RINGO | Readiness of ICOS

Readiness of ICOS for Necessities of integrated Global Observations

D1.4

Requirements for the monitoring of land-ocean carbon fluxes at pan-European scale

RINGO (GA no 730944)

DRAFT

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Deliverable: Report describing the ideal and minimum requirements of an aquatic transport and fluxes observation system including possible role of ICOS RI and resulting costs.

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Deliverable Review Checklist

A list of checkpoints has been created to be ticked off by the Task Leader before finalizing the deliverable. These checkpoints are incorporated into the deliverable template where the Task Leader must tick off the list.

- Appearance is generally appealing and according to the RINGO template. Cover page has been updated according to the Deliverable details. √
- The executive summary is provided giving a short and to the point description of the deliverable. √
- All abbreviations are explained in a separate list. √
- All references are listed in a concise list. √
- The deliverable clearly identifies all contributions from partners and justifies the resources used. √
- A full spell check has been executed and is completed. √

	Name	Partner	Date
From	Daniel J. Mayor	NOC/NERC	21/07/2020
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Executive Summary

The export of carbon (C) from land to sea via the Land-Ocean Aquatic Continuum (LOAC) is a substantial component of the global C cycle, with the lateral transport of C through aquatic environments stimulating a vertical exchange of gaseous C between the LOAC and the atmosphere. Aquatic environments are highly dynamic, and subject to a multitude of environmental pressures linked to global climate change and human activities. In order to understand the effect of these pressures on the global C cycle, a high-quality monitoring network is required to resolve spatial and temporal variability. This report provides guidance on the requirements for such a network at pan-European scale, including the extent to which monitoring might be integrated within existing infrastructure.

We discuss the transport of terrigenous C along the LOAC (land – stream – river – estuary – coastal zone – ocean), and consider additional linked environments such as groundwater, lakes, wetlands, and constructed water bodies. We outline the requirements for monitoring lateral and vertical C fluxes associated with each of these environments, and suggest a blueprint by which monitoring of these fluxes may be achieved.

The requirements of the proposed monitoring programme are outlined as follows: (1) regular monitoring of the lateral movement of C through the LOAC, conducted at broad spatial scale by national agencies under the guidance of the European Environment Agency (EEA), and according to site selection and methodological criteria provisionally set forth in this report; (2) regular monitoring of the vertical movement of C between the LOAC and the atmosphere, conducted at key 'super-sites' and administered by the Integrated C Observatory System (ICOS) and other research infrastructure and institutes; and (3) focussed studies to understand the processes that act upon C fluxes along the LOAC, conducted by research centres and driven by targeted research calls. Investment in autonomous systems is advised, with examples of existing technologies provided.

As a next step, we recommend the formation of a new LOAC Thematic Centre (LTC) to oversee a preparatory phase, with the goal of initiating a pan-European land-ocean C monitoring network within 10 years. This timeline is short, but is considered necessary given the significance of these fluxes to large-scale C budgeting and the current lack of consistent data sets.

The study of land-ocean-atmosphere C fluxes necessitates collaboration across the traditional disciplines of terrestrial, freshwater, marine, and atmospheric science, the sharing of knowledge and experience, and the use of a common language. This report has been written in that spirit.

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1. Introduction

1.1 Important definitions

The Land Ocean Aquatic Continuum (LOAC) refers to the network of aquatic environments which link the terrigenous and marine environments, including groundwater, fluvial systems, lakes, constructed water bodies (i.e. ponds, reservoirs, ditches), wetlands, transitional waters (i.e. estuaries, fjords, deltas, lagoons, coastal waters), and finally the ocean.

In the context of this report, the Land-Ocean C Flux consists of three components, where 'aquatic' covers the full spectrum of salinities observed across the LOAC. These are:

1. Lateral C fluxes (land – aquatic)
2. Vertical C fluxes (aquatic – atmosphere)
3. Vertical C fluxes (aquatic – sediment)

1.2 Objectives of RINGO Task 1.4

This strategic scoping task brought together an interdisciplinary group of experts who are actively investigating the fate of C across a range of aquatic ecosystems. That group was tasked with the following objectives:

1. Determine the status of pan-European land-ocean C flux monitoring, and identify the associated methodologies;

2. Identify poorly-monitored regions with significant and/or changing land-ocean C fluxes; and

3. Provide guidance on future requirements for continual land-ocean C flux monitoring, including:

    (a) The integration and expansion of existing infrastructure, including ICOS and other national infrastructures and data products; and

    (b) How such a monitoring network might be sustained.

Land-ocean-atmosphere C fluxes span the terrestrial, freshwater, marine, and atmospheric realms and thus transcend the traditional boundaries found within environmental science. Their study necessitates collaboration and cooperation across disciplines and specialisms. A critical aspect of Task 1.4 was knowledge exchange, designed to foster such collaboration through the creation of a shared vocabulary and knowledge base. This was facilitated through a series of workshops and field visits to existing infrastructure in a range of environments. The motivation was to foster a better appreciation of the LOAC as a whole, and how different research communities study and understand it.

2. Knowledge Review

2.1 Land-ocean carbon fluxes: an important knowledge gap

Anthropogenic perturbation of the global carbon (C) cycle is driving a rapid increase in atmospheric greenhouse gas (GHG) concentrations, with consequences for the global climate system (i.e. Stocker et al., 2013). Successfully reducing and/or mitigating these consequences is hampered by large uncertainties in global C budgets. We must therefore improve our understanding of the C cycle, including the wide range of complex processes and feedback mechanisms within it, as a matter of urgency.

Until recently, the global estimate of land-freshwater C transport was 1.9 Pg C yr^{-1} (Cole et al., 2007). This is approximately equal to the total annual uptake of anthropogenic carbon dioxide (CO_2) by the biosphere (Stocker et al., 2013), and hence represents a significant term in the global C budget. Subsequent estimates have continually increased the size of the estimated flux of terrigenous C into inland waters, with the most recent estimate being 5.1 Pg C yr^{-1} (Drake et al., 2018). The uncertainties associated with this estimate remain large becasue our ability to quantify the flux of terrigenous C from land into aquatic systems remains in its infancy.

Freshwater systems are linked to the open ocean via the Land Ocean Aquatic Continuum (LOAC), a complex fluid network which links aquatic environments of every kind, and provides a conduit through which C is transported from land to the ocean (Cole et al., 2007; Drake et al., 2018; Regnier et al., 2013). It includes mountainous headwater streams, groundwaters, fluvial systems, lakes, wetlands, transitional waters (i.e. estuaries, fjords, deltas, lagoons, and coastal waters), constructed water bodies (i.e. ponds, reservoirs, and ditches), shelf seas, and the open ocean. The flux of terrigenous C via the LOAC consists of three components, where 'aquatic' covers the full spectrum of observed salinities. These are:

1. Lateral C fluxes (land – aquatic)
2. Vertical C fluxes (aquatic – atmosphere)
3. Vertical C fluxes (aquatic – sediment)

These three fluxes are comprised of a number of different C species, including: dissolved organic C (DOC); dissolved inorganic C (DIC), which itself consists of: aqueous CO_2 ($CO_{2\,(aq)}$); carbonic acid (H_2CO_3), carbonate (HCO_3^-) and bicarbonate (CO_3^{2-}) ions; particulate organic C (POC); particulate inorganic C (PIC); and gasses (carbon dioxide ($CO_{2\,(g)}$); and methane ($CH_{4\,(g)}$, a GHG with ~28 fold higher global warming potential than CO_2 (Myhre et al., 2013)). In this report, CO_2 and CH_4 refer specifically to gaseous form. The relative composition and concentration of these species are controlled by a wide range of environmental factors including climate, land use and land cover (LULC), soil organic carbon (SOC) content and other soil properties (e.g. clay content, pH, carbonate content, erodability), geology, catchment characteristics (e.g. catchment size, catchment slope), net primary production (NPP), hydrology and water residence time. The fate of this material is dependent on external environmental factors, and likely to be highly variable in both space and time.

How an ecosystem takes up, stores, and releases C influences how that ecosystem interacts with the LOAC. Net Primary Production (NPP) is the amount of C absorbed by plants during photosynthesis. Net Ecosystem Production (NEP) combines C taken in by plants and C released by soils, or rather the net C exchange between the ecosystem and the atmosphere. The balance between the two is a contributing factor in determining the quantity and type of terrigenous organic carbon (OC) found in the LOAC (i.e. relatively recalcitrant (resistant to degradation) soil organic matter (SOM) vs labile (susceptible to degradation), fresh biological production). In low-latitude regions, increased DOC export is thought to be linked to high rates of NPP, which makes the total amount of terrestrial OC available for entrainment and delivery to aquatic systems greater than in other global biome types (e.g. high lattitudes; Li et al., 2019). Conversely, in high latitude regions where NPP is significantly lower, high DOC export is sustained by much higher SOC stores, particularly in peatland and permafrost environments, where decomposition rates are constrained by waterlogging or freezing, so that NEP rather than NPP controls export. A similar imbalance between NPP and decomposition also occurs in tropical peatlands, which generate some of the highest DOC export fluxes in the world (e.g. Moore et al., 2013). For the Boreal region, Hastie et al., (2018) recently presented a C budget in which 3% - 5% of terrestrial NPP is transported into the aquatic continuum. In human-influenced systems, a further fraction of OC results from anthropogenic sources, typically from fertiliser use, animal faeces, sewage outflows, and similar. As this terrigenous OC moves along the LOAC, the majority will undergo either aggregation/ flocculation and/or burial in lacustrine and fluvial sediments (Kirschbaum et al., 2019), or remineralisation and/or outgassing, returning to the atmosphere as either CO_2 or CH_4 (e.g. Sawakuchi et al., 2017). In this way, the lateral flux of OC from land to sea stimulates a vertical flux of inorganic carbon (IC) to the atmosphere (Figure 4), the magnitude of which is largely controlled by the relative rates of different transformation and transport processes along the LOAC. The remaining fraction (approximately 10% as DOC) is exported into the world's estuaries (Kirschbaum et al., 2019) where highly variable transfer efficiencies are observed (Abril et al., 2002; Dürr et al., 2011).

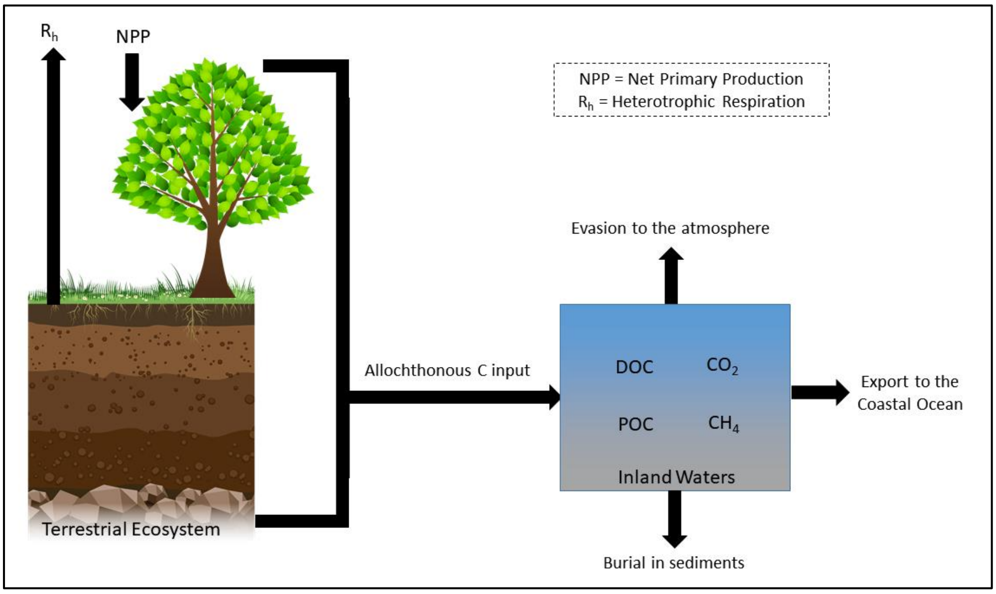

Figure 4: Diagrammatic representation of the transport of terrigenous OC along the LOAC, adapted from Lauerwald et al., 2017.

Various processes remove OC pool during transport across the LOAC. Heterotrophic metabolism results in the remineralisation of both DOC and POC, with the resultant C evaded into the atmosphere as CO_2 along with CH_4 produced by the breakdown and/or fermentation of organic substrates, in particular detrital POC. A portion of DOC assimilates/aggregates into the POC pool by flocculation, some of which is incorporated into sediments.

Photodegradation acts upon the coloured organic fraction, breaking up larger molecules and resulting in transformations to gaseous form (either chemically or via enhanced remineralisation) and eventual evasion to the atmosphere. What remains is exported into transitional waters. Each of these processes is influenced by a range of factors including the concentration and lability of organic matter, microbial community activity, water residence time, salinity and light attenuation (Parker and Mitch, 2016; Soares et al., 2019; Vähätalo and Wetzel, 2004). Variation in bio-and photo-degradation rates is illustrated in Wiegner and Seitzinger, (2001), where a study of forested and agricultural catchments found that 6 to 14% of DOC was utilised by bacteria, whilst light exposure did not have a significant effect. Other studies have shown much higher levels of photochemical degradation, particularly in humic waters where up to 50% of DOC can be removed under natural light conditions, whilst non-coloured OM such as sugars exuded by algae a tend to exhibit much lower rates of photodegradation (0.2%) (see Wiegner and Seitzinger, 2001 and references therein).

Terrigenous inorganic C (IC) originates in carbonate-mineral rocks and soils, released by chemical and/or physical weathering and washed into aquatic systems via precipitation. It can also originate from root and soil respiration on land, and be washed into the aquatic system via porewater and runoff. Once it has entered the LOAC, the fate of this terrigenous IC is not notably different from IC derived from other sources (i.e. atmospheric or biogenic IC), being determined by the local carbonate cycle (Figure 5), the environmental conditions which control it (in particular, pH, hydrology, weather, and water temperature), and the local respiration / photosynthesis balance. In carbonate-rich systems, or those experiencing acidification, additional but less significant inputs are likely to occur due to the dissolution of biogenic structures and/or suspended matter. Combined, these local factors determine the balance of aquatic and atmospheric concentrations, and thus drive a water – atmosphere flux, the direction of which varies in space and time. What is not evaded to the atmosphere will continue downstream.

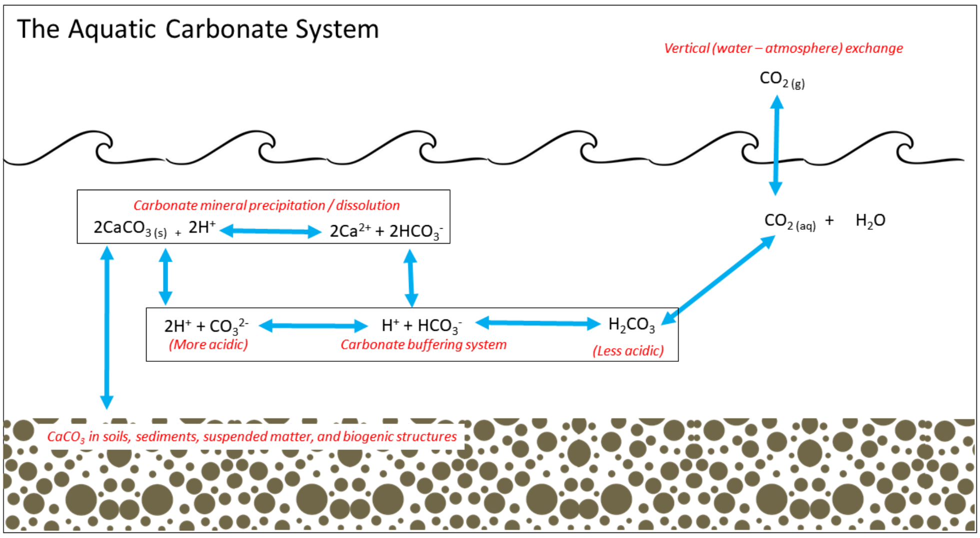

Figure 5: Diagrammatic representation of the aquatic carbonate cycle.

For a long time, it was assumed that the flux of terrigenous OC from land to sea had remained unchanged since pre-industrial times, but current estimates indicate that it is now ~1 Pg greater than it was in pre-industrial times, and that this number is likely still increasing (Regnier et al., 2013). Changes in the magnitude and/or direction of the component fluxes can have wide-ranging biogeochemical and ecological effects. Alterations in OC concentrations have been shown to influence the physical, photochemical, biochemical, and biological processes that control the metabolism and functioning of aquatic environments (Queimaliños et al., 2019). Increased allochthonous (externally produced) OC inputs can lead to increased light attenuation and altered thermal structure, which can inhibit primary production (Sandberg et al., 2004), increased benthic OM loadings, which can both stimulate and smother benthic communities (Frouin, 2000) and alter the coposition of microbial communities (Lindh et al., 2015). More broadly, changes to the organic matter (OM) within which OC is typically bound (both in terms of concentration or composition) can alter aquatic nutrient dynamics with wide-ranging knock-on effects for ecosystem function (Graeber et al., 2015; Stutter et al., 2018). The consequences of increased terrigenous nutrient input can be eutrophication, algal and microbial blooms, and deoxygenation resulting from increased remineralisation of the associated autochthonous OM (Dagg et al., 2008). Degradation leads to an increase in IC as respiring microorganisms produce CO_2. When biodegradation rates are high, the produced IC can amplify the effect of increasing atmospheric CO_2 uptake in many aquatic systems, and this is often compounded in regions where rivers flow through carbonate rocks. Ocean acidification is thought to contribute towards the declining resilience and health of coastal ecosystems, and river outflows originating in carbonate-rich geology can serve to amplify this. (Bates et al., 2014; Carstensen and Duarte, 2019; Doney et al., 2009; Fabry et al., 2008; Sabine and Feely, 2004). Indeed, the cumulative effect of downstream movement of fresh water bodies means that these effects can exert negative effects in transitional and coastal waters, where pollution from upstream human activities (i.e. agricultural runoff and untreated sewage) via riverine discharge is recognised as a major driver for change (Regnier et al., 2013). Each of these effects has the potential to dramatically restructure the local ecosystem, and each is intrinsically linked to the flow of terrigenous C from land to sea.

