. *Water Res.* **2019**, *165*, 114966, doi:10.1016/j.watres.2019.114966.

178. Jaeger, A.; Posselt, M.; Betterle, A.; Schaper, J.; Mechelke, J.; Coll, C.; Lewandowski, J. Spatial and temporal variability in attenuation of polar trace organic compounds in an urban lowland stream. *Environ. Sci. Technol.* **2019**, *53*, 2383–2395, doi:10.1021/acs.est.8b05488.

179. Ren, J.H.; Packman, A.I. Stream-subsurface exchange of zinc in the presence of silica and kaolinite colloids. *Environ. Sci. Technol.* **2004**, *38*, 6571–6581, doi:10.1021/es035090x.

180. Karwan, D.L.; Saiers, J.E. Hyporheic exchange and streambed filtration of suspended particles. *Water Resour. Res.* **2012**, *48*, W01519, doi:10.1029/2011WR011173.

181. Fox, A.; Packman, A.I.; Boano, F.; Phillips, C.B.; Arnon, S. Interactions between suspended kaolinite Deposition and hyporheic exchange flux under losing and gaining flow conditions. *Geophys. Res. Lett.* **2018**, *45*, 4077–4085, doi:10.1029/2018GL077951.

182. Wharton, G.; Mohajeri, S.H.; Righetti, M. The pernicious problem of streambed colmation: A multi-disciplinary reflection on the mechanisms, causes, impacts, and management challenges. *Wiley Interdiscip. Rev. Water* **2017**, e1231, doi:10.1002/wat2.1231.

183. Jones, I.; Growns, I.; Arnold, A.; McCall, S.; Bowes, M. The effects of increased flow and fine sediment on hyporheic invertebrates and nutrients in stream mesocosms. *Freshw. Biol.* **2015**, *60*, 813–826, doi:10.1111/fwb.12536.

184. Descloux, S.; Datry, T.; Marmonier, P. Benthic and hyporheic invertebrate assemblages along a gradient of increasing streambed colmation by fine sediment. *Aquat. Sci.* **2013**, *75*, 493–507, doi:10.1007/s00027-013-0295-6.

185. Mathers, K.L.; Millett, J.; Robertson, A.L.; Stubbington, R.; Wood, P.J. Faunal response to benthic and hyporheic sedimentation varies with direction of vertical hydrological exchange. *Freshw. Biol.* **2014**, *59*, 2278–2289, doi:10.1111/fwb.12430.

186. Dunscombe, M.; Robertson, A.; Peralta Maraver, I.; Shaw, P. Community structure and functioning below the stream bed across contrasting geologies. *Sci. Total Environ.* **2018**, *630*, 1028–1035, doi:10.1016/j.scitotenv.2018.02.274.

187. Kemp, P.; Sear, D.A.; Collins, A.L.; Naden, P.S.; Jones, J.I. The impacts of fine sediment on riverine fish. *Hydrol. Process.* **2011**, *25*, 1800–1821, doi:10.1002/hyp.7940.

188. Sear, D.A.; Jones, J.I.; Collins, A.L.; Hulin, A.; Burke, N.; Bateman, S.; Pattison, I.; Naden, P.S. Does fine sediment source as well as quantity affect salmonid embryo mortality and development? *Sci. Total Environ.* **2016**, *541*, 957–968, doi:10.1016/j.scitotenv.2015.09.155.

189. Larsen, L.; Harvey, J.; Skalak, K.; Goodman, M. Fluorescence-based source tracking of organic sediment in restored and unrestored urban streams. *Limnol. Oceanogr.* **2015**, *60*, 1439–1461, doi:10.1002/lno.10108.

190. Wagner, M.; Scherer, C.; Alvarez-Muñoz, D.; Brennholt, N.; Bourrain, X.; Buchinger, S.; Fries, E.; Grosbois, C.; Klasmeier, J.; Marti, T. Microplastics in freshwater ecosystems: What we know and what we need to know. *Environ. Sci. Eur.* **2014**, *26*, 12, doi:10.1186/s12302-014-0012-7.