Changing land-ocean C fluxes can also have significant social, economic, and human-health implications. For example, over the last 50 years aquatic DOC concentrations across Europe and North America (Monteith et al., 2007) have increased significantly. This has made the extraction of potable water more expensive, increased greenhouse gas (GHG) emissions associated with water treatment plants, and resulted in potentially deleterious human health impacts as a result of carcinogenic by-products of DOC removal from drinking water (Jones et al., 2016; Lavonen et al., 2013). Increases in the amount of POC flowing down major rivers has been linked to a shallowing of estuaries and an increased financial burden in terms of maintaining shipping routes. Increasing DIC concentrations have been linked to decreasing yields from fresh and coastal fisheries, resulting in increased fish and shellfish mortality, decreased livelihoods, and increasing consumer cost.

Despite these and other myriad biogeochemical, ecological, social, economic, and human health implications associated with changing land-ocean C fluxes, we currently lack understanding of the spatio-temporal variability associated with the input, processing, and removal of terrigenous C across the LOAC. As a result, we cannot adequately predict how changes to land-ocean C fluxes will influence aquatic C cycling or atmospheric CO_2 levels. Quantifying these fluxes is made particularly difficult by the degree of variability observed across the varied environments that compose the LOAC, a description of which follows.

2.2 Environments of the land-ocean aquatic continuum (LOAC)

Our discussion of the environments which constitute the European LOAC includes: soil and groundwater; fluvial waters (headwaters, streams, and rivers); lakes and freshwater wetlands/bogs; constructed waterbodies (reservoirs, ponds, and ditches); and transitional waters (estuaries, fjords, lagoons, deltas, saltmarsh and seagrass, and shelf seas).

2.2.1 Soil water and groundwater

The transfer of C from land to sea begins with subsurface soil and groundwater flows that can be conceptualised across different spatial and temporal scales, both of which strongly affect internal C processing and transport (Figure 6).

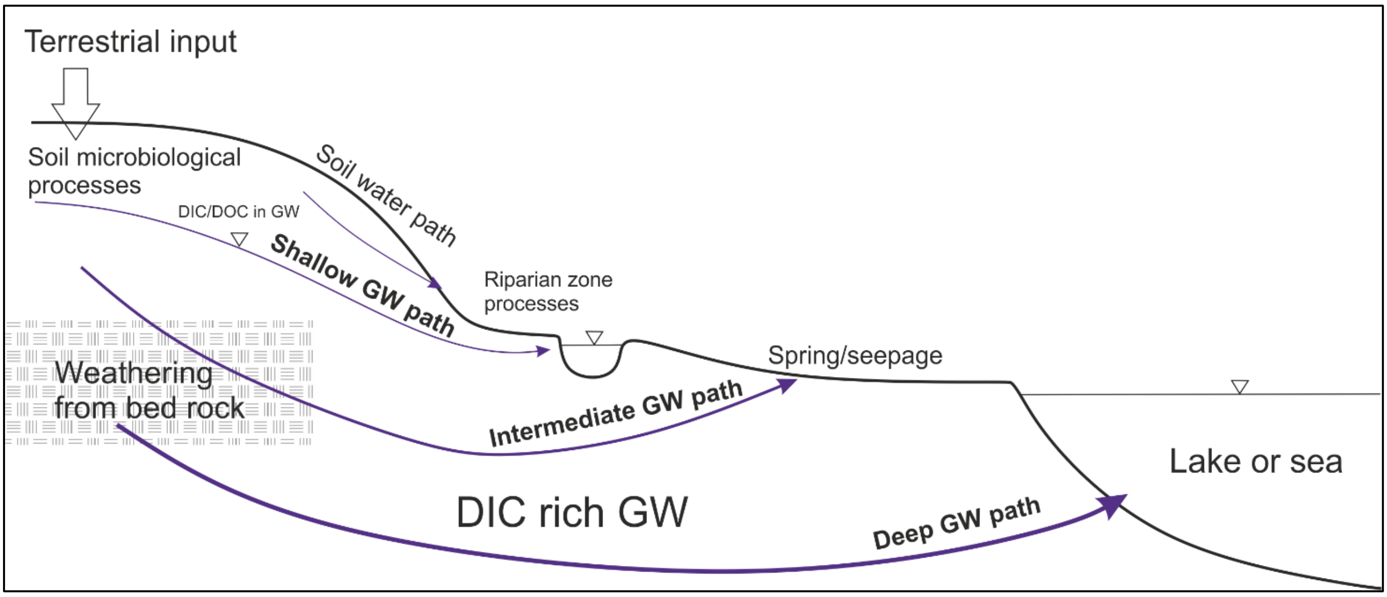

Figure 6: Shallow, intermediate, and deep groundwater (GW) flow baths bring C to fluvial systems on differing temporal and spatial scales. This excludes the short-circuiting effects of groundwater withdrawals.

Deep and intermediate groundwater flow paths exhibit residence times ranging from decades to millennia, operating at spatial resolutions ranging from regional to continental (Lapworth et al., 2018), whilst shallow flow paths through soils and superficial deposits exhibit relatively short residence times in the order of days to weeks to years typically, and operate at hillslope scales or smaller (Gooddy et al., 2006; Laudon and Sponseller, 2018). Water flowing over the soil surface or via very shallow flow paths within the soil can also transport DOM derived from plants and surface litter. This is a conceptual simplification of subsurface groundwater flows, and in reality there is a residence time continuum in that is controlled by a range of hydrogeological processes that operate at a variety of temporal and spatial scales (Tóth, 1963).

In most groundwater systems (with the exception of karstic and other fracture aquifers) larger colloids and particulates (POC and PIC) initially present are effectively filtered out as groundwater recharge passes through top soil and deeper porous material due to small matrix pore sizes. DOM produced in surface organic soils is also efficiently retained and removed via precipitation, adsorption and remineralisation in mineral soils and porous bedrock, and this weakly soluble 'humic' component of the DOM is also therefore largely absent from deeper groundwater. As a consequence, dissolved forms (certain fractions of DOC, and DIC) dominate (Stuart and Lapworth, 2016).

Deeper groundwater typically contains lower DOC concentrations, between 0.5-1 mg/L, due to microbial and physico-chemical processes which remove DOC in the shallow subsurface (McDonough et al., 2020). Shallow sub-surface flows typically contain DOC picked up whilst passing through organic soil material. This soil DOC undergoes transformation via oxidation, microbial utilization, adsorption and metal co-precipitation (Shen et al., 2015; Wassenaara et al., 1991), partitioning into a relatively labile DOC pool which is rapidly remineralized to DIC, and a relatively recalcitrant DOC pool (including humic and fulvic acids; Regan et al., 2017) which persists in the organic soil, but is prone to precipitation and adsorption in mineral soils and porous bedrock. As a result, most DOC input to surface waters derives from shallow subsurface flow through organic soils (e.g. Evans et al., 2007), whereas DIC tends to be transported via deeper groundwater flow.

Subsurface inflows, via base flow, provide rivers with both DOC and DIC, thereby contributing relatively persistent C inputs to surface water and controlling CO_2 evasion patterns, but episodic events (i.e. heavy rainfall/drought) can move flow paths between mineral and organic soil layers, generating occasional large pulses of DOC input (Lupon et al., 2019; Rawlins et al., 2014). The more dominant inorganic C species in groundwater are geologically mediated via bedrock weathering, and soil-mediated via heterotrophic activity and root respiration, which elevates soil pCO_2 and produces dissolved (bi)carbonate ions (Winterdahl et al., 2016). Deirmendjian et al. (2018) found that approximately 75% of the DIC exported into streams in this manner degassed rapidly as CO_2, providing the pathway for a GW mediated land-aquatic-atmosphere flux.

An added complication is the significant anthropogenic use of groundwater e.g. for drinking water and irrigation which perturbs the natural groundwater C cycle described above, global groundwater withdrawals are estimated to be c. 980 $km^3\ yr^{-1}$ (Margat and Gun, 2013; Siebert et al., 2010). Through this process a significant amount of DIC and DOC held in groundwater C stocks are redistributed to the surface, where it can enter the riverine and surface water system or is once again recharged and committed to the groundwater system. For example, groundwater withdrawals for drinking water in the UK is estimated to account for up to 0.05% of all UK CH_4 emissions (Gooddy and Darling, 2005). This and other aspects of groundwater withdrawals are never accounted for in C budget and flux estimates.

Groundwater also transfers dissolved C directly to surface water bodies such as lakes, wetlands and oceans, (Downing and Striegl, 2018). This can be particularly relevant in areas such as the Mediterranean Sea, where submarine groundwater discharge is a major source of dissolved inorganic nutrients that is comparable to riverine and atmospheric inputs (Rodellas et al., 2015). Submarine springs can be a significant source of nutrients for the ocean (Slomp and Van Cappellen, 2004), but DIC and DOC fluxes are currently unknown. GW therefore represents a potentially significant factor in the regional C balance, and excluding it from land-ocean C budgets (as is common practice) almost certainly biases balance estimates.

2.2.2 Fluvial waters

Headwaters are the first part of the LOAC to receive inputs of OM from the surrounding land, giving them a unique association with the terrestrial surface environment. As a result, allochthonous (externally supplied), terrigenous material dominates OC cycling in these upstream environments (Royer and David, 2005). Further downstream, this allochthonous OC combines with various autochthonous (locally produced) forms, resulting from i.e. algae, submerged vegetation, as well as other allochthonous inputs from anthropogenic sources such as sewage, wetlands, and agricultural runoff. As OC moves downstream, the proportion of relatively recalcitrant material increases as labile material is preferentially utilised (Catalán et al., 2016). Some evidence exists of the so-called 'priming effect', whereby the local microorganism community are able to metabolise highly recalcitrant OM in the presence of specific labile compounds (e.g. agricultural associated compounds), and so rivers have the potential to act as hotspots for the remineralisation of terrigenous OM (Blanchet et al., 2017).

Increased concentrations of autochthonous C may lead to an increase in aquatic respiration and photolysis, whilst increasing residence time with distance downstream promotes the photooxidation of allochthonous C, both of which produce CO_2. Coupled with inputs from DIC supersaturated GW sources, streams are typically supersaturated with CO_2 and the associated degassing represents a significant fraction of catchment scale CO_2 losses (e.g. Butman and Raymond, 2011). Indeed, fluvial waters are disproportionately large sources of both CO_2 and CH_4 to the atmosphere given their area, and global emissions have been estimated at 1.8 Pg C yr^{-1}, of which 27 Tg is in the form of CH_4, (Borges et al., 2015; Raymond et al., 2013; Wallin et al., 2018). Drake et al. (2018) put forward a revised value of 3.9 Pg C yr^{-1}, the difference partly explained by the inclusion of smaller order streams.

River floodplains often behave similarly to wetlands during flood periods, exporting significant amounts of OC as surface soil C and vegetation contribute to aquatic DOC concentrations (Abril and Borges, 2019; Raymond and Spencer, 2015). Similarly, intermittent (seasonal or episodic) wetting imposes physical disturbance and alters the biogeochemistry (i.e. oxic status) of soils with knock-on effects on C cycling. Ephemeral events can have disproportionate influence on C export to the LOAC (Raymond et al., 2016; von Schiller et al., 2017, 2019) yet are rarely captured during monitoring activities.

2.2.3 Lakes and freshwater wetlands

Lakes are strongly influenced by the surrounding catchment, and inputs from land are often considerably larger than internal lake production via photosynthesis (Cole et al., 1994). Lake sediments represent a very stable C sink (e.g. not sensitive to fire, subject to limited disturbance), and accrue at an estimated 0.6 Pg C yr^{-1} globally (Kortelainen et al., 2004; Stallard, 1998; Tranvik et al., 2009). Lakes can also modify the flux and composition of DOM. The dominant removal process is typically bacterial mineralisation (Koehler et al., 2014; Berggren et al., 2018), but photochemical breakdown may also be important within the upper photic zone, preferentially removing the highly coloured humic fraction of the DOM pool. Rates of DOM processing tend to decrease over time as the more biologically labile and photochemically reactive fractions of the DOM pool become depleted (Catalan et al., 2016; Vachon et al., 2016; Evans et al., 2017). As a result, rates of DOM removal will tend to be highest in lower-residence time lakes receiving fresh OM inputs from their catchments. However, this general decline in DOM removal rates is counterbalanced by very long residence times in some lakes (years, decades or even centuries in the largest waterbodies) which allow a very high fraction of the total DOM input to be remineralised. The importance of internal processing in lakes was recently highlighted by a land-ocean modelling study which found that the inclusion of an 'average' UK lake (residence time =

109 days) in the LOAC reduced the amount of DOC that becomes sequestered in the open ocean from 5% to 3% (Anderson et al., 2019).

Estimates of GHG emissions from lakes range from 0.3 – 1.2 Pg C yr^{-1} (Raymond et al., 2013; Tranvik et al., 2009), although some discrepancy exists as to the inclusion (or otherwise) of reservoirs in these figures. Approximately ~75 Tg C yr^{-1} of the vertical lake flux is CH_4 (Bastviken et al., 2011), much of which originates from sediment ebullition (bubbling). This is regulated by e.g. water depth and the amount of organic substrates supplied by the surrounding catchment, with the presence of labile OC favouring CH_4 production (Duc et al., 2010). Due to the depth dependency, near the shore and mostly in wind shadow can account for ~50% of the total lake CH_4 fluxes (Natchimuthu et al., 2016). The remaining CO_2 and CH_4 not emitted in the lake follows the outflowing water downstream and joins fluvial waters.

There is a risk of 'double counting' GHG emissions, because wetland area definitions often include many small lakes (Saunois et al., 2016). The low-oxygen, water-saturated soils found in wetlands result in high rates of OC accrual, whilst the connectivity between these soils, the overlying vegetation, and overlying water results in the transfer of large amounts of OC into surrounding lakes and fluvial waters. They are among the most productive environments in the world, and so are net contributors of atmospheric C to waters via high rates of primary production (Abril et al., 2014). The C they export is generally modern, and contains a relatively labile component which is more bio-accessible than terrigenous matter, but less bio-accessible than e.g. autocthonous phytoplankton exudates (Raymond and Spencer, 2015). Quantifying the flux of DOC from wetlands into inland waters can be problematic, particularly in fen-type peatlands that receive C from surrounding mineral soils and precipitation relative to bog-type (ombrotrophic) wetlands that receive C via precipitation alone. Indeed, to discuss the complexity of freshwater wetlands in terms of C cycling would warrant a separate report, and so we do not attempt to give a comprehensive overview. Instead, we note that these environments represent an important part of the LOAC, and will require careful consideration in any future monitoring network.

2.2.4 Transitional waters and coastal wetlands

Estuaries are thought to act as 'dynamic filters', exchanging material and energy with the ocean to varying degrees according to physical, hydrological, and biogeochemical conditions. They tend to be net heterotrophic (Heip et al., 1995), and can be strong sources of CO_2 and CH_4 to the atmosphere. The atmospheric flux of CO_2 from European estuaries is thought to represent a sum equal to 5 – 10% of Western Europe's anthropogenic emissions (Frankignoulle et al., 1998). However, a great deal of uncertainty surrounds degassing rates as they vary in space and time, with the relative abundance of pelagic (i.e. phytoplankton dominated) versus benthic (i.e. seagrass or benthic algal dominated) production, both of which are influenced by land-ocean OM flows, playing a major role. Organic matter inputs from catchments (Raymond and Bauer, 2001) and/or adjacent tidal wetlands (Bauer et al., 2013; Wang and Cai, 2004) vary from system to system, and the processing of these inputs determines the trophic balance in transitional (estuarine) waters.

Estuaries can serve as significant long-term organic C sinks through sedimentation of terrestrial inputs and, where present, the burial of vegetation, particularly seagrass and saltmarsh organic matter originating from coastal wetlands

(Duarte et al., 2004; McLeod et al., 2011; Nellemann et al., 2009). Coastal wetland environments represent only a small fraction of the global coastline (<1%; Nellemann et al., 2009), but are amongst the world's most intense C sink habitats per unit area (Duarte et al., 2005; Luisetti et al., 2019; Nellemann et al., 2009). Their small total area means that these vegetated habitats make small contributions to global C budgets, but their inclusion in land-ocean C budgeting is appropriate given their potential to sequester significant portions of C from incoming fluvial and/or estuarine waters, and their tendency to export significant fractions of their above-ground biomass beyond the immediate environment (e.g. seagrass, ~50%). The extent of European saltmarsh and seagrass has been estimated at 330 thousand and 2.5 million ha, respectively (Luisetti et al., 2013), with global sequestration and burial values generally used in lieu of regional ones.