191. Dris, R.; Imhof, H.; Sanchez, W.; Gasperi, J.; Galgani, F.; Tassin, B.; Laforsch, C. Beyond the ocean: Contamination of freshwater ecosystems with (micro-) plastic particles. *Environ. Chem.* **2015**, *12*, 539–550, doi:10.1071/EN14172.

192. Mani, T.; Hauk, A.; Walter, U.; Burkhardt-Holm, P. Microplastics profile along the Rhine River. *Sci. Rep.* **2015**, *5*, 17988, doi:10.1038/srep17988.

193. Alimi, O.S.; Hernandez, L.M.; Tufenkji, N. Microplastics and nanoplastics in aquatic environments: Aggregation, deposition, and enhanced contaminant transport. *Environ. Sci. Technol.* **2018**, *52*, 1704–1724, doi:10.1021/acs.est.7b05559.

194. Browne, M.A.; Crump, P.; Niven, S.J.; Teuten, E.; Tonkin, A.; Galloway, T.; Thompson, R. Accumulation of microplastic on shorelines worldwide: Sources and sinks. *Environ. Sci. Technol.* **2011**, *45*, 9175–9179, doi:10.1021/es201811s.

195. Magnusson, K.; Norén, F. *Screening of Microplastic Particles in and Down-Stream a Wastewater Treatment Plant*; Report C55; Swedish Environmental Research Institute: Stockholm, Sweeden, 2014; p. 22. Available online: http://www.diva-portal.org/smash/get/diva2:773505/FULLTEXT01.pdf (accessed on 23 October 2019).

196. Vogelsang, C.; Lusher, A.L.; Dadkhah, M.E.; Sundvor, I.; Umar, M.; Ranneklev, S.B.; Eidsvoll, D.; Meland, S. *Microplastics in Road Dust–Characteristics, Pathways and Measures*; Research Report 7361-2019; Institute of Transport Economics, Norwegian Centre for Transport Research: Oslo, Norway, 2019; p. 174. Available online: https://niva.brage.unit.no/niva-xmlui/handle/11250/2493537 (accessed on 23 October 2019).

197. Kooi, M.; Besseling, E.; Kroeze, C.; Van Wezel, A.P.; Koelmans, A.A. Modeling the fate and transport of plastic debris in freshwaters: Review and guidance. In: *Freshwater Microplastics*; Springer: Cham, Switzerland, 2018; pp. 125–152, doi:10.1007/978-3-319-61615-5.

198. Besseling, E.; Quik, J.T.; Sun, M.; Koelmans, A.A. Fate of nano-and microplastic in freshwater systems: A modeling study. *Environ. Pollut.* **2017**, *220*, 540–548, doi:10.1016/j.envpol.2016.10.001.

199. Castañeda, R.A.; Avlijas, S.; Simard, M.A.; Ricciardi, A. Microplastic pollution in St. Lawrence river sediments. *Can. J. Fish. Aquat. Sci.* **2014**, *71*, 1767–1771, doi:10.1139/cjfas-2014-0281.

200. Hoellein, T.J.; Shogren, A.J.; Tank, J.L.; Risteca, P.; Kelly, J.J. Microplastic deposition velocity in streams follows patterns for naturally occurring allochthonous particles. *Sci. Rep.* **2019**, *9*, 3740, doi:10.1038/s41598-019-40126-3.

201. Nel, H.A.; Dalu, T.; Wasserman, R.J. Sinks and sources: Assessing microplastic abundance in river sediment and deposit feeders in an Austral temperate urban river system. *Sci. Total Environ.* **2018**, *612*, 950–956, doi:10.1016/j.scitotenv.2017.08.298.

202. Hurley, R.; Woodward, J.; Rothwell, J.J. Microplastic contamination of river beds significantly reduced by catchment-wide flooding. *Nat. Geosci.* **2018**, *11*, 251–257, doi:10.1038/s41561-018-0080-1.

203. Maazouzi, C.; Galassi, D.; Claret, C.; Cellot, B.; Fiers, F.; Martin, D.; Marmonier, P.; Dole-Olivier, M.J. Do benthic invertebrates use hyporheic refuges during streambed drying? A manipulative field experiment in nested hyporheic flowpaths. *Ecohydrology* **2017**, *10*, e1865, doi:10.1002/eco.1865.

204. Malcolm, I.A.; Soulsby, C.; Youngson, A.F.; Hannah, D.M.; McLaren, I.S.; Thorne, A. Hydrological influences on hyporheic water quality: Implications for salmon egg survival. *Hydrol. Process.* **2004**, *18*, 1543–1560, doi:10.1002/hyp.1405.

205. Febria, C.M.; Beddoes, P.; Fulthorpe, R.R.; Williams, D.D. Bacterial community dynamics in the hyporheic zone of an intermittent stream. *ISME J.* **2012**, *6*, 1078–1088, doi:10.1038/ismej.2011.173.

206. Datry, T.; Larned, S.T.; Tockner, K. Intermittent rivers: A challenge for freshwater ecology. *BioScience* **2014**, *64*, 229–235, doi:10.1093/biosci/bit027.

207. Bonada, N.; Doledec, S.; Statzner, B. Taxonomic and biological trait differences of stream macroinvertebrate communities between mediterranean and temperate regions: Implications for future climatic scenarios. *Glob. Chang. Biol.* **2007**, *13*, 1658–1671, doi:10.1111/j.1365-2486.2007.01375.x.

208. Ward, A.S.; Zarnetske, J.P.; Baranov, V.; Blaen, P.J.; Brekenfeld, N.; Chu, R.; Derelle, R.; Drummond, J.; Fleckenstein, J.; Garayburu-Caruso, V.; et al. Co-located contemporaneous mapping of morphological, hydrological, chemical, and biological conditions in a 5th order mountain stream network, Oregon, USA. *Earth Syst. Sci.* **2019**. doi:10.5194/essd-2019-45.

209. Zheng, L.; Cardenas, M.B.; Wang, L.; Mohrig, D. Ripple effects: Bedform morphodynamics cascading into hyporheic zone biogeochemistry. *Water Resour. Res.* **2019**, *55*, 7320–7342, doi:10.1029/2018WR023517.

210. Odum, H.T. Primary production in flowing waters. *Limnol. Oceanogr.* **1956**, *1*, 102–117, doi:10.4319/lo.1956.1.2.0102.

211. Mulholland, P.J.; Houser, J.N.; Maloney, K.O. Stream diurnal dissolved oxygen profiles as indicators of in-stream metabolism and disturbance effects: Fort Benning as a case study. *Ecol. Indic.* **2005**, *5*, 243–252, doi:10.1016/j.ecolind.2005.03.004.

212. Roberts, B.J.; Mulholland, P.J.; Hill, W.R. Multiple scales of temporal variability in ecosystem metabolism rates: Results from 2 years of continuous monitoring in a forested headwater stream. *Ecosystems* **2007**, *10*, 588–606, doi:10.1007/s10021-007-9059-2.

213. Rajwa-Kuligiewicz, A.; Bialik, R.J.; Rowiński, P.M. Dissolved oxygen and water temperature dynamics in lowland rivers over various timescales. *J. Hydrol. Hydromech.* **2015**, *63*, 353–363, doi:10.1515/johh-2015-0041.

214. Brandt, T.; Vieweg, M.; Laube, G.; Schima, R.; Goblirsch, T.; Fleckenstein, J.H.; Schmidt, C. Automated in situ oxygen profiling at aquatic–terrestrial interfaces. *Environ. Sci. Technol.* **2017**, *51*, 9970–9978, doi:10.1021/acs.est.7b01482.