Coastal inlets such as fjords are recognised as globally important sites for C burial, and their proximity to the terrestrial environment renders them effective 'traps' for terrigenous matter before it can reach the ocean. A recent study in the fjordic Loch Sunart, Scotland, 42% of the sediment OC was terrigenous, making it a more effective C store than the surrounding catchment (Smeaton and Austin, 2017). The mud-flat sediments characteristic of deltaic and lagoon systems are also very effective C storage environments, but can also be intense sites of C processing (Mayor et al., 2018). Little or no CO_2 flux data are available for fjords, deltas, or coastal lagoons. These environments represent an important knowledge gap. Other coastal inlets, such as the Rias Baixas on the west coast of the Iberian Peninsula, are influenced by seasonal near-shore upwelling of nutrient-rich deep-waters. This pulse input of nutrients fuels high levels of primary production and the sedimentation of organic matter. In turn, this drives respiration and methanogenesis in sediments with substantial efflux of CH_4 to the atmosphere through diffusion and direct ebullition (de Carlos et al., 2017; Kitidis et al., 2007).

Fluvial waters can strongly influence the coastal zone, transferring large amounts of dissolved and particulate C across a range of environments known collectively as 'transitional waters' (i.e. estuaries, fjords, deltas, lagoons) and the vegetated habitats which surround them. Evidence suggests that the delivery of terrigenous C to these transitional waters (and beyond) via the LOAC is a significant term, for example a recent synthesis paper estimated that rivers deliver approximately 60% of the total C input to the transitional waters which border the North West European shelf seas (NWES; Legge et al., 2020). It is likely that the majority of this input is microbially and photochemically transformed to CO_2 which outgasses in estuaries and the near-shore coastal zone (Kitidis et al., 2019). This proportion is similar to that published for the North American shelf (Fennel et al., 2019), despite obvious differences in geography and location.

Transport of terrigenous C beyond transitional waters is poorly defined. Whilst estuaries tend to be net CO_2 sources and shelf seas tend to be net CO_2 sinks, it has been suggested that riverine OC might effectively bypass the estuarine zone and thus contributed to open ocean C cycling (Cai, 2011). Greater riverine OC inputs would therefore mean greater oceanic CO_2 emissions. Approximately 30% of terrigenous DOC is thought to survive to the shelf, contributing ~30% of oceanic sedimentary burial (Burdige, 2007; Kandasamy and Nagender Nath, 2016). However, the transfer efficiency of DOC through transitional systems is highly variable (Dürr et al., 2011). A study of the Celtic Sea reported that up to 30% of the DOC at the shelf edge is terrigenous (Carr et al., 2019), whilst another of the North Sea found little evidence of terrigenous material beyond coastal waters (Painter et al., 2018). On the Western Adriatic shelf, the POC flux to the seabed is estimated to be ~309 Gt C yr^{-1}, whilst POC burial is ~180 Gt C yr^{-1}, corresponding to an overall burial efficiency of ~59%. Deposition in this region represents 62% of terrigenous OC inputs (Tesi et al., 2013). Such variability necessitates the study of specific C dynamics within the full range of transitional environments.

2.2.5 Modified (constructed) water bodies

Modified or 'constructed' water bodies, defined as *"water bodies where human activities have changed the hydrology of existing natural water bodies thereby altering water residence times and/or sedimentation rates… and water bodies that have been created by excavation, such as canals, ditches, and ponds"* (Lovelock et al., 2019), have been shown to make significant contributions to land-ocean C processing. Any emissions from such water bodies must be considered to be, at least partly, anthropogenic in origin. Their inclusion in lateral and vertical C flux monitoring network is therefore important for C and GHG accounting, especially as these systems are disproportionately large sources of CH_4. In particular, we recommend attention be paid to reservoirs, ponds, and ditches with clear connectivity to the land-ocean continuum.

2.2.5.1 Reservoirs

Globally, reservoirs are reported to bury ~60 Tg C yr^{-1} (Mendonça et al., 2017). This storage is greatest in tropical and subtropical regions, but it is also likely to be significant across Europe. However, these large water bodies are also estimated to produce 770 Tg CO_2 *eq* yr^{-1}, with CH_4 being the prime contributor to this flux (18 Tg CH_4 yr^{-1} / 504 Tg CO_2 *eq* yr^{-1}; Deemer et al., 2016; using CO_2 *eq* value from Myhre et al., 2013). The nutrient status of reservoirs has been suggested as the main driver of CH_4 emissions (Deemer et al., 2016; DelSontro et al., 2018) although latitudinal patterns also exist in the GHG emissions from these environments (Barros et al., 2011; Deemer et al., 2016). It should be noted that untangling the full C/GHG budget of reservoirs requires extensive monitoring. This is because of potentially high emissions from outflowing rivers, turbines, and spillways which arise as a result of elevated GHG concentrations in discharging reservior hypolimnion waters (Guérin et al., 2006).

2.2.5.2 Ponds

Compared to reservoirs, significantly less research has been conducted on constructed ponds, although similar patterns of biogeochemistry have been found for these small waterbodies. Specifically, diffusive emissions of CH_4 and CO_2 can be considerable (Holgerson and Raymond, 2016; Ollivier et al., 2019; Peacock et al., 2019; Webb et al., 2019), but ebullitive emissions of CH_4 tend to be larger still (van Bergen et al., 2019; Grinham et al., 2018; Natchimuthu et al., 2014; Panneer Selvam et al., 2014). Like reservoirs, C burial in these systems can be sizeable (Taylor et al., 2019), but it is likely that burial is not large enough to offset their C/GHG emissions (van Bergen et al., 2019). Recent work has demonstrated that the combination of high C fluxes and cumulatively large surface area can result in constructed ponds being significant sources of GHGs on a national scale (Grinham et al., 2018; Ollivier et al., 2019). Globally, the area occupied by constructed ponds is similar to that occupied by large reservoirs (Downing, 2010) and a coarse estimate of global CH_4 emissions from ponds is 3-8 Tg yr^{-1} (Saunois et al., 2019).

2.2.5.3 Ditches

Numerous studies have measured GHG emissions from ditches, although the majority of studies have focused on ditches in organic soils (Evans et al., 2016). Synthesised data suggests that ditch CH_4 emissions are larger than those from ponds and that, as for reservoirs and ponds, CH_4 is the largest contributor to climatic warming from these systems (Lovelock et al., 2019). Additionally, ditches can have impacts on fluvial OC dynamics; fluxes and concentrations of DOC and POC have, in some cases, been shown to increase following drainage of organic soils (Evans et al., 2016), and the effect of this increase has been observed downstream in large rivers (Asmala et al., 2019). In some heavily drained countries (e.g. The Netherlands, Finland, the UK) the total length of ditches can exceed that of natural watercourses (Brown et al., 2006; Verdonschot et al., 2011), suggesting that the contribution of ditches to C and GHG cycling could be extensive.

2.3 Factors controlling land-ocean carbon transport

2.3.1 Hydrology and residence time

Hydrology influences the source of aquatic OC, with higher discharge resulting in a greater portion of terrigenous material being transferred into the LOAC (Li et al., 2019). This is because periods of higher discharge typically co-occur with periods of increase surface runoff and/or increased leaching of organic-rich soil horizons and surface litter (Raymond et al., 2016; Raymond and Spencer, 2015). On the other hand, during periods of lower discharge the water flowing through the LOAC typically contains more geogenic (rock derived) IC, and experiences longer flow paths and/or longer residence times which increase the potential for active biogeochemical cycling of what OM is present via photochemical degradation or microbial processing.

Residence time (the length of time OC spends within a given environment or indeed within the LOAC), provides a powerful control on C processing. By definition, headwater streams have short residence times. Water moves quickly through them into larger streams and rivers. Hence, whilst they receive large volumes of organic material directly from the catchment, there may be limited potential for biogeochemical processing to occur. The increasing residence time of downstream aquatic systems, as streams drain into rivers, lacustrine and coastal environments, may mean that C cycling becomes a more important control on overall C budgets with distance downstream. Conversely, the extent to which the material has already been degraded in the upstream aquatic environment may mean that further processing is limited (Catalán et al., 2016). The construction of water bodies (i.e. reservoirs, ponds, ditches) increases the residence time of water in the LOAC, resulting in downstream C contribution that is older and, as a result of prior processing, more recalcitrant. This can have significant spatio-temporal implications for OC processing (Evans et al., 2017b; Müller et al., 2013).

Deeper groundwater flow paths exhibit residence times ranging from decades to millennia, whilst shallow flow paths exhibit relatively short residence times in the order of weeks to years typically, and operate at hillslope scales or smaller (Gooddy et al., 2006; Lapworth et al., 2018; Laudon and Sponseller, 2018). The groundwater C inflow, via base flow, to surface waters contributes a significant amount of C with long residence times. The composition of this C has been modified due to subsurface processes and has different reactivity compared to surface and in-situ derived C in surface water bodies (Lapworth et al., 2009; Tye and Lapworth, 2016).

2.3.2 Physical catchment characteristics

A number of physical attributes have been shown to strongly influence land-ocean C fluxes. Geology is an important consideration, with some rock forms being more prone to weathering than others, and more permeable and calcareous geology resulting in higher concentrations of DIC in surrounding waterbodies (Shin et al., 2011). This is particularly true in intermediate and deep GW flows where water flows through bedrock before resurfacing supersaturated with DIC dissolved into the water during transit.

Catchment scale has an effect on regional C budgets, with larger catchments producing larger contributions of dissolved and particulate matter (i.e. for GW contributions, see Laudon and Sponseller, 2018). Mean catchment slope has been identified as a potential driver of global land to ocean C fluxes (Ludwig and Probst, 1996; Raymond and Spencer, 2015). Slope is inversely related to DOC flux, as catchments with steeper morphologies are suggested to have a higher proportion of surface runoff where water contact time with soil horizons is restricted (Ludwig and Probst, 1996), as well as tending to have thinner and less organic-rich soils. Leaching of organic material from soils enriches runoff with DOC, therefore water leaving catchments with shallower slopes and a higher proportion of throughflow relative to surface runoff will to be more concentrated in DOC, all other factors being equal. Shallower slopes also allow for more extensive wetlands and riparian zones, which can influence OC export (Mulholland, 2003). Physical catchment characteristics are relatively stable (i.e. not subject to ongoing, large scale, rapid change)

2.3.3 Land use/land cover (LULC) and land use change

LULC is a primary driver of changing fluvial organic C exports to the coastal ocean (Bauer et al., 2013), influencing soil OC stocks (Li et al., 2019) and the age, composition and lability of exported DOC (Butman et al., 2015; Parr et al., 2015; Wilson and Xenopoulos, 2009). Natural forested watersheds typically export aromatic, structurally complex DOM that is biologically recalcitrant compared to DOM exported from anthropogenically modified agricultural watersheds that is characterised by reduced structural complexity and increased microbial contributions (Butman et al., 2015). However, this aromatic DOM also tends to be highly coloured, and susceptible to photodegradation, to the extent that overall rates of reactivity may be similar between these contrasting DOM pools (Anderson et al., 2019). Globally, deforestation and agricultural expansion are the major factors influencing LULC modification, but the trend across much of Europe is towards afforestation. A number of studies have linked the presence of forestry with higher DOC concentrations in freshwaters. Sobek et al. (2007) found that conifer boreal forest positively related to lake DOC concentration in a study of 7,500 global lakes. In a 75 year data set collected from a river in Sweden, long-term change in water colour was partly explained by an increased presence of Norway spruce (*Picea abies*) in the catchment (Škerlep et al., 2019). A study of fluvial DOC fluxes in North America found that export was higher in forests than in pasture or cropland, and that fluxes were greatest from coniferous forest relative to broadleaf (Lauerwald et al., 2012), whilst another found a significant positive correlation between CO_2 in boreal lakes and the percentage of needle-leaved evergreen trees (Hastie et al., 2018). Drainage of peatland also appears to contribute to the mobilisation of higher (and typically older) DOC fluxes from deeper horizons (Evans et al., 2014, 2016; Moore et al., 2013). In headwater streams in the blanket bog of the Flow Country, Northern Scotland, DOC concentrations were 30% higher in drained afforested catchments relative to both drained and undrained controls (Pickard et al., *in prep*.) Driving mechanisms behind this relationship remain unclear, although it is now largely established that planting coniferous forestry on organic-rich soils, particularly peatlands, can precipitate a destabilisation of the soil C store. Large-scale expansion of tree planting is not anticipated in areas with historically stable forest cover such as Fenno-Scandia, yet other countries in Europe are increasing tree planting in line with national scale C reduction and climate change mitigation strategies. To broaden our mechanistic understanding of forestry related DOC increases, more extensive monitoring is required. Conversely, we have no reason to expect mass-deforestation at a pan-European scale, however where it does occur it will likely lead to increased delivery of OC to the LOAC, increased stream metabolism, and higher rates of CO_2 evasion to the atmosphere, at least in the short-term due to soil disturbance.

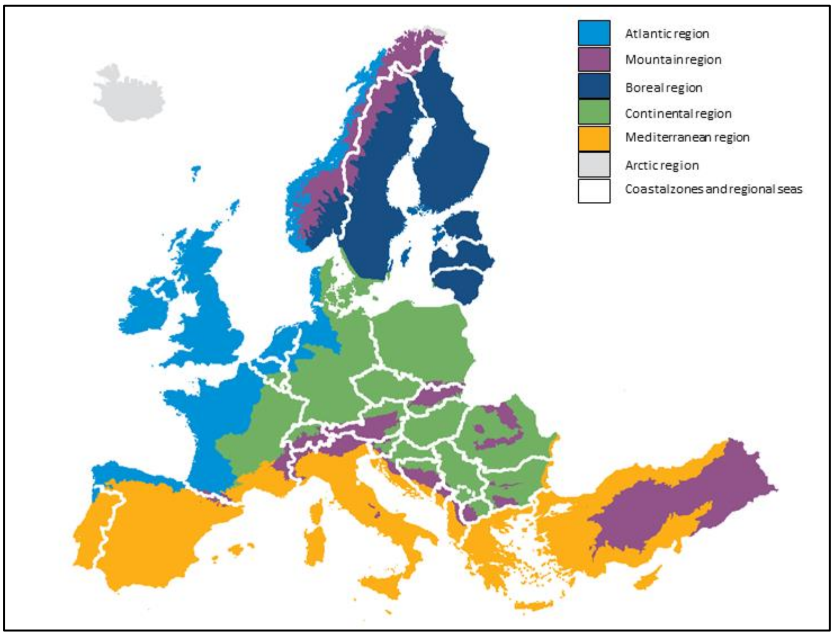

Figure 7: Map of Europe showing the seven climate regions used by the EEA (adapted from EEA Report No 01/2017 "Climate change, impacts, and vulnerability in Europe 2016").

Other human activities also have an effect. Dam construction has decreased sediment and OC delivery to the LOAC, whilst fertiliser use has increased nutrient fluxes, leading to an increase in autochthonous DOM production (Bianchi and Allison, 2009; Galloway et al., 2008). Long-term (1970 – 2015) study of the Seine River found that in-stream CO_2 was closely related to urban water pollution (Marescaux et al., 2018). The overall effect of these changes may be a moderate increase in CO_2 emissions across the LOAC, and a possible decrease in OC delivery to the coastal ocean, but much uncertainty surrounds this assessment. Land use change is an ongoing process, operating at global scale, according to human requirements (e.g. need for farmland) and values (e.g. desire for conservation), and acts with other drivers in combination, making predictions of future trajectories challenging.

*Table 4: Predicted near-future climate change-related shifts pertaining to the land-ocean C cycle, split by climatic region (data obtained from EEA report No 01/2017). *Also predicted for coastal zone: Increased sea surface temperature, acidity, dead zon*

	Mediterranean	Boreal	Continental	Atlantic	Arctic	Mountain	Coastal*
Temperature	Increase	Increase	Increase	Increase	Above av. increase	Above av. increase	Increase
Temperature extremes	Increase		Increase				
Precipitation	Increase	Increase	Decrease in summer	increase			
Flood		Increase	Increase	Increase			Increase + sea level rise
Drought	Increase		Increase				
Fires	Increase		Increase				
Water demand	Increase		Increase				
Ice / snow cover		Less ice/snow			Decrease in Permafrost	Decrease in glacial cover	Decrease in sea ice

2.3.4 Climate and climate change

The European Environment Agency (EEA) partitions Europe into seven climate regions: Mediterranean, Boreal, Continental, Atlantic, Arctic, and Mountain, plus the coastal zones and regional seas (figure 7). Current predictions of climate change-related shifts across each of these regions are shown in Table 4, and discussed below.

2.3.4.1 Temperature increase and extremes

Temperatures are expected to increase across all European regions, which have the potential to drive myriad effects in relation to the LOAC. This includes decreased GHG drawdown. For example, the world's ocean has absorbed 41% of all anthropogenic CO_2 emitted as a result of fossil fuel burning and cement manufacture (Khatiwala et al., 2009), but an increase in sea surface temperature and eventual saturation of CO_2 in surface waters may reduce the efficiency of the ocean carbon sink (McKinley et al., 2016). In the medium to long term, this uptake is limited by changes in the overturning circulation which entrains carbon into deep waters with residence times in the order of hundreds to thousands of years. In the short term (next century), models predict enhanced thermal stratification of the upper layers of the ocean, including continental shelf waters (Gröger et al., 2013; Holt et al., 2012). This would increase the residence time of terrestrial OC in the sunlit surface mixed layer and hence enhanced photolysis in coastal and shelf waters (see removal processes).

2.3.4.2 Precipitation

The duration, intensity, and frequency of rainfall influence the transfer of terrigenous C into the LOAC. Short periods of rainfall are usually absorbed by soils and vegetation, whilst long (or particularly intense) periods of rainfall can lead to saturated soils and increased runoff. When seasonality leads to dry and wet periods, soil surfaces can become baked hard and lose the capacity to absorb rains, thus the first rains of the season can also cause enhanced runoff. When runoff is high, a greater volume of terrigenous C is carried into the LOAC. In some cases, precipitation is the major explanatory variable for DOC export (e.g. Pumpanen et al., 2014).