215. Gilbert, J.; Dole-Oliver, M.J.; Marmonier, P.; Vervier, P. Surface water-groundwater ecotones. In *The Ecology and Management of Aquatic–Terrestrial Ecotones*; Naiman, R.J., Décamps, H., Eds.; Unesco: Paris, France, 1990; pp. 199–225.

216. Townsend, C.R.; Scarsbrook, M.R.; Dolédec, S. The intermediate disturbance hypothesis, refugia, and biodiversity in streams. *Limnol. Oceanogr*. **1997**, *42*, 938–949, doi:10.4319/lo.1997.42.5.0938.

217. Robertson, A.L. Lotic meiofaunal community dynamics: Colonisation, resilience and persistence in a spatially and temporally heterogeneous environment. *Freshw. Biol.* **2000**, *44*, 135–147, doi:10.1046/j.1365-2761.2000.00595.x.

218. Morén, I.; Wörman, A.; Riml, J. Design of remediation actions for nutrient mitigation in the hyporheic zone. *Water Resour. Res.* **2017**, *53*, 8872–8899, doi:10.1002/2016WR020127.

219. Grant, S.B.; Azizian, M.; Cook, P.; Boano, F.; Rippy, M.A. Factoring stream turbulence into global assessments of nitrogen pollution. *Science* **2018**, *359*, 1266–1269, doi:10.1126/science.aap8074.

220. Wörman, A.; Packman, A.I.; Marklund, L.; Harvey, J.W.; Stone, S.H. Fractal topography and subsurface water flows from fluvial bedforms to the continental shield. *Geophys. Res. Lett.* **2007**, *34*, L07402, doi:10.1029/2007GL029426.

221. Stonedahl, S.H.; Harvey, J.W.; Wörman, A.; Salehin, M.; Packman, A.I. A multiscale model for integrating hyporheic exchange from ripples to meanders. *Water Resour. Res.* **2010**, *46*, W12539, doi:10.1029/2009WR008865.

222. Bridge, J.W. *High Resolution In-Situ Monitoring of Hyporheic Zone Biogeochemistry*; Science Report SC030155/SR3; Environment Agency: Bristol, UK; 2005; p. 51 Available online: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/291498/scho0605bjco-e-e.pdf (accessed on 23 October 2019).

223. Posselt, M.; Jaeger, A.; Schaper, J.L.; Radke, M.; Benskin, J.P. Determination of polar organic micropollutants in surface and pore water by high-resolution sampling-direct injection-ultra high performance liquid chromatography-tandem mass spectrometry. *Environ. Sci. Process. Impacts* **2018**, *20*, 1716–1727, doi:10.1039/C8EM00390D.

224. Saenger, N.; Kitanidis, P.K.; Street, R. A numerical study of surface-subsurface exchange processes at a riffle-pool pair in the Lahn River, Germany. *Water Resour. Res.* **2005**, *41*, 12424, doi:10.1029/2004WR003875.

225. Cardenas, M.B.; Wilson, J.L. Hydrodynamics of coupled flow above and below a sediment-water interface with triangular bed-forms. *Adv. Water Resour.* **2007**, *30*, 301–313, doi:10.1016/j.advwatres.2006.06.009.

226. Cardenas, M.B.; Wilson, J.L. Effects of current-bed form induced fluid flow on the thermal regime of sediments. *Water Resour. Res.* **2007**, *43*, W08431, doi:10.1029/2006WR005343.

227. Cardenas, M.B.; Wilson, J.L. Dunes, turbulent eddies, and interfacial exchange with permeable sediments. *Water Resour. Res.* **2007**, *43*, W08412, doi:10.1029/2006WR005787.

228. Bardini, L.; Boano, F.; Cardenas, M.B.; Revelli, R.; Ridolfi, L. Nutrient cycling in bedform induced hyporheic zones. *Geochim. Cosmochim. Acta* **2012**, *84*, 47–61, doi:10.1016/j.gca.2012.01.025.

229. Trauth, N.; Schmidt, C.; Maier, U.; Vieweg, M.; Fleckenstein, J.H. Coupled 3-D stream flow and hyporheic flow model under varying stream and ambient groundwater flow conditions in a pool-riffle system. *Water Resour. Res.* **2013**, *49*, 5834–5850, doi:10.1002/wrcr.20442.

230. Chen, X.B.; Cardenas, M.B.; Chen, L. Three-dimensional versus two-dimensional bed form-induced hyporheic exchange. *Water Resour. Res.* **2015**, *51*, 2923–2936, doi:10.1002/2014WR016848.

231. Chen, X.; Cardenas, M.B.; Chen, L. Hyporheic exchange driven by three-dimensional sandy bed forms: Sensitivity to and prediction from bed form geometry. *Water Resour. Res.* **2018**, *54*, doi:10.1029/2018WR022663.

232. Ren, J.; Wang, X.; Zhou, Y.; Chen, B.; Men, L. An analysis of the factors affecting hyporheic exchange based on numerical modeling. *Water* **2019**, *11*, 665, doi:10.3390/w11040665.

233. Brunner, P.; Simmons, C.T. HydroGeoSphere: A fully integrated, physically based hydrological model. *Groundwater* **2012**, *50*, 170–176, doi:10.1111/j.1745-6584.2011.00882.x.

234. Oxtoby, O.; Heyns, J.; Suliman, R. A finite-volume solver for two-fluid flow in heterogeneous porous media based on OpenFOAM. Paper presented at the Open Source CFD International Conference, Hamburg, Germany, 24–25 October 2013.

235. Broecker, T.; Teuber, K.; Elsesser, W.; Hinkelmann, R. Multiphase modeling of hydrosystems using OpenFOAM. In *Advances in Hydroinformatics*; Springer: Singapore, 2018; pp. 1013–1029, doi:10.1007/978-981-10-7218-5_71.

236. Broecker, T.; Teuber, K.; Sobhi Gollo, V.; Nützmann, G.; Hinkelmann, R. Integral flow modelling approach for surface water-groundwater interaction along a rippled streambed. *Water* **2019**, *11*, 1517, doi:10.3390/w11071517.

237. Honti, M.; Bischoff, F.; Moser, A.; Stamm, C.; Baranya, S.; Fenner, K. Relating Degradation of Pharmaceutical Active Ingredients in a Stream Network to Degradation in Water-Sediment Simulation Tests. *Water Resour. Res.* **2018**, *54*, 9207–9223, doi:10.1029/2018WR023592.

238. Lindim, C.; van Gils, J.; Cousins, I.T. A large-scale model for simulating the fate & transport of organic contaminants in river basins. *Chemosphere* **2016**, *144*, 803–810, doi:10.1016/j.chemosphere.2015.09.051.

239. Feijtel, T.; Boeije, G.; Matthies, M.; Young, A.; Morris, G.; Gandolfi, C.; Hansen, B.; Fox, K.; Holt, M.; Koch, V.; et al. Development of a geography-referenced regional exposure assessment tool for European rivers-great-er contribution to great-er #1. *Chemosphere* **1997**, *34*, 2351–2373, doi:10.1016/S0045-6535(97)00048-9.

240. Coll, C.; Lindim, C.; Sobek, A.; Sohn, M.D.; MacLeod, M. Prospects for finding Junge variability-lifetime relationships for micropollutants in the Danube river. *Environ. Sci. Process. Impacts* **2019**, doi:10.1039/C9EM00283A.

241. Frei, S.; Peiffer, S. Exposure times rather than residence times control redox transformation efficiencies in riparian wetlands. *J. Hydrol.* **2016**, *543*, 182–196, doi:10.1016/j.jhydrol.2016.02.001.

242. Pittroff, M.; Frei, S.; Gilfedder, B.S. Quantifying nitrate and oxygen reduction rates in the hyporheic zone using ^{222}Rn to upscale biogeochemical turnover in rivers. *Water Resour. Res.* **2017**, *53*, 563–579, doi:10.1002/2016WR018917.