Precipitation can also influence the supply of DIC into the LOAC. Acid rain enhances carbonate rock weathering, and as atmospheric C concentrations continue to increase, the transport of DIC into the LOAC is also increasing. Increased precipitation also increases GW flows, which can strengthen and dissipate in response to variations in precipitation patterns (Laudon and Sponseller, 2018). For example, elevated DIC concentrations are associated with base flow conditions when surficial water flow paths are inactive (Wallin et al., 2010), or in winter when precipitation is highest and flows are therefore maximal, driving DIC exchange between these deep flows and overlying streams/rivers (Lyon et al., 2010). In lake systems, upwelling of C rich deep water is precipitation-driven and coupled with associated seasonal increases in lateral OC inputs (i.e. Denfeld et al., 2015) and a resultant increase in remineralisation and surface CO_2 concentrations. In boreal systems, these seasonal emission peaks generally occur in spring and autumn when rains are maximal. However, Nydahl et al., (2017) found either a negative or no relationship between CO_2 and precipitation in boreal lakes over a 17 year period in Sweden, and suggest that this may be due to the dilution of CO_2 rich groundwater by increased surface water runoff. Environmental conditions underpin cause and effect.

Precipitation is expected to increase in the Mediterranean, Boreal, and Atlantic regions, where we might expect increased runoff, an increase in the contribution of terrigenous C to the land-ocean C cycle, and perhaps an increase in LOAC-atmosphere C flux. In the Continental region, a decrease in precipitation is predicted which might serve to elevate GW DIC concentrations, similarly enhancing fluvial CO_2 evolution. This may be partially offset by decreased lake upwelling in the region. A recent study by McDonough et al (2020) found that global changes groundwater DOC are in part driven by changes in climate, including temperature and precipitation, as well as urbanisation.

2.3.4.3 Flood, drought, fire, and water demand

Flooding can temporarily convert flood plains and surrounding land into what are essentially wetland systems, increasing wetted area and therefore contributing additional terrigenous OC to the LOAC during episodic events. Conversely, a lack of precipitation can lead to drought conditions which can lead to elevated OC concentrations and fluxes in subsequent years (i.e. Lepistö et al., 2014). Incidences of wildfire have been shown to influence aquatic C cycling, and are linked to a preceding lack of precipitation/drought spell. Due to the dynamic and unpredictable nature of wildfire, there are limited before-after data sets to assess the potential influence on aquatic C concentrations and export, and there remains a lack of consensus as to the directional effect of wildfire on DOC. However, in a study of a wild fire in N Ireland where before-after data were available, DOC concentrations were considerably lower after the fire due to increased acidity of the soil (Evans et al., 2017a). Increased prevalence of wildfire may facilitate further study of this soil acidity affect. A substantial proportion of the biomass-C is converted into pyrogenic-C (charcoal) during wildfires which is resistant to degradation over centuries-millennia (Kuhlbusch and Crutzen, 1995; Santín et al., 2015). Therefore, pyrogenic-C represents a substantial long-term sink for C in terrestrial ecosystems and the LOAC, accounting for 12 % of direct emission to the atmosphere globally (Jones et al., 2019). The impact of wildfire on LOAC C-transfer is unknown in the Mediterranean climate region where wildfires are more common and the LOAC is characterized by a predominance of ephemeral waterways.

2.3.4.4 Ice/snow cover

The formation of thermokarst lakes as a result of permafrost melt also release large amounts of CH_4 by bubbling (reviewed by Wik et al., 2016). There are strong indications that sediment production of CO_2 and CH_4, and the associated fluxes to the atmosphere, are positively and exponentially affected by increasing temperatures (Gudasz et al., 2010; Marotta et al., 2014; Natchimuthu et al., 2016; Wik et al., 2016; Yvon-Durocher et al., 2014), whilst precipitation-driven upwelling can bring deep water rich in both CH_4 and CO_2 and to the surface, producing periods of enhanced emissions (Karlsson et al., 2013).

2.4 Knowledge Gaps

There are geographical biases across a range of scales that present a considerable issue for the environmental sciences (e.g. Metcalfe et al., 2018). There is a literature focus on large rivers (Dai et al., 2012), despite the fact that smaller rivers and headwater streams draining mountainous catchments and organic-rich soils can be important conduits for fluvial C export (Milliman and Syvitski, 1992; Worrall et al., 2012), and may make a disproportionately large contribution to land-ocean C fluxes (Williamson et al., submitted). In addition, the majority of relevant research has been conducted in North America and Central / Northern Europe, areas which have historically been strongly influenced by industrialisation, land use change, and acid deposition. There is a notable absence of examples that have incorporated the quantification of groundwater C stores and fluxes in large-scale C flux estimates, or the impact of anthropogenic use and redistribution of groundwater at the surface, this is an important knowledge gap in current C flux estimates. Temporal bias also exists, with sampling occuring more frequently in fair-weather (i.e. spring/summer). This is particularly notable in high latitude systems where ice-cover makes aquatic systems inaccessible during the winter months, and where storms make seagoing more treacherous.

As well as large-scale geographical and temporal sampling issues, there are also problems relating to sampling frequency. Long-term, high-frequency measurements of C concentration and water discharge are now possible and provide valuable insights into fine-scale C dynamics (e.g. Kirchner, 2003; Kyung Yoon et al., 2016) but are typically outside the budget of, and/or precluded by the 3-5 year funding model typically used to support academic studies. This reduces capacity to adequately account for changes over time, especially during storm events when failing to account for changes to organic C dynamics can lead to both under- and over-estimation of annual exports (Clark et al., 2007; Dhillon and Inamdar, 2013, 2014). There are further issues arising from divergences in analytical methods, such as varying pore sizes being used for filtering water samples between different research disciplines (e.g. marine vs. fresh water), different modes of analytically quantifying C, and the use of indirect rather than direct measurement techniques (Abril et al., 2015; Karanfil et al., 2002; Sugimura and Suzuki, 1988; Vodacek et al., 1995).

Although these may seem like trivial concerns, they do have real-world implications. For example, the traditional use of 0.45 µm as a filter pore size for DOC analysis has resulted in a significant fraction of colloidal OC (COC) being classified as DOC (Yan et al., 2018). DOC has a key role in binding and transporting harmful trace metals (Dai et al., 1995), and the form of OC directly affects its reactivity (Attermeyer et al., 2018), thus accurate quantification of OC form is necessary for modelling C degradation and effects on aquatic ecosystem health. Finally, there are philosophical issues arising from the paradigms adopted by different research communities (Marín-Spiotta et al., 2014). The global export of terrestrial C into and through inland waters, and on into the ocean encompasses the disciplines of soil, freshwater and marine science. The paradigm in soil science is that environmental and biological controls mediate OC stability (Schmidt et al., 2011), whilst for aquatic systems molecular composition is considered key (Kellerman et al., 2015). Thus, separate communities have used different methods to investigate similar questions. Furthermore, the diversity of aquatic environmental typologies around Europe (and the world) has resulted in the development and implementation of a range of strategies for aquatic C flux monitoring. Understanding and integrating data generated via different methodologies in different components of this continuum represents a major challenge for generating land-ocean C flux budgets at every scale (i.e. local, regional, continental, and global).

2.5 Building modelling capacity

Data obtained from monitoring and process studies can be used in a variety of ways, including the production of conceptual budgets of carbon cycling across the LOAC and for exploring the skill of existing modelling capabilities. Perhaps more importantly, as our knowledge of fluxes and the underlying processes increases, so our capacity to develop mechanistic numerical models grows. In turn, this increases confidence in our ability to accurately predict future land-ocean-atmosphere C fluxes and how they will respond to LULC and climate change. The complexity of C cycling poses great difficulties in this regard (Le Quéré et al., 2014). As a consequence, C transfer across the LOAC, from soils through fluvial systems and into the open ocean, has not been explicitly represented using mechanistic parameterisations in global or pan-European scale C budgets, including those generated using Earth System Models (Ciais et al., 2013). Various research groups have developed a range of models that represent individual parts of the LOAC, representing C cycling in freshwater systems (e.g. Futter et al., 2007; Rowe et al., 2014; Tipping et al., 2016) and the ocean (e.g. Anderson and Williams, 1998; Keller and Hood, 2013; Polimene et al., 2006). There is, however, little consistency in approach between models of different disciplines in terms of chosen state variables, representation of processes of production and turnover, and nomenclature, meaning that the different models cannot be easily joined together to predict C fluxes across the entirety of the LOAC. We are only aware of a single, processed-based model that is capable of operating across the LOAC (UniDOM; Anderson et al., 2019).

2.5.1 Land - freshwater models

Land-surface models, using land cover as the predictor variable, are commonly used to estimate the leaching of DOC from soils into fluvial waters and the transport of that DOC downstream. The LPJ GUESS model is one example, but has so far only been applied to sub-arctic catchments in Northern Sweden (Tang et al., 2018). ORCHILEAK (Lauerwald et al., 2017), a new branch of the ORCHIDEE land surface model (Krinner et al., 2005), is another. It is somewhat more developed, and has recently been applied at pan-European scale to simulate the seasonal and interannual variation in fluvial DOC transport over the period 1978-2014 (Gommet et al., in prep) as part of the EU project Verify. Other successful applications of ORCHIDEE have been undertaken at regional scale for the Amazon basin (Hastie et al., 2019; Lauerwald et al., 2017), the Congo Basin (Hastie et al., 2020), and the Lena basin (Bowring et al., 2019, 2020).

Estimating fluvial fluxes of terrigenous POC, which is mobilized from terrestrial ecosystems through erosion of soil material and litter, and through litterfall onto the water surface, arguably poses an even greater challenge for the modelling community. Strong, non-linear relationships between erosion and water flow, and in particular the strong contributions of ephemeral extreme events (e.g. Hughes, 2005) are particularly difficult to capture with any degree of realism. Simulating the deposition of sediment and terrigenous POC in aquatic sediments and on floodplains, for example, would require the representation of even smaller dams and reservoirs as well as of the small-scale topography of river channels, banks, and flood plains. A relatively simple approach to include fluvial fluxes of POC together with those of DOC has been realised in the land surface model DLEM (Dynamic Land Ecosystem Model). Although DLEM can run at global (and therefore pan-European) scale, simulation of fluvial DOC and POC fluxes have so far only been published for the Eastern USA (Tian et al., 2015). For the representation of sediment and POC erosion into the river network, DLEM makes use of the relatively simple to parameterize, event-based erosion model MUSLE (Modified Universal Soil Loss Equation; Williams, 1975). A similar approach has recently been implemented into ORCHIDEE and has so far been evaluated for the Rhine basin (Zhang et al., *in revision*).

Besides the ongoing developments in the land surface model community, a few more specialised river transport and biogeochemistry models deserve mention. Those that focus on processes within the river network, and require mobilization fluxes of C and nutrients from land to the river network as pre-processed model inputs, include the RIVERSTRAHLER model (Billen et al., 1994). RIVERSTRAHLER simulates all major biogeochemical processes in a river network involving DOC, POC, and nutrients (i.e. N, P, and Si), relating not only to soil erosion and leaching but to sewage injections and in-stream algal biomass production. Recently, representation of DIC fluxes related to chemical rock weathering and respiration, both within soils and the river) was added to the model (Marescaux et al., 2019). However, because of the great efforts required to parameterize this model, its application has been largely limited to the Seine River. Nonetheless, a recent study that utilised RIVERSTRAHLER to simulate eutrophication of the NE Atlantic (Desmit et al., 2018) demonstrates its utility at a more extensive, regional scale.

Other models of interest are CARBON-DISC (van Hoek et al., 2019), MADOC (Rowe et al., 2014), and INCA-C (Futter et al., 2007). CARBON-DISC is designed as a global scale model that represents fluvial transport of DOC, POC, and DIC at 0.5-degree resolution, including processes such as decomposition of DOC and POC, instream production of POC, and CO_2 exchange between the river and the atmosphere. Until now, the model has only been evaluated for the Rhine basin, showing that more model development and calibration will be needed before the model can be applied at regional scales. MADOC was developed to investigate the drivers of long-term DOC variation across freshwater systems. It investigates the turnover of SOM in relation to DIC dynamics (i.e. pH and alkalinity effects), and was parameterised using targeted field studies. INCA-C was the first model of DOC cycling to explicitly include the effects of different LULC types, hydrological flow paths, in-soil biogeochemistry, and surface water processes on in-stream DOC concentrations, and is specifically useful in temperate and boreal forested and peat-dominated catchments.

Lake models of note include that of Tipping et al., (2016) which includes biogeochemical and sedimentation behaviour of C and other macronutrients in a large lake setting, and of Stepanenko et al., (2016) which couples physical processes and biogeochemistry to solve water column pCO_2 and pCH_4 and related vertical fluxes to the atmosphere.

2.5.2 Ocean models

The global nature of the oceans lends itself to the global coupled ocean-atmosphere General Circulation Models (GCMs). However, the extreme heterogeneity in terrestrial catchment characteristics observed across Europe suggests such smaller scale models might be most appropriate when modelling the influence of their outflows on the marine system. As yet, there has been little explicit modelling of the fluxes and fate of terrigenous DOM in ocean systems, with the exception of the UniDOM model (section 2.5.3). Rather, ocean models have focused on autochthonous (in situ) production of DOC and how this contributes to the cycling and storage of C in the ocean (e.g. Druon et al., 2010; Schlitzer, 2002; Yamanaka and Tajika, 1997) and paid less attention to terrigenous DOM (although see Anderson et al., 2019). DOC is a heterogeneous mix of substrates that have different labilities (timescales of turnover) that are discretised in models, e.g., a typical classification in ocean models is to divide DOC into labile, semi-labile and refractory pools (Carlson and Ducklow, 1995; Cherrier et al., 1996). Existing oceanic C models generally utilise production and consumption terms which are derived from an enormous range of formulations and parameterisations and where, in many if not all cases, we lack sufficient biological (i.e taxa) and chemical (i.e. concentrations and fluxes) data to adequately test them. To some degree, differences in parameterisation can be attributed to variations in objectives and focus (Anderson et al., 2015).

GCMs are well suited to making large-scale predictions, but operate at a scale that often renders high levels of complexity impractical. Smaller, more regional models tend to be better suited to simulating multiple source terms, mixed organic matter labilities, and high levels of environmental heterogeneity (Anderson et al., 2015), but their utility is limited by their scale and they can prove difficult to parameterise without system-specific data. A noteable exception to this is the European Regional Seas Ecosystem Model (ERSEM; Butenschön et al., 2016), which is currently running in several global GCMs at broad scale, representing a range of complex biogeochemical and ecological processes (Figure 8).

It should be noted that, whilst a single model linking all environments transitional and oceanic environments may be desirable, specific questions define the compromise required between the need for complexity and the need for computational efficiency. For example, computationally-efficient, intermediate complexity models are required for global climate projections (e.g. 1 degree resolution NEMO-MEDUSA; Yool et al., 2013) while more complex models of higher resolution may be used to resolve shelf-sea processes (e.g. 7km NEMO-ERSEM, (Butenschön et al., 2016), and even higher resolution complex models may be used to resolve estuarine processes (e.g. <20m resolution FVCOM-ERSEM; Ge et al., 2020). The same logic is true of freshwater models, and indeed of models linking the full LOAC. The perceived simplicity of a singular model may well be overtaken by bespoke, question- and system-specific requirements

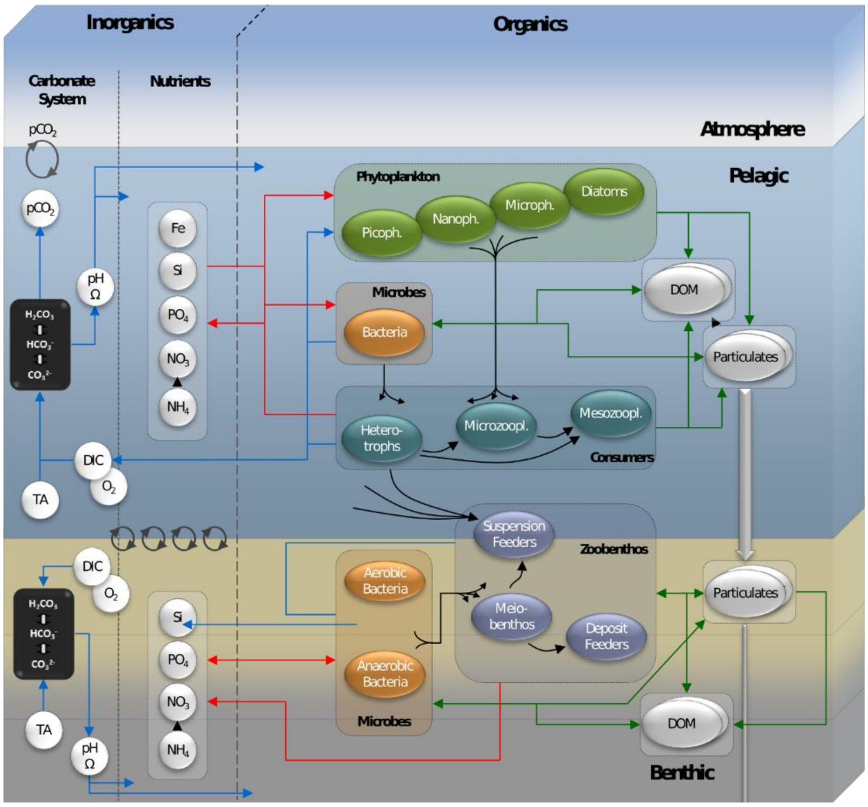

Figure 8: A schematic of the ERSEM model, taken from Butenschön et al., 2016.

Modelling of ocean DIC is relatively well constrained in ERSEM and other models (e.g. MEDUSA 2.0; Yool et al., 2013), largely due to the existence of databases such as SOCAT, the World Ocean Database, and the Global Ocean Data Analysis Project (GLODAP) which provide the large-scale, internally consistent datasets required to adequately test model parameterisation. Adequate expertise in land-ocean IC modelling did not exist within the working group, and such expertise should be sought out as part of any future preparatory phase to determine the relative importance of including this term in future efforts.

Until recently, the integration of terrigenous C fluxes into such models had received relatively little attention as a research field. The contribution of terrigenous OC to the oceanic DOM/DOC pool is generally thought to be small, with most undergoing mineralization or burial in ocean margins (e.g. Bianchi, 2011; Fichot and Benner, 2014; Hedges et al., 1997; Opsahl and Benner, 1997) and the perceived benefits of modelling it have, in the past, outweighed by the inherent complexity of the task. However, a growing body of evidence now exists that demonstrates the potential significance of terrigenous C in ocean C cycling (e.g. Medeiros et al., 2016; Regnier et al., 2013), and recent modelling efforts have led to significant advances in our ability to standardise state variables across fresh and marine environments such that the influence of terrigenous OC on the marine C cycle can be approximated (Anderson et al., 2019).

2.5.3 Linking land and ocean – UniDOM

The recently published UniDOM (Unified model of DOM) model (Anderson et al., 2019; Figure 1) is the first of its kind to represent DOC transfer across the different environments of the LOAC using a single, unified set of equations and parameters. Results of the model, which was parameterised for the waters of Great Britain, indicate that ~5% of the DOC originating in streams may make its way into the open ocean. This estimate was, however, "preliminary" given that there are many uncertainties associated with the model parameterisation, given the limited information available for this purpose (Anderson et al., 2019).

In UniDOM (figure 9), terrigenous DOC is divided into two pools, T_1 (strongly-UV absorbing, prone to photooxidation but microbially resistant) and T_2 (non- or weakly-UV absorbing, not photo-oxidised and relatively prone to biological turnover). In general terms, T_1 represents structural compounds such as lignin that are prone to photooxidation and are susceptible to microbial decomposition. Importantly, T_1 and T_2 are amenable to routine measurement using specific UV absorbance (SUVA), providing the means to integrate field programmes and modelling. The model provided an analysis of the relative roles of flocculation, photooxidation and microbial turnover in the turnover of terrigenous organic matter. Perhaps surprisingly, predicted flocculation was low, although the associated literature is equivocal on this matter and the model parameterisation quantitatively uncertain. Photooxidation and microbial both accounted for significant turnover. A key feature of the model is a novel parameterisation whereby these rates decrease with increasing DOC age, representing increasing recalcitrance as labile substrates are stripped out. The flocculation, whereas T_2 compounds are less prone to photooxidation and are susceptible to microbial decomposition. development of UniDOM highlights the perennial challenge of understanding and modelling the dynamics of DOM, namely that of dealing with a heterogeneous mix of substrates where lability depends on a multitude of factors including biochemical structure, the microbial community, concentration and the presence/absence of competing substrates (Anderson et al., 2015).

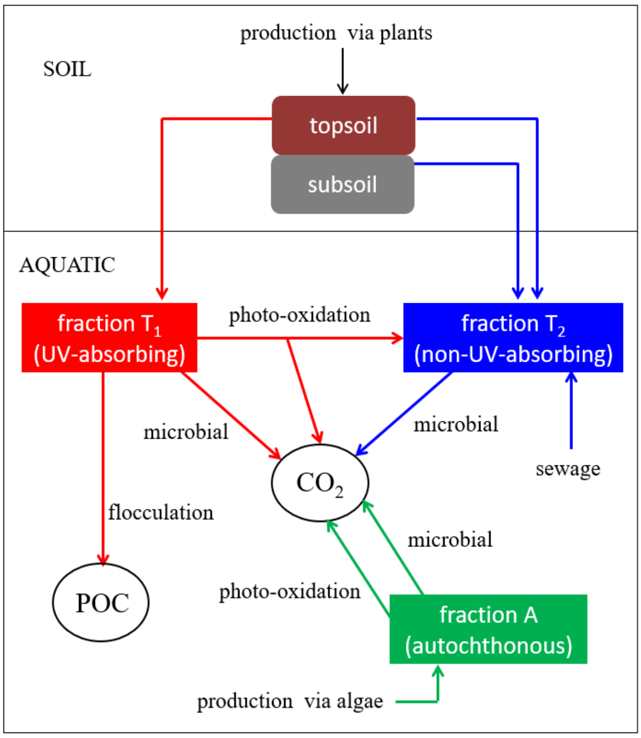

Figure 9: Flow diagram of the UniDOM model, with two terrigenous state variables (T1, T2) and one autochthonous (A), and turnover via microbes, photo-oxidation and flocculation (Anderson et al., 2019).

The greatest challenge to modelling fluxes of terrigenous DOC across the LOAC is to derive a common set of state variables and parameterisations that span the different environments, and which are also amenable to routine measurement so as to link with field research. The UniDOM model has made a significant step forward in this regard, based on the T_1 and T_2 state variables that can be readily approximated via absorbance spectrophotometry. Much work still needs to be done, however, to validate this model against data, provide better constrained values for the parameters associated with flocculation, photooxidation and microbial degradation, all of which potentially influence DOC turnover, and to incorporate and test UniDOM in 3-D modelling frameworks. Of course, it may be that other models are also developed with alternate representations of terrigenous DOC, but the task of bringing together the different disciplines is large, requiring close collaboration between modellers and field scientists. Any decision on the definition of model state variables and parameterisations should be amenable to both the soil modelling community and measurement in the field.

Applying UniDOM more widely, e.g., at pan-European and global scales, will require input terms from the various systems feeding into the fluvial-estuary-ocean pathway. There are many complicating factors, including groundwater flows, constructed waterbodies, wetlands, etc. There is likewise a need for validation data to fully test models and we again emphasise the need for collaboration between modellers and field scientists. The development of appropriate soil models is another key aspect of future development, generating DOC fluxes that enter the aquatic systems that are consistent with the aquatic systems. Modellers also face the major challenge of simulating the full 3-D environment all the way from freshwaters to the ocean. The UniDOM model was tested in a simple linear physical framework (effectively, a pipe) where there was no lateral mixing. Moving to 3-D is complicated for this model because of the age-dependent parameterisation for turnover of terrigenous DOC by photooxidation and microbial degradation. It may be that a compromise parameterisation should be developed where this age-dependent parameterisation is approximated by different state variables of fixed lability, such as the labile, semi-labile and refractory pools described earlier.

In summary, the UniDOM model has made a significant stride forward in developing a model that spans the different environments of the LOAC, but much work needs to be done to refine the parameterisations of this model, to extend its geographical range and to provide validation data. Of course, it may be that other such models are developed and diversity in approach is always to be welcomed. It is important to bear in mind the need for synergy not just in model parameterisation across the different environments of the LOAC, but also between models and data. Development of cross-system models thus constitutes a major exercise necessitating, from the outset, close collaboration between terrestrial, freshwater and marine scientists, including both those working in the field and modellers.

3. Monitoring requirements and recommendations

3.1 The current status of pan-European land-ocean carbon flux monitoring

There are no recent estimates of European scale land-ocean C fluxes available. In order to determine the status of land-ocean C flux measurements within Europe, three data sources were identified and investigated: (1) monitoring data stored by national agencies; (2) data held in European repositories; (3) data contained within recently published literature.

How data are held by national agencies varies according to the purpose and location of the monitoring activity. Data gathered in response to EU legislation (i.e. obligated under the Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD)) are reported to, and held by, the European Environment Agency (EEA). Whilst C parameters are not listed as priority substances and thus not measured in their own right, they are routinely measured when required as context for a substance which is (i.e. DOC is measured alongside Cu). The EEA does therefore hold a significant amount of potentially useful data for countries which have historically been part of their monitoring frameworks (such as the WFD and MSFD), although this is less true for those who have recently joined. Monitoring conducted under the remit of the country itself, whether in response to government objectives or as part of national statutory monitoring of, for example, industrial plants, is held by national monitoring agencies (e.g., in England, this would be the Environment Agency). In both cases, very few C parameters are measured across a large area. Various repositories exist at European scale which store relevant data, for example the European Marine Observation and

Data Network (EMODnet), the Water Information System for Europe (WISE). These data sources are relevant as the data held within them are freely accessible, and go beyond the scope of national agencies into more targeted research.

Beyond these two sources, academic literature holds countless examples of in-depth studies where a large range of C parameters are measured, albeit usually across a much smaller area (e.g. Evans et al., 2018; Lapworth et al., 2013; Peacock et al., 2017, 2019; although see Williamson et al., submitted). A number of more recent, smaller-scale estimates do exist, each falling broadly into one of three categories: studies of small (<1 - 50km^2) discrete catchments; studies targeted at representative sections of a single river system; and total output studies which focus on the lower reaches of larger basins (Hope et al., 1994; Worrall et al., 2018). The former are frequently used to investigate the effects of different types of land-use or disturbance on C fluxes, either through comparison or with paired catchments, whilst the latter tend more towards building a broader understanding of river-ocean C export.

Both data sources carry pros and cons. Monitoring data are usually historic, spanning at least a number of years, whereas academic studies may be singular events, covering anything from days to years but tending towards shorter periods. The transfer of monitoring data from measurement to availability is in the order of 2 - 5 years, whilst publishing an academic study takes upwards of a year, often significantly longer, and with no guarantee that the data from a given study will ever become publicly available. Monitoring data can generally be accessed by submitting a well-considered formal request to the agency in question, but requires some prior knowledge of which data may exist. Accessing academic data requires painstaking literature searches across numerous disciplines and environments, with a need to regularly revise those searches in pursuit of new studies, whilst new monitoring data are predictable in both their frequency and source. Monitoring methodologies are usually consistent across countries, whereas academic methodologies are often less comparable due methodological diffrences between studies (e.g. which method of DOC quantification is used), differences between disciplines (e.g. filter pore size), and varying demands of different environmental systems (e.g. freshwater vs. marine). Monitoring work typically operates to capture either point-breaches of environmental limits or general trends across large areas. By contrast, academic-focused studies tend towards smaller scale, targeted studies that often examine processes rather than simply gathering data and examining trends.

We suggest that monitoring and academic research are, individually, insufficient to allow the construction of an accurate accounting of current pan-European land-ocean C fluxes. Rather, a combination of the two would allow the synthesis of baseline fluxes against which future measurements could be compared. Gathering and synthesising data from these sources would, however, require a signficiant investment of time and researcher effort.

3.2 Proposal from the RINGO Task 1.4 working group

We propose a bespoke monitoring network, designed to deliver appropriate data to (1) enable the synthesis of a pan-European land-ocean C flux budget; and (2) improve our knowledge on the cycling and fate of C from source to sea. Such a network would allow the creation of a carefully planned and comprehensive sampling program, addressing temporal and spatial variations in aquatic C dynamics across the LOAC. Consistent analytical and sampling methods could be deployed to allow total comparability across measurements. Data would be fully archived, and made available to research and stakeholder communities.

The scientific benefits of highly standardised methods, adopted across a global range, have previously been demonstrated in aquatic ecosystems (Tiegs et al., 2019). Similarly, global networks that measure C already exist in the environmental sciences. For example, FLUXNET is a global network that uses eddy covariance towers to measure ecosystem-atmosphere exchanges of CO_2, water vapour and energy. Baldocchi et al., (2001), in introducing FLUXNET, state “large-scale, multi-investigator projects have been the keystone of many scientific and technological advances in the twentieth century.” We agree with their assessment, and believe that a similar, aquatic systems-focussed network, would bring numerous scientific rewards and advancements in our understanding of C cycling from soils, through inland waters, and into the marine system. We also recognise that the suggestions provided here represent a starting point for broader discussions amongst the wider community of researchers studying C fluxes across the LOAC within Europe and beyond. The costs associated with comissioning such a network would necessitate a feasibility study.

3.2.1 Defining the geographical scope

Land ocean C fluxes do not obey political boundaries, but we nevertheless recognise that monitoring these across Europe will necessarily involve a political dimension. Therefore, we must first define the scope of any proposed monitoring structure. We consider those countries which are ICOS member states and/or subject to the European Environment Agency (EEA) as having relevance (Table 5), and henceforth ‘Europe’ will be used to refer to these countries. It is important to note that the bordering countries, in particular Russia, play a significant role in riverine discharge throughout Northern Europe, and that the inclusion of those rivers upstream of where they cross into EEA territory would be optimal.

Table 5: EU countries and associated information, ranked by the percentage of EU rivers contained within each each. Number of rivers and percentage values taken from EEA Surface Water Body database on 30/10/2018.

Country	ICOS Member	EEA Member	# Rivers	% of EU Rivers
Sweden	Yes	Yes	15092	16.9
France	Yes	Yes	10706	12.0
Germany	Yes	Yes	8998	10.1
Austria	No	Yes	8065	9.0
Denmark	Yes	Yes	7776	8.7
Italy	Yes	Yes	7493	8.4
UK	Yes	No	7506	8.4
Poland	No	Yes	4596	5.1
Spain	No	Yes	4390	4.9
Romania	No	Yes	2891	3.2
Finland	Yes	Yes	1913	2.1
Portugal	No	Yes	1899	2.1
Croatia	No	Yes	1484	1.7
Slovak Republic	No	Yes	1510	1.7
Czech Republic	Yes	Yes	1044	1.2
Hungary	No	Yes	963	1.1
Bulgaria	No	Yes	873	1.0

Estonia	No	Yes	645	0.7
Belgium	Yes	Yes	527	0.6
The Netherlands	Yes	Yes	246	0.3
Cyprus	No	Yes	174	0.2
Latvia	No	Yes	203	0.2
Slovenia	No	Yes	137	0.2
Luxembourg	No	Yes	110	0.1
Greece	No	Yes	No data	<0.1
Ireland	No	Yes	No data	<0.1
Lithuania	No	Yes	No data	<0.1
Norway	No	Yes	No data	N/A
Iceland	No	Yes	No data	N/A
Switzerland	Observer	No	No data	N/A

3.2.2 Site selection criteria

Adequate site selection is central to the success of any monitoring network, and thus it is important to identify the major drivers of land-ocean C fluxes, and to design sampling schemes around them which also have the required spatial and temporal resolution with which to capture their influence. We recommend monitoring design and site selection be undertaken on a nation-by-nation basis, utilising local knowledge of geography, infrastructure, and existing sampling programmes to maximise coverage given available resources. The controlling factors outlined above should be referenced to ensure adequate sampling of key drivers and environments.

Land cover mapping utilising the various satellite products available at pan-European scale (i.e. COPERNICUS; SENTINEL) will undoubtedly play an important role in any future monitoring network, both in terms of ensuring adequate spatial cover of key environments and when scaling up estimates. For example, LULC specific estimates of OC transfer from land to the LOAC exist at sub-European scale, and such estimates could be scaled up at a broad scale to reduce the requirement for catchment-scale quantification. However, the influence of LULC operates at sub-catchment scales and thus should be monitored as broadly as possible.

3.2.3 Required parameters

There are three primary fluxes of C that should desirably be measured by a pan-European land-ocean flux network. These are listed below in order of importance, where ‘aquatic’ covers the full spectrum of salinities observed across the LOAC.

3.2.3.1 Term 1: Lateral C fluxes (land – aquatic)

A large number of parameters are inconsistently measured in studies that quantify the land-aquatic flux. Those considered essential and desirable are listed in Table 6. Concentration measurements of the various C pools (DOC, POC, DIC, and PIC) and gaseous forms (CO_2 and CH_4) are considered essential, along with core meta-parameters (water temperature, conductivity, and pH). Discharge measurements which are required to calculate flux values (i.e. concentration per unit volume per unit time) are also essential. Discharge measurements are made by water boards and national agencies at a large number of sites, and are generally readily available for download (e.g. the UK’s National River Flow Archive (NRFA) available at https://nrfa.ceh.ac.uk/). In many cases, this will be sufficient.

Table 6: List of essential and useful parameters with relevance to quantifying horizontal land-ocean C fluxes

Essential	Desirable
DOC	Nutrients (NO_3, NO_2, NH_4, SRP, $Si(OH)_4$,TN, TP)
POC	Selected major ions / cations (i.e. sulphate and iron)
DIC	Biochemical Oxygen Demand (BOD)
PIC	Chromophoric Dissolved Organic Matter (CDOM)
CO_2 (pCO_2)	Fluorescent Dissolved Organic Matter (FDOM)
CH_4 (pCH_4)	Alkalinity
Water temperature	Dissolved Oxygen (DO)
Conductivity	Turbidity
pH	Turbulence
Water discharge	Depth

3.2.3.2 Term 2: Vertical C fluxes (aquatic – atmosphere)

Quantification of the aquatic – atmosphere flux should consider gaseous CO_2 and CH_4. Within ICOS, Eddy Covariance (EC) flux towers are considered the primary method to solve for the exchange of these gasses at the water-air interface. A dedicated ICOS Working Group is currently writing a standardised protocol for making these measurements in waterbodies (see http://www.icos-etc.eu/icos/working-groups/work-group?wgroup=18 for updates), which is based upon flux tower set-up and maintenance aspects for terrestrial ecosystems which have already been described in the existing ICOS flux measurement protocols (Rebmann et al, 2018; Sabbatini et al, 2018; Nemitz et al, 2018). However, the local heterogeneity and small spatial scales associated with some aquatic environments and sub-environments within the LOAC (e.g. low order streams, small water bodies, and near-shore parts of lakes) represent challenges for EC measurements which should be considered, and sites must be carefully selected for suitability with testing undertaken to verify that EC fluxes are representative of total aquatic fluxes at selected sites. This process will create a bias in terms of what types of aquatic environments can be reliably studied using this methodology, and so alternative methodologies such as flux chambers and mass balance approaches may be more appropriate in some cases. Such flexibility would minimise the systemic bias associated with EC, with methodology selected based on the characteristics of the measurement site. However, each methodological approach operates on a different spatiotemporal scale, and so it is important to verify method comparability using long-term and spatially distributed averages, more of which are required. Where EC towers are considered the most appropriate methodology, particular attention should be given to establishing stations over meaningful eco-physical sections the LOAC. Defining what constitutes a 'meaningful eco-physical section' is beyond the scope of this report.