243. Grabowski, R.C.; Gurnell, A.M. Diagnosing problems of fine sediment delivery and transfer in a lowland catchment. *Aquat. Sci.* **2016**, *78*, 95–106, doi:10.1007/s00027-015-0426-3.

244. Grabowski, R.C.; Gurnell, A.M.; Burgess-Gamble, L.; England, J.; Holland, D.; Klaar, M.J.; Morrissey, I.; Uttley, C.; Wharton, G. The current state of the use of large wood in river restoration and management. *Water Environ. J.* **2019**, *33*, 366–377, doi:10.1111/wej.12465.

245. Azinheira, D.L.; Scott, D.T.; Hession, W.; Hester, E.T. Comparison of effects of inset floodplains and hyporheic exchange induced by in-stream structures on solute retention. *Water Resour. Res.* **2014**, *50*, 6168–6190, doi:10.1002/2013WR014400.

246. Lammers, R.W.; Bledsoe, B.P. What role does stream restoration play in nutrient management? *Crit. Rev. Environ. Sci. Technol.* **2017**, *47*, 335–371, doi:10.1080/10643389.2017.1318618.

247. Herzog, S.P.; Higgins, C.P.; Singha, K.; McCray, J.E. Performance of engineered streambeds for inducing hyporheic transient storage and attenuation of resazurin. *Environ. Sci. Technol.* **2018**, *52*, 10627–10636. doi:10.1021/acs.est.8b01145.

248. Ward, A.S.; Morgan, J.A.; White, J.R.; Royer, T.V. Streambed restoration to remove fine sediment alters reach-scale transient storage in a low-gradient fifth-order river, Indiana, USA. *Hydrol. Process.* **2018**, *32*, 1786–1800, doi:10.1002/hyp.11518.

249. Herzog, S.P.; Higgins, C.P.; McCray, J.E. Engineered streambeds for induced hyporheic flow: Enhanced removal of nutrients, pathogens, and metals from urban streams. *J. Environ. Eng.* **2015**, *142*, 04015053, doi:10.1061/(ASCE)EE.1943-7870.0001012.

250. Bernhardt, E.S.; Palmer, M.A. Restoring streams in an urbanizing world. *Freshw. Biol.* **2007**, *52*, 738–751. doi:10.1111/j.1365-2427.2006.01718.x.

251. Mutz, M.; Kalbus, E.; Meinecke, S. Effect of instream wood on vertical water flux in low-energy sand bed flume experiments. *Water Resour. Res.* **2007**, *43*, 1–10, doi:10.1029/2006WR005676.

252. Thompson, M.S.A.; Brooks, S.J.; Sayer, C.D.; Woodward, G.; Axmacher, J.C.; Perkins, D.M.; Gray, C. Large woody debris "rewilding" rapidly restores biodiversity in riverine food webs. *J. Appl. Ecol.* **2018**, *55*, 895–904, doi:10.1111/1365-2664.13013.

253. Palmer, M.A.; Menninger, H.L.; Bernhardt, E. River restoration, habitat heterogeneity and biodiversity: A failure of theory or practice? *Freshw. Biol.* **2010**, *55*, 205–222, doi:10.1111/j.1365-2427.2009.02372.x.

254. Magliozzi, C.; Coro, G.; Grabowski, R.C.; Packman, A.I.; Krause, S. A multiscale statistical method to identify potential areas of hyporheic exchange for river restoration planning. *Environ. Model. Softw.* **2019**, *111*, 311–323, doi:10.1016/j.envsoft.2018.09.006.

255. Betterle, A.; Schirmer, M.; Botter, G. Characterizing the spatial correlation of daily streamflows. *Water Resour. Res.* **2017**, *53*, 1646–1663, doi:10.1002/2016WR019195.

256. Betterle, A.; Schirmer, M.; Botter, G. Flow dynamics at the continental scale: Streamflow correlation and hydrological similarity. *Hydrol. Process.* **2018**, *33*, 627–646, doi:10.1002/hyp.13350.