3.2.3.3 Term 3: Vertical C fluxes (aquatic – sediment)

The quantification of aquatic – sediment fluxes should be conducted in major transport channels and in a sub-sample of smaller streams to allow for process modelling and ground-truthing. The freshwater/seawater interface represents a hotspot for flocculation and adsorption of DOC onto mineral surfaces due to changes in ionic strength and local particle resuspension(Morris et al., 1978; Nedwell et al., 1999; Zhou et al., 1994). Sorption and desorption reactions lead to partitioning of the fluvial input (Kaiser and Guggenberger, 2000). In this context, "turbidity" should be an essential variable (Table 6). Measurement of term 3 will require observations in the low salinity region of the estuary.

As this is not a fixed geographic position, but dependent on tidal state (spring vs. neap tides), observations of the core parameters are best made from a boat or autonomous vessel (section 3.2.4.1). Financial and logistical considerations may limit this activity to a small number of representative supersites (section 3.2.4.2)

If the priority is to quantify the flux of terrigenous C that reaches the ocean, the minimum requirement would be to ensure term 1 measurements were made at a sufficiently representative selection of freshwater limits. Such measurements would provide a measure of what enters the estuarine /marine environment, and could represent a boundary for interpreting the upstream conditions. However, the variable transfer efficiency of estuaries described in Durr et al., (2012) means that effort would be required in terms of process studies to more completely understand the processes at play in the estuaries and transitional waters associated with those river mouth sites in order to fully appreciate the flux to the ocean. If the priority is to quantify the vertical flux of C to the atmosphere, stimulated by that lateral flux, a more complex monitoring network is required.

A combination of all three-measurement terms would allow for a complete characterisation of the net C transport by water bodies in absolute terms. However, due to the expense and time involvement, not all three fluxes can practically be measured at the frequency and spatial resolutions necessary to prove useful at continent-scale. We therefore propose a monitoring network which operates at varying scales. Quantification of term 1 should be undertaken at maximum spatial and temporal resolution, taking into consideration the range of factors influencing lateral land-ocean C transport to ensure adequately representative coverage is achieved. Quantification of terms (2) and (3) should occur at where possible, with all three coming together at selected 'supersite' locations where the complete picture of C transport and accumulation can be constructed using site-specific measurements. These site-level values can then be scaled up across the continent via remote sensing and modelling. Each of the three fluxes above require different methodological approaches and measurement protocols.

3.2.4 Proposed monitoring activities

Given the differing scales required to monitor the three flux terms outlined above, we propose a three-tier approach whereby national agencies incorporate regular, wide-spread monitoring of term 1 (land-aquatic), and a combination of ICOS and research centres / academic intitutions undertake site-specific monitoring of terms 2 (aquatic-atmosphere) and 3 (aquatic-sediment) at designated 'super sites', and at other suitable locations.

3.2.4.1 Broad-scale lateral flux montoring

It is our determination that the most appropriate route for delivery of lateral C flux monitoring is through national environmental agencies, with monitoring programmes enforced and outputs collated by the EEA and associated legislation following the templates set out by the WFD and/or MSFD (i.e. pre-determined parameters, with fixed and universal levels by which water body health is determined, and mandatory reporting at regular intervals to a centralised body). The EEA currently mandates the measurement of a limited number of parameters relevant to land-ocean C fluxes. It is more cost effective to incorporate additional parameters into existing monitoring frameworks than to instigate new ones. The existing EEA framework is proven, reliable, and has a relatively secure funding path, although some additional resources will be required. Member states have already 'bought in' to and are practiced at reporting along WFD and MSFD lines, and the addition of specific parameters should therefore be accepted and integrated relatively easily.

One option for data handling would be to extract the relevant data streams from the EEA or national agencies, and to display these via the ICOS C portal (CP) or other recognised data storage repository. Whilst engagement with the EEA offers economy of scale by utilising existing structures and logistics, such a data reporting structure would lengthen the timescale for data delivery (order of months). Alternatively, direct reporting would shorten the data delivery timescale, but would duplicate some reporting commitments from national monitoring agencies. Either approach would require some financial support. We recommend data extraction as the most cost-effective option.

An inherent weakness in the exploiting the existing EEA monitoring framework for land ocean C flux monitoring is that it rarely goes into headwater regions. Another is the lack of connectedness between the freshwater, transitional, and coastal sections of most national agency programmes. In addition, much of the monitoring activity undertaken by national agencies is point-source pollution monitoring of outflows. Such locations are not useful in the context of land-ocean C-fluxes, and so the number of potential locations where useful data could be collected is much lower than the total number of locations currently monitored. However, if additional sites could be added upstream of point-sources, these trips could be optimised to suit both purposes.

3.2.4.2 Integrating lateral and vertical fluxes

We believe that site-specific, integrated monitoring of all 3 flux terms at key locations would be required to (a) incorporate vertical (aquatic-sediment and aquatic-atmosphere) fluxes; and (b) ground-truth modelling based on the more extensive lateral flux monitoring data.

The ideal land-ocean 'supersites' would be located at the closure of a river drainage basin, in proximity of the ocean. This would limit confounding factors and simplify the study of land-ocean C fluxes from catchment to coast. Many ICOS sites are located in lakes, wetlands, coastal, and open waters, but the majority do not meet all off these criteria. However, a few examples of ICOS marine sites have the potential to investigate land-ocean C-fluxes. For example, the Belgian marine component consists of two research vessels operating in coastal waters out of the port of Ostend in the River Scheldt estuary as well as a fixed buoy in the English Channel. Similarly, the UK's "Western Channel Observatory" incorporates a fixed buoy and a research vessel operating out of Plymouth at the mouth of the River Tamar. Estuarine sampling transects would require additional resources, but much of the infrastructure is already in place. Effective monitoring of net C transport along the full land-ocean continuum would therefore require additional investment in infrastructure, or creative collaboration with other Research Infrastructures and/or institutes.

Whilst not exhaustive, Table 8 lists sites belonging to established (ICOS and eLTER) and preparatory (Danubius) European research infrastructure that might be utilised in this way. It is of note that several sites not associated with these infrastructures do exist, for instance those associated with the Swedish Infrastructure for Ecosystem Science (SITES) water network (https://www.fieldsites.se/). New sites are also coming on line currently, for example an EC flux tower directly over the harbour of Ostend, set up to meet ICOS specifications (Flanders Marine Institute/VLIZ).

3.2.4.3 Research centre monitoring

Where expedient, additional resources should be utilised to obtain a more complete coverage of the LOAC. For example, monitoring the flux of terrigenous C at the tidal extent can be embedded within existing sampling activities undertaken by national agencies, but the most cost-effective means of sampling water across estuarine gradients would likely be best achieved by exploiting existing sea-going sampling operations run by Research Centres (which encompasses government and academic institutions) that run offshore monitoring stations (e.g. L4) which require regular maintenance. This would only be achievable in a sub-set of locations.

Table 7: Potential sites of interest for land-ocean-atmosphere C flux measurements, integrating the ICOS network and other existing national and research infrastructures.RI = Research Infrastructure; ZA = Zone Atelier; LTSER = Long Term Socioecological Research; eLTER = European Long Term Ecological Research.

Site	Location	Country	RI	Notes
ZA Seine	River	France	eLTER	LTSER
ZA Bassin du Rhone	River	France	eLTER	
ZA Brest-Iroise	Interface Land/Sea	France	eLTER	
Delta Po Lagoons	Lagoon	Italy	eLTER	
Venice Lagoon	Lagoon	Italy	eLTER	
Northern Adriatic Sea - Italy	Coastal	Italy	eLTER	
Po Delta– Venice Lagoon	Delta/lagoon	Italy	Danubius	Supersite
PALOMA	Coastal	Italy	ICOS	Ocean
Miramare	Coastal	Italy	ICOS	Ocean
Minho Estuary	Estuary	Portugal	eLTER	
Mira Estuary	Estuary	Portugal	eLTER	
Mondego Estuary	Estuary	Portugal	eLTER	
Danube Delta Biosphere Reserve	Delta	Romania	eLTER	
Danube Delta	Delta	Romania	Danubius	Supersite
Delta del Ebro	Delta	Spain	eLTER	
Ebro-Llobregat Deltaic System	Delta	Spain	Danubius	Supersite
Doñana LTSER	Lagoon	Spain	eLTER	LTSER
L4	Coastal	UK	n/a (PML)	Ocean
River Stinchar	River	UK	eLTER	
River Frome	River	UK	eLTER	
River Esk	River	UK	eLTER	
River Coquet	River	UK	eLTER	
River Spey	River	UK	eLTER	
River Ewe	River	UK	eLTER	
River Cree	River	UK	eLTER	
River Bush	River	UK	eLTER	
Western Channel Observatory	Coastal	UK	ICOS	Ocean
Thames Estuary	Estuary	UK	Danubius	Supersite
Baltic Sea Centre	Coastal	Sweden	eLTER	
Ore estuary	Estuary	Sweden	eLTER	
Östergarnsholm	Coastal	Sweden	ICOS	Eco/Ocean
Thornton Buoy	Coastal	Belgium	ICOS	Ocean
Uto	Coastal	Finland	ICOS	Atm(Ocean)
Bothnian Bay	Coastal	Finland	eLTER	LTSER
Western Gulf of Finland	Coastal	Finland	eLTER	LTESR
River Salaca - Latvia	River	Latvia	eLTER	
Elbe Estuary	Estuary	Germany	Danubius	Supersite
Nestos	Delta	Greece	Danubius	Supersite

3.2.4.4 Approximate costing of monitoring activities

The cost of monitoring activities cannot be fully ascertained without more specific information re: the exact number of sites, their locations, frequency of measurement, and the parameters to be measured, and we reccomend costing be performed as part of a feasibility study which should preceed a preparatory phase. However, a rough costing is provided based upon the LOCATE (www.locate.ac.uk) 1-year GB-scale monitoring programme administered by NERC (2017-18). This programme covered ~35% of the GB landmass by catchment area, undertaking discrete, manual sampling of 40 rivers and 12 estuaries on a monthly basis. Fieldwork days cost between £120 and £890 per day (land based vs. boat-based), with each trip requiring a minimum of 2 field personell and 2 days of laboratory work, equating to 4 FT days. Multiple sites can be visited per day, but this is dependent on distance from home institute – in the case of LOCATE, 2-3 rivers were sampled per team, per day. Overnight stays were avoided by utilising a research centre network, but would of course attract further costs. Overhead costs (which vary by institute) and analyitical costs (which vary by sample number, parameter and laboratory) are not approximated here, but should be asscertained by a feasibility study once number of sites, specific parameters, and mode of sampling / measurement have been determined. Further detail of this study can be found in Williamson et al., (submitted).

3.2.6 Proposed process understanding activities

Coordinated academic study represents a significant opportunity to improve understanding of land-ocean C fluxes, and so we recommend that ICOS facilitate research on the processes which influence the fate of C across the LOAC and the environmental controls therein. We recommend the publication of priority research questions and environments, produced in consultation with the wider research community, to target individual studies in areas of greatest need. This would ideally be followed by dedicated funding calls for research projects which clearly take into account these priority questions, and which offer access to ICOS facilities and 'supersites'. A centralised land-ocean C flux database (section 3.2.8) containing up to date details of ongoing studies and, where possible, historic data should be created. The inclusion of process-study data should be encouraged, according to best practice, and made mandatory for ICOS-funded studies.

Addressing the following process questions will enable more robust estmates of the pan-European (and global) land-ocean C flux, and to develop modelling tools to understand how those fluxes will likely evolve in the future. They will also help us develop priorities for future work.

- Q1. What is the relative importance of biodegradation, photdegradation, and aggregation/ flocculation across the various LOAC environments, and what controls these processes?
- Q2. What fraction of the OC discharged by rivers is buried in estuarine and coastal sediments?
- Q3. What fraction of riverine/terrigenous OC is respired by planktonic and benthic prokaryotes?
- Q4. What fraction of riverine/terrigenous OC is utilised in the trophic chain (i.e. by filter feeders, deposit feeders)?
- Q5. Are mixing zones in deltas and estuaries sinks or sources of CO_2 and CH_4?
- Q6. What controls estuarine C transfer across varied geophysical environments?

Q7. Where are the greatest uncertainties associated with LOAC C fluxes and how can we reduce these?

Q8. Can we reach greater agreement over measurement protocols across LOAC environments?

This list is by no means exhaustive.

3.2.7 Sampling methodologies: manual vs. autonomous

A range of sampling techniques are available which can most easily be grouped as ‘manual’ (physical, in-person sampling collection at a single point in time or space) and ‘autonomous’ (automated sampling and/or sensing which does not require a physical presence and can occur across a period of time or space). Some of the key advantages and disadvantages of these sampling types are given in Table 8. It is not possible to adequately account for all possible methodologies, but some examples are given below.

Table 8. Advantages and disadvantages of water and sensor-based sampling activities

Method	Advantage	Disadvantage
Water sampling (discrete, manual)	Generates definitive data	High labour costs (time and travel costs) to visit distant/multiple locations
	Can be added to existing sampling activities (e.g. those already undertaken by national Environment Agencies)	Limited temporal resolution. Can miss important but ephemeral events (e.g. flash floods)
		Periodic sensor recalibration required.
	Per sample processing costs may be trivial	Sample analysis may take a long time
In-situ observations (high temporal resolution, autonomous)	High temporal resolution (e.g. every minute or second). Can catch ephemeral events (e.g. flash floods)	High capital costs; Limits number of units; Poses security requirements
	Can generate data in [near] real-time	Potentially requires fixed power supply
		Requires routine maintenance (e.g. cleaning and sensor replacement) Permanently exposed: Risk of theft; Risk of damage by moving debris

The recommendations of this report focus on manual water sampling as a universally available (at least in a pan-European context), easily scalable, reliable option. However, consideration should also be given to autonomy, particularly in locations where high spatial resolution has been obtained but where temporal data are lacking. In such cases, data acquisition should, where affordable, be supplemented via sensors that allow temporal patterns to be identified, and the origin of the material determined via sampling (e.g. for stable isotope analysis) or discerned via in-situ measurements (e.g. spectrolyser). Observations made with continuous sensors from autonomous platforms must be supplemented by manual sampling at regular intervals in order to ensure data quality via instrument calibration. Examples of existing autonomy follows (Appendix II), the first providing high-resolution temporal data with limited spatial coverage, and the second providing high-resolution spatial coverage with limited capacity for temporal replication. It is of note that these are just two examples of autonomy currently in use by the authors, and do not necessarily represent the most appropriate options for a proposed monitoring network. Indeed, autonomy can be wide ranging, from throwing tennis ball-sized temperature sensors from a bridge to installing an array of sensors onto a floating raft-like platform mid-lake.

3.2.8 Coordinating data sharing and ensuring optimal utilisation

We recommend that ICOS encourage data sharing and dissemination through the existing ICOS C Portal. This would ideally include data obtained via academic research as well as from national agency and ICOS specific monitoring activities, but we appreciate that data storage and dissemination can prove costly and so this may not be feasible. Buy-in from the ICOS membership and national agencies might be expected with relative ease, but coordination of academic study will require motivation on the part of a large number of institutions and individuals and therefore may be more problematic to achieve.

The Surface Ocean CO_2 Atlas (SOCAT; www.socat.info) might serve as a useful example of how such broad-scale buy-in from the research community can be obtained. SOCAT focusses on collection of monitoring data by research institutes, and has solidified the ocean going CO_2 community such that data sharing on the associated platform is now standard practice. A strict 'cookbook' is provided for methodology and data QC, as with existing ICOS practices. Volunteers coordinate on a regional scale and provide QC services free-of charge, although more recently some funding has been achieved to cover activities such as analysis of key analytical uncertainties. However, much of the work within SOCAT is done on a voluntary basis or intermittently funded through research grants with insecure futures. This works because of the dedication of a few individuals, but the end-product is in a persistently precarious position. In terms of their motivation, volunteers signpost co-authorship on higher impact outputs than might be achieved alone, a sense of community ownership, and a feeling that what is being created is important. A similar platform for the land-ocean C flux community may be more complex to build and advertise, given a higher number of parameters and environments under consideration, but it is certainly feasible that the research community could be motivated to use it as a central point for the storage and dissemination of data which could be used to supplement more formal monitoring activities. It is important to note, however, that such an endeavour would represent a considerable investment of time that should not be taken lightly. These activities should therefore be coordinated by a dedicated thematic centre to operate alongside the ICOS OTC, ETC and ATC. A dedicated team is required to administer the RI and coordinate data management and QC processes.

3.2.9 The LOAC Thematic Centre and preparatory phase

Quantification of the LOAC C fluxes by ICOS will require a distinct LOAC thematic centre (LTC) akin to the atmospheric (ATC), environmental (ETC) and oceanic (OTC) thematic centres already in existence within ICOS. This thematic centre will adopt existing practices from the other ICOS TCs where appropriate and establish new ones where necessary through appropriate working groups (e.g. analytical protocols specific to the LOAC). Whilst there is substantial overlap with existing TCs, the methodologies and tasks involved are sufficiently different than the establishment of a distinct TC is warranted.

The LTC will coordinate inter-calibration activities, evaluation of new methodologies, and data collation. We envisage an initial preparatory phase during which these activities will be undertaken, analytical protocols will be adopted, and station selection criteria as well as the relevant data-QC and data-handling procedures will be established. A substantial component of this initial phase would be a 'data mining' exercise, collating existing but disparate data from the EEA and other sources (academic and research institutes as well as NGOs) to identify key regions for monitoring and to construct an initial pan-European land-ocean C budget which will thereafter act as a baseline against which future change can be judged.

The LTC will also coordinate training workshops and networking opportunities (e.g. methodological workshops with representatives of sensor manufacturers, environmental regulators and consultants; summer schools) which will allow the diverse community of researchers, initiated by this task and essential to the success off the LTC itself, to stay connected and to expand, both in number and expertise.

4. Conclusion

The export of carbon (C) from land to sea via the land-ocean aquatic continuum (LOAC) is a substantial component of the global C cycle, with the lateral transport of C through aquatic environments stimulating a vertical exchange of gaseous C between the LOAC and the atmosphere. Aquatic environments are highly dynamic, and subject to a multitude of environmental pressures linked to human activities and global climate change. Understanding how these pressures affect the global C cycle requires new information on the spatial and temporal variability of C fluxes across the LOAC. This report has provided guidance on the requirements for a high-quality, pan-European monitoring network, including the extent to which monitoring might be integrated within existing infrastructure.

The proposed monitoring programme involves (1) regular monitoring of the lateral movement of C through the LOAC, conducted at broad spatial scale by national agencies under the guidance of the European Environment Agency (EEA), and according to site selection and methodological criteria provisionally set forth in this report; (2) regular monitoring of the vertical movement of C between the LOAC and the atmosphere, conducted at key 'super-sites' and administered by the Integrated C Observatory System (ICOS) and other research infrastructure and institutes; (3) focussed studies to understand the processes that act upon C fluxes along the LOAC, conducted by research centres and driven by targeted research calls. As a next step, we recommend the formation of a new LOAC Thematic Centre (LTC) to oversee a preparatory phase, with the goal of initiating a pan-European land-ocean C monitoring network within 10 years. This timeline is short, but is considered necessary given the significance of these fluxes to large-scale C budgeting and the current lack of consistent data sets and understanding.

The study of land-ocean-atmosphere C fluxes necessitates collaboration across the traditional disciplines of terrestrial, freshwater, marine, and atmospheric science, the sharing of knowledge and experience, and the use of a common language. In producing this report, such collaboration has been fostered.

5. Abbreviations

The following abbreviations are used in this report (in alphabetical order):

A	Autochthonous (internally produced) DOM, used in UniDOM model
ATC	Atmospheric Thematic Centre
C	Carbon
cDOM	Chromophoric dissolved organic matter
CH_4	Methane
CO_2	Carbon dioxide
CP	ICOS Carbon Portal
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
eLTER	European Long Term Ecological Research
ETC	Ecosystem Thematic Centre
fDOM	Fluorescent dissolved organic matter
GHG	Greenhouse Gasses
IC	Inorganic Carbon
ICOS	Integrated Carbon Observatory System
LOAC	Land-ocean aquatic continuum
LTC	LOAC Thematic Centre (proposed)
LTSR	Long Term Socioecological Research
LULC	Land Use / Land Cover
OC	Organic Carbon
OM	Organic Matter
OTC	Ocean Thematic Centre
PIC	Particulate Inorganic Carbon
POC	Particulate Organic Carbon
RI	Research Infrastructure
SUVA	Specific Ultra Violet Absorbance
T_1	Chromophoric DOM compounds prone to photooxidation, used in UniDOM model
T_2	Chromophoric DOM compounds less prone to photooxidation, used in UniDOM model
ZA	Zone Atelier

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7. References

Abril, G. and Borges, A. V.: Ideas and perspectives: Carbon leaks from flooded land: Do we need to replumb the inland water active pipe?, Biogeosciences, doi:10.5194/bg-16-769-2019, 2019.

Abril, G., Nogueira, M., Etcheber, H., Cabeçadas, G., Lemaire, E. and Brogueira, M. J.: Behaviour of organic carbon in nine contrasting European estuaries, Estuar. Coast. Shelf Sci., doi:10.1006/ecss.2001.0844, 2002.

Abril, G., Martinez, J. M., Artigas, L. F., Moreira-Turcq, P., Benedetti, M. F., Vidal, L., Meziane, T., Kim, J. H., Bernardes, M. C., Savoye, N., Deborde, J., Souza, E. L., Albéric, P., Landim De Souza, M. F. and Roland, F.: Amazon River carbon dioxide outgassing fuelled by wetlands, Nature, doi:10.1038/nature12797, 2014.

Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C. R., Marwick, T. R., Tamooh, F., Ochieng Omengo, F., Geeraert, N., Deirmendjian, L., Polsenaere, P. and Borges, A. V.: Technical note: Large overestimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters, Biogeosciences, doi:10.5194/bg-12-67-2015, 2015.

Anderson, T. R. and Williams, P. J. L. B.: Modelling the seasonal cycle of dissolved organic carbon at station E1 in the English channel, Estuar. Coast. Shelf Sci., doi:10.1006/ecss.1997.0257, 1998.

Anderson, T. R., Christian, J. R. and Flynn, K. J.: Modeling DOM Biogeochemistry, in Biogeochemistry of Marine Dissolved Organic Matter: Second Edition., 2015.

Anderson, T. R., Rowe, E. C., Polimene, L., Tipping, E., Evans, C. D., Barry, C. D. G., Hansell, D. A., Kaiser, K., Kitidis, V., Lapworth, D. J., Mayor, D. J., Monteith, D. T., Pickard, A. E., Sanders, R. J., Spears, B. M., Torres, R., Tye, A. M., Wade, A. J. and Waska, H.: Unified concepts for understanding and modelling turnover of dissolved organic matter from freshwaters to the ocean: the UniDOM model, Biogeochemistry, 1, 1–19, doi:10.1007/s10533-019-00621-1, 2019.

Asmala, E., Carstensen, J. and Raike, A.: Multiple anthropogenic drivers behind upward trends in organic carbon concentrations in boreal rivers, Environ. Res. Lett., doi:10.1088/1748-9326/ab4fa9, 2019.

Baldocchi, D., Falge, E., Gu, L., Olson, R., Hollinger, D., Running, S., Anthoni, P., Bernhofer, C., Davis, K., Evans, R., Fuentes, J., Goldstein, A., Katul, G., Law, B., Lee, X., Malhi, Y., Meyers, T., Munger, W., Oechel, W., Paw, U. K. T., Pilegaard, K., Schmid, H. P., Valentini, R., Verma, S., Vesala, T., Wilson, K. and Wofsy, S.: FLUXNET: A New Tool to Study the Temporal and Spatial Variability of Ecosystem-Scale Carbon Dioxide, Water Vapor, and Energy Flux Densities, Bull. Am. Meteorol. Soc., doi:10.1175/1520-0477(2001)082<2415:FANTTS>2.3.CO;2, 2001.

Barros, N., Cole, J. J., Tranvik, L. J., Prairie, Y. T., Bastviken, D., Huszar, V. L. M., Del Giorgio, P. and Roland, F.: Carbon emission from hydroelectric reservoirs linked to reservoir age and latitude, Nat. Geosci., doi:10.1038/ngeo1211, 2011.

Bastviken, D., Tranvik, L. J., Downing, J. A., Crill, P. M. and Enrich-Prast, A.: Freshwater methane emissions offset the continental carbon sink, Science (80-.)., doi:10.1126/science.1196808, 2011.

Bates, N. R., Astor, Y. M., Church, M. J., Currie, K., Dore, J. E., González-Dávila, M., Lorenzoni, L., Muller-Karger, F., Olafsson, J. and Santana-Casiano, J. M.: A time-series view of changing surface ocean chemistry due to ocean uptake of anthropogenic CO2 and ocean acidification, Oceanography, doi:10.5670/oceanog.2014.16, 2014.

Bauer, J. E., Cai, W.-J., Raymond, P. a, Bianchi, T. S., Hopkinson, C. S. and Regnier, P. a G.: The changing carbon cycle of the coastal ocean., Nature, 504(7478), 61–70, doi:10.1038/nature12857, 2013.

van Bergen, T. J. H. M., Barros, N., Mendonça, R., Aben, R. C. H., Althuizen, I. H. J., Huszar, V., Lamers, L. P. M., Lürling, M., Roland, F. and Kosten, S.: Seasonal and diel variation in greenhouse gas emissions from an urban pond and its major drivers, Limnol. Oceanogr., doi:10.1002/lno.11173, 2019.

Bianchi, T. S.: The role of terrestrially derived organic carbon in the coastal ocean: A changing paradigm and the priming effect, Proc. Natl. Acad. Sci. U. S. A., doi:10.1073/pnas.1017982108, 2011.

Bianchi, T. S. and Allison, M. A.: Large-river delta-front estuaries as natural “recorders” of global environmental change, Proc. Natl. Acad. Sci. U. S. A., doi:10.1073/pnas.0812878106, 2009.

Billen, G., Garnier, J. and Hanset, P.: Modelling phytoplankton development in whole drainage networks: the RIVERSTRAHLER Model applied to the Seine river system, Hydrobiologia, doi:10.1007/BF00007414, 1994.

Blanchet, M., Pringault, O., Panagiotopoulos, C., Lefèvre, D., Charrière, B., Ghiglione, J. F., Fernandez, C., Aparicio, F. L., Marrasé, C., Catala, P., Oriol, L., Caparros, J. and Joux, F.: When riverine dissolved organic matter (DOM) meets labile DOM in coastal waters: changes in bacterial community activity and composition, Aquat. Sci., 79(1), 27–43, doi:10.1007/s00027-016-0477-0, 2017.

Borges, A. V., Abril, G., Darchambeau, F., Teodoru, C. R., Deborde, J., Vidal, L. O., Lambert, T. and Bouillon, S.: Divergent biophysical controls of aquatic CO2 and CH4 in the World's two largest rivers, Sci. Rep., doi:10.1038/srep15614, 2015.

Bowring, S. P. K., Lauerwald, R., Guenet, B., Zhu, D., Guimberteau, M., Tootchi, A., Ducharne, A. and Ciais, P.: ORCHIDEE MICT-LEAK (r5459), a global model for the production, transport, and transformation of dissolved organic carbon from Arctic permafrost regions - Part 1: Rationale, model description, and simulation protocol, Geosci. Model Dev., doi:10.5194/gmd-12-3503-2019, 2019.

Bowring, S. P. K., Lauerwald, R., Guenet, B., Zhu, D., Guimberteau, M., Regnier, P., Tootchi, A., Ducharne, A. and Ciais, P.: ORCHIDEE MICT-LEAK (r5459), a global model for the production, transport, and transformation of dissolved organic carbon from Arctic permafrost regions - Part 2: Model evaluation over the Lena River basin, Geosci. Model Dev., doi:10.5194/gmd-13-507-2020, 2020.

Brown, C. D., Turner, N., Hollis, J., Bellamy, P., Biggs, J., Williams, P., Arnold, D., Pepper, T. and Maund, S.: Morphological and physico-chemical properties of British aquatic habitats potentially exposed to pesticides, Agric. Ecosyst. Environ., doi:10.1016/j.agee.2005.10.015, 2006.

Burdige, D. J.: Preservation of organic matter in marine sediments: Controls, mechanisms, and an imbalance in sediment organic carbon budgets?, Chem. Rev., 107(2), 467–485, doi:10.1021/cr050347q, 2007.

Butenschön, M., Clark, J., Aldridge, J. N., Icarus Allen, J., Artioli, Y., Blackford, J., Bruggeman, J., Cazenave, P., Ciavatta, S., Kay, S., Lessin, G., Van Leeuwen, S., Van Der Molen, J., De Mora, L., Polimene, L., Sailley, S., Stephens, N. and Torres, R.: ERSEM 15.06: A generic model for marine biogeochemistry and the ecosystem dynamics of the lower trophic levels, Geosci. Model Dev., doi:10.5194/gmd-9-1293-2016, 2016.

Butman, D. and Raymond, P. A.: Significant efflux of carbon dioxide from streams and rivers in the United States, Nat. Geosci., doi:10.1038/ngeo1294, 2011.

Butman, D. E., Wilson, H. F., Barnes, R. T., Xenopoulos, M. A. and Raymond, P. A.: Increased mobilization of aged carbon to rivers by human disturbance, Nat. Geosci., doi:10.1038/ngeo2322, 2015.

Cai, W.-J.: Estuarine and coastal ocean carbon paradox: CO2 sinks or sites of terrestrial carbon incineration?, Ann. Rev. Mar. Sci., 3, 123–145, doi:10.1146/annurev-marine-120709-142723, 2011.

de Carlos, A., Martínez-Carreño, N., Barros-García, D., Luis, J. R. and García-Gil, S.: Geochemical and microbial context of the gassy sediments in the Ría de Vigo (NW of Spain), Mar. Geol., doi:10.1016/j.margeo.2016.12.004, 2017.

Carlson, C. A. and Ducklow, H. W.: Dissolved organic carbon in the upper ocean of the central equatorial Pacific Ocean, 1992: Daily and finescale vertical variations, Deep. Res. Part II, doi:10.1016/0967-0645(95)00023-J, 1995.

Carr, N., Davis, C. E., Blackbird, S., Daniels, L. R., Preece, C., Woodward, M. and Mahaffey, C.: Seasonal and spatial variability in the optical characteristics of DOM in a temperate shelf sea, Prog. Oceanogr., doi:10.1016/j.pocean.2018.02.025, 2019.

Carstensen, J. and Duarte, C. M.: Drivers of pH Variability in Coastal Ecosystems, Environ. Sci. Technol., doi:10.1021/acs.est.8b03655, 2019.

Catalán, N., Marcé, R., Kothawala, D. N. and Tranvik, L. J.: Organic carbon decomposition rates controlled by water retention time across inland waters, Nat. Geosci., doi:10.1038/ngeo2720, 2016.

Cherrier, J., Bauer, J. E. and Druffel, E. R. M.: Utilization and turnover of labile dissolved organic matter by bacterial heterotrophs in eastern North Pacific surface waters, Mar. Ecol. Prog. Ser., doi:10.3354/meps139267, 1996.

Clark, J. M., Lane, S. N., Chapman, P. J. and Adamson, J. K.: Export of dissolved organic carbon from an upland peatland during storm events: Implications for flux estimates, J. Hydrol., doi:10.1016/j.jhydrol.2007.09.030, 2007.

Cole, J. J., Caraco, N. F., Kling, G. W. and Kratz, T. K.: Carbon dioxide supersaturation in the surface waters of lakes, Science (80-.)., doi:10.1126/science.265.5178.1568, 1994.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J. and Melack, J.: Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, Ecosystems, 10(1), 171–184, doi:10.1007/s10021-006-9013-8, 2007.

Dagg, M., Sato, R., Liu, H., Bianchi, T. S., Green, R. and Powell, R.: Microbial food web contributions to bottom water hypoxia in the northern Gulf of Mexico, Cont. Shelf Res., 28(9), 1127–1137, doi:10.1016/j.csr.2008.02.013, 2008.

Dai, M., Martin, J. M. and Cauwet, G.: The significant role of colloids in the transport and transformation of organic carbon and associated trace metals (Cd, Cu and Ni) in the Rhône delta (France), Mar. Chem., doi:10.1016/0304-4203(95)00051-R, 1995.

Dai, M., Yin, Z., Meng, F., Liu, Q. and Cai, W. J.: Spatial distribution of riverine DOC inputs to the ocean: An updated global synthesis, Curr. Opin. Environ. Sustain., doi:10.1016/j.cosust.2012.03.003, 2012.

Deemer, B. R., Harrison, J. A., Li, S., Beaulieu, J. J., Delsontro, T., Barros, N., Bezerra-Neto, J. F., Powers, S. M., Dos Santos, M. A. and Vonk, J. A.: Greenhouse gas emissions from reservoir water surfaces: A new global synthesis, Bioscience, doi:10.1093/biosci/biw117, 2016.

Deirmendjian, L., Loustau, D., Augusto, L., Lafont, S., Chipeaux, C., Poirier, D. and Abril, G.: Hydro-ecological controls on dissolved carbon dynamics in groundwater and export to streams in a temperate pine forest, Biogeosciences, doi:10.5194/bg-15-669-2018, 2018.

DelSontro, T., del Giorgio, P. A. and Prairie, Y. T.: No Longer a Paradox: The Interaction Between Physical Transport and Biological Processes Explains the Spatial Distribution of Surface Water Methane Within and Across Lakes, Ecosystems, doi:10.1007/s10021-017-0205-1, 2018.

Denfeld, B. A., Wallin, M. B., Sahlée, E., Sobek, S., Kokic, J., Chmiel, H. E. and Weyhenmeyer, G. A.: Temporal and spatial carbon dioxide concentration patterns in a small boreal lake in relation to ice-cover dynamics, Boreal Environ. Res., 2015.

Desmit, X., Thieu, V., Billen, G., Campuzano, F., Dulière, V., Garnier, J., Lassaletta, L., Ménesguen, A., Neves, R., Pinto, L., Silvestre, M., Sobrinho, J. L. and Lacroix, G.: Reducing marine eutrophication may require a paradigmatic change, Sci. Total Environ., doi:10.1016/j.scitotenv.2018.04.181, 2018.

Dhillon, G. S. and Inamdar, S.: Extreme storms and changes in particulate and dissolved organic carbon in runoff: Entering uncharted waters?, Geophys. Res. Lett., doi:10.1002/grl.50306, 2013.

Dhillon, G. S. and Inamdar, S.: Storm event patterns of particulate organic carbon (POC) for large storms and differences with dissolved organic carbon (DOC), Biogeochemistry, doi:10.1007/s10533-013-9905-6, 2014.

Doney, S. C., Fabry, V. J., Feely, R. A. and Kleypas, J. A.: Ocean Acidification: The Other CO 2 Problem, Ann. Rev. Mar. Sci., 1(1), 169–192, doi:10.1146/annurev.marine.010908.163834, 2009.

Downing, J. A.: Emerging global role of small lakes and ponds: Little things mean a lot, Limnetica, 2010.

Downing, J. A. and Striegl, R. G.: Size, age, renewal, and discharge of groundwater carbon, Inl. Waters, doi:10.1080/20442041.2017.1412918, 2018.

Drake, T. W., Raymond, P. A. and Spencer, R. G. M.: Terrestrial carbon inputs to inland waters: A current synthesis of estimates and uncertainty, Limnol. Oceanogr. Lett., 3(3), 132–142, doi:10.1002/lol2.10055, 2018.

Druon, J. N., Mannino, A., Signorini, S., McClain, C., Friedrichs, M., Wilkin, J. and Fennel, K.: Modeling the dynamics and export of dissolved organic matter in the Northeastern U.S. continental shelf, Estuar. Coast. Shelf Sci., doi:10.1016/j.ecss.2010.05.010, 2010.

Duarte, C. M., Middelburg, J. J. and Caraco, N.: Major role of marine vegetation on the oceanic carbon cycle, Biogeosciences Discuss., 1(1), 659–679, doi:10.5194/bgd-1-659-2004, 2004.

Duarte, C. M., Middelburg, J. J. and Caraco, N.: Major role of marine vegetation on the oceanic carbon cycle, Biogeosciences, 2, 1–8, doi:10.5194/bgd-1-659-2004, 2005.

Duc, N. T., Crill, P. and Bastviken, D.: Implications of temperature and sediment characteristics on methane formation and oxidation in lake sediments, Biogeochemistry, doi:10.1007/s10533-010-9415-8, 2010.

Dürr, H. H., Laruelle, G. G., van Kempen, C. M., Slomp, C. P., Meybeck, M. and Middelkoop, H.: Worldwide Typology of Nearshore Coastal Systems: Defining the Estuarine Filter of River Inputs to the Oceans, Estuaries and Coasts, 34(3), 441–458, doi:10.1007/s12237-011-9381-y, 2011.

Evans, C. D., Renou-Wilson, F. and Strack, M.: The role of waterborne carbon in the greenhouse gas balance of drained and re-wetted peatlands, Aquat. Sci., doi:10.1007/s00027-015-0447-y, 2016.

Evans, C. D., Malcolm, I. A., Shilland, E. M., Rose, N. L., Turner, S. D., Crilly, A., Norris, D., Granath, G. and Monteith, D. T.: Sustained Biogeochemical Impacts of Wildfire in a Mountain Lake Catchment, Ecosystems, doi:10.1007/s10021-016-0064-1, 2017a.

Evans, C. D., Futter, M. N., Moldan, F., Valinia, S., Frogbrook, Z. and Kothawala, D. N.: Variability in organic carbon reactivity across lake residence time and trophic gradients, Nat. Geosci., doi:10.1038/NGEO3051, 2017b.

Evans, C. D., Peacock, M., Green, S. M., Holden, J., Chapman, P. J., Lebron, I., Callaghan, N., Grayson, R. and Baird, A. J.: The impact of ditch blocking on fluvial carbon export from a UK blanket bog, Hydrol. Process., doi:10.1002/hyp.13158, 2018.

Fabry, V. J., Seibel, B. A., Feely, R. A. and Orr, J. C.: Impacts of ocean acidification on marine fauna and ecosystem processes, in ICES Journal of Marine Science, vol. 65, pp. 414–432., 2008.

Fennel, K., Alin, S., Barbero, L., Evans, W., Bourgeois, T., Cooley, S., Dunne, J., Feely, R. A., Martin Hernandez-Ayon, J., Hu, X., Lohrenz, S., Muller-Karger, F., Najjar, R., Robbins, L., Shadwick, E., Siedlecki, S., Steiner, N., Sutton, A., Turk, D., Vlahos, P. and Aleck Wang, Z.: Carbon cycling in the North American coastal ocean: A synthesis, Biogeosciences, doi:10.5194/bg-16-1281-2019, 2019.

Fichot, C. G. and Benner, R.: The fate of terrigenous dissolved organic carbon in a river-influenced ocean margin, Global Biogeochem. Cycles, doi:10.1002/2013GB004670, 2014.

Frankignoulle, M., Abril, G., Borges, A., Bourge, I., Canon, C., Delille, B., Libert, E. and Théate, J. M.: Carbon dioxide emission from European estuaries, Science (80-.)., doi:10.1126/science.282.5388.434, 1998.

Frouin, P.: Effects of anthropogenic disturbances of tropical soft-bottom benthic communities, Mar. Ecol. Prog. Ser., 194, 39–53, doi:10.3354/meps194039, 2000.

Futter, M. N., Butterfield, D., Cosby, B. J., Dillon, P. J., Wade, A. J. and Whitehead, P. G.: Modeling the mechanisms that control in-stream dissolved organic carbon dynamics in upland and forested catchments, Water Resour. Res., doi:10.1029/2006WR004960, 2007.

Galloway, J. N., Townsend, A. R., Erisman, J. W., Bekunda, M., Cai, Z., Freney, J. R., Martinelli, L. A., Seitzinger, S. P. and Sutton, M. A.: Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions, Science (80-.)., doi:10.1126/science.1136674, 2008.

Ge, J., Torres, R., Chen, C., Liu, J., Xu, Y., Bellerby, R., Shen, F., Bruggeman, J. and Ding, P.: Influence of suspended sediment front on nutrients and phytoplankton dynamics off the Changjiang Estuary: A FVCOM-ERSEM coupled model experiment, J. Mar. Syst., doi:10.1016/j.jmarsys.2019.103292, 2020.

Gooddy, D. C. and Darling, W. G.: The potential for methane emissions from groundwaters of the UK, Sci. Total Environ., doi:10.1016/j.scitotenv.2004.07.019, 2005.

Gooddy, D. C., Darling, W. G., Abesser, C. and Lapworth, D. J.: Using chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF6) to characterise groundwater movement and residence time in a lowland Chalk catchment, J. Hydrol., doi:10.1016/j.jhydrol.2006.04.011, 2006.

Graeber, D., Goyenola, G., Meerhoff, M., Zwirnmann, E., Ovesen, N. B., Glendell, M., Gelbrecht, J., Teixeira De Mello, F., González-Bergonzoni, I., Jeppesen, E. and Kronvang, B.: Interacting effects of climate and agriculture on fluvial DOM in temperate and subtropical catchments, Hydrol. Earth Syst. Sci., 19(5), 2377–2394, doi:10.5194/hess-19-2377-2015, 2015.

Grinham, A., Albert, S., Deering, N., Dunbabin, M., Bastviken, D., Sherman, B., Lovelock, C. E. and Evans, C. D.: The importance of small artificial water bodies as sources of methane emissions in Queensland, Australia, Hydrol. Earth Syst. Sci., doi:10.5194/hess-22-5281-2018, 2018.

Gröger, M., Maier-Reimer, E., Mikolajewicz, U., Moll, A. and Sein, D.: NW European shelf under climate warming: Implications for open ocean - Shelf exchange, primary production, and carbon absorption, Biogeosciences, doi:10.5194/bg-10-3767-2013, 2013.

Gudasz, C., Bastviken, D., Steger, K., Premke, K., Sobek, S. and Tranvik, L. J.: Temperature-controlled organic carbon mineralization in lake sediments, Nature, doi:10.1038/nature09186, 2010.

Guérin, F., Abril, G., Richard, S., Burban, B., Reynouard, C., Seyler, P. and Delmas, R.: Methane and carbon dioxide emissions from tropical reservoirs: Significance of downstream rivers, Geophys. Res. Lett., doi:10.1029/2006GL027929, 2006.

Hastie, A., Lauerwald, R., Weyhenmeyer, G., Sobek, S., Verpoorter, C. and Regnier, P.: CO2 evasion from boreal lakes: Revised estimate, drivers of spatial variability, and future projections, Glob. Chang. Biol., doi:10.1111/gcb.13902, 2018.

Hastie, A., Lauerwald, R., Ciais, P. and Regnier, P.: Aquatic carbon fluxes dampen the overall variation of net ecosystem productivity in the Amazon basin: An analysis of the interannual variability in the boundless carbon cycle, Glob. Chang. Biol., doi:10.1111/gcb.14620, 2019.

Hastie, A., Lauerwald, R., Ciais, P., Papa, F. and Regnier, P.: Historical and future contributions of inland waters to the Congo basin carbon balance, Earth Syst. Dyn. Discuss., doi:10.5194/esd-2020-3, 2020.

Hedges, J. I., Keil, R. G. and Benner, R.: What happens to terrestrial organic matter in the ocean?, in Organic Geochemistry., 1997.

Heip, C. H. R., Goosen, N. K., Herman, P. M. J., Kromkamp, J., Middelburg, J. J. and Soetaert, K.: Production and consumption of biological particles in temperate tidal estuaries, Oceanogr. Mar. Biol. an Annu. Rev. Vol. 33, 1995.

van Hoek, W. J., Vilmin, L., Beusen, A. H. W., Mogollón, J. M., Liu, X., Langeveld, J. J., Bouwman, A. F. and Middelburg, J. J.: CARBON-DISC 1.0 – A coupled, process-based model of global in-stream carbon biogeochemistry, Geosci. Model Dev. Discuss., doi:10.5194/gmd-2019-205, 2019.

Holgerson, M. A. and Raymond, P. A.: Large contribution to inland water CO2 and CH4 emissions from very small ponds, Nat. Geosci., doi:10.1038/ngeo2654, 2016.

Holt, J., Butenschön, M., Wakelin, S. L., Artioli, Y. and Allen, J. I.: Oceanic controls on the primary production of the northwest European continental shelf: Model experiments under recent past conditions and a potential future scenario, Biogeosciences, doi:10.5194/bg-9-97-2012, 2012.

Hope, D., Billett, M. F. and Cresser, M. S.: A review of the export of carbon in river water: Fluxes and processes, Environ. Pollut., doi:10.1016/0269-7491(94)90142-2, 1994.

Hughes, D. A.: Hydrological issues associated with the determination of environmental water requirements of ephemeral rivers, River Res. Appl., doi:10.1002/rra.857, 2005.

Jones, M. W., Santín, C., van der Werf, G. R. and Doerr, S. H.: Global fire emissions buffered by the production of pyrogenic carbon, Nat. Geosci., doi:10.1038/s41561-019-0403-x, 2019.

Jones, T. G., Evans, C. D. and Freeman, C.: The greenhouse gas (GHG) emissions associated with aquatic carbon removal during drinking water treatment, Aquat. Sci., doi:10.1007/s00027-015-0458-8, 2016.

Kaiser, K. and Guggenberger, G.: The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils, in Organic Geochemistry., 2000.

Kandasamy, S. and Nagender Nath, B.: Perspectives on the Terrestrial Organic Matter Transport and Burial along the Land-Deep Sea Continuum: Caveats in Our Understanding of Biogeochemical Processes and Future Needs, Front. Mar.

Sci., 3(December), 1–18, doi:10.3389/fmars.2016.00259, 2016.

Karanfil, T., Schlautman, M. A. and Erdogan, I.: Survey of DOC and UV measurement practices with implications for SUVA determination, J. / Am. Water Work. Assoc., doi:10.1002/j.1551-8833.2002.tb10250.x, 2002.

Karlsson, J., Giesler, R., Persson, J. and Lundin, E.: High emission of carbon dioxide and methane during ice thaw in high latitude lakes, Geophys. Res. Lett., doi:10.1002/grl.50152, 2013.

Keller, D. P. and Hood, R. R.: Comparative simulations of dissolved organic matter cycling in idealized oceanic, coastal, and estuarine surface waters, J. Mar. Syst., doi:10.1016/j.jmarsys.2012.01.002, 2013.

Kellerman, A. M., Kothawala, D. N., Dittmar, T. and Tranvik, L. J.: Persistence of dissolved organic matter in lakes related to its molecular characteristics, Nat. Geosci., doi:10.1038/NGEO2440, 2015.

Khatiwala, S., Primeau, F. and Hall, T.: Reconstruction of the history of anthropogenic CO2 concentrations in the ocean, Nature, doi:10.1038/nature08526, 2009.

Kirchner, J. W.: A double paradox in catchment hydrology and geochemistry, Hydrol. Process., doi:10.1002/hyp.5108, 2003.

Kirschbaum, M. U. F., Zeng, G., Ximenes, F., Giltrap, D. L. and Zeldis, J. R.: Towards a more complete quantification of the global carbon cycle, Biogeosciences, 16(3), 831–846, doi:10.5194/bg-16-831-2019, 2019.

Kitidis, V., Tizzard, L., Uher, G., Judd, A., Upstill-Goddard, R. C., Head, I. M., Gray, N. D., Taylor, G., Durán, R., Diez, R., Iglesias, J. and García-Gil, S.: The biogeochemical cycling of methane in Ria de Vigo, NW Spain: Sediment processing and sea-air exchange, J. Mar. Syst., doi:10.1016/j.jmarsys.2006.03.022, 2007.

Kitidis, V., Shutler, J. D., Ashton, I., Warren, M., Brown, I., Findlay, H., Hartman, S. E., Sanders, R., Humphreys, M., Kivimäe, C., Greenwood, N., Hull, T., Pearce, D., McGrath, T., Stewart, B. M., Walsham, P., McGovern, E., Bozec, Y., Gac, J. P., van Heuven, S. M. A. C., Hoppema, M., Schuster, U., Johannessen, T., Omar, A., Lauvset, S. K., Skjelvan, I., Olsen, A., Steinhoff, T., Körtzinger, A., Becker, M., Lefevre, N., Diverrès, D., Gkritzalis, T., Cattrijsse, A., Petersen, W., Voynova, Y. G., Chapron, B., Grouazel, A., Land, P. E., Sharples, J. and Nightingale, P. D.: Winter weather controls net influx of atmospheric CO2 on the north-west European shelf, Sci. Rep., doi:10.1038/s41598-019-56363-5, 2019.

Kortelainen, P., Pajunen, H., Rantakari, M. and Saarnisto, M.: A large carbon pool and small sink in boreal Holocene lake sediments, Glob. Chang. Biol., doi:10.1111/j.1365-2486.2004.00848.x, 2004.

Krinner, G., Viovy, N., de Noblet-Ducoudré, N., Ogée, J., Polcher, J., Friedlingstein, P., Ciais, P., Sitch, S. and Prentice, I. C.: A dynamic global vegetation model for studies of the coupled atmosphere-biosphere system, Global Biogeochem. Cycles, doi:10.1029/2003GB002199, 2005.

Kuhlbusch, T. A. J. and Crutzen, P. J.: Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO2 and a source of O2, Global Biogeochem. Cycles, doi:10.1029/95GB02742, 1995.

Kyung Yoon, T., Jin, H., Oh, N. H. and Park, J. H.: Technical note: Assessing gas equilibration systems for continuous pCO2 measurements in inland waters, Biogeosciences, doi:10.5194/bg-13-3915-2016, 2016.

Lapworth, D. J., Gooddy, D. C., Allen, D. and Old, G. H.: Understanding groundwater, surface water, and hyporheic zone biogeochemical process in a Chalk catchment using fluorescence properties of dissolves and colloidal organic matter, J. Geophys. Res. Biogeosciences, doi:10.1029/2009JG000921, 2009.

Lapworth, D. J., Gooddy, D. C., Kent, F., Heaton, T. H. E., Cole, S. J. and Allen, D.: A combined geochemical and hydrological approach for understanding macronutrient sources, J. Hydrol., doi:10.1016/j.jhydrol.2013.07.006, 2013.

Lapworth, D. J., Zahid, A., Taylor, R. G., Burgess, W. G., Shamsudduha, M., Ahmed, K. M., Mukherjee, A., Gooddy, D. C., Chatterjee, D. and MacDonald, A. M.: Security of Deep Groundwater in the Coastal Bengal Basin Revealed by Tracers, Geophys. Res. Lett., doi:10.1029/2018GL078640, 2018.

Laudon, H. and Sponseller, R. A.: How landscape organization and scale shape catchment hydrology and biogeochemistry: insights from a long-term catchment study, Wiley Interdiscip. Rev. Water, doi:10.1002/wat2.1265, 2018.

Lauerwald, R., Hartmann, J., Ludwig, W. and Moosdorf, N.: Assessing the nonconservative fluvial fluxes of dissolved organic carbon in North America, J. Geophys. Res. Biogeosciences, doi:10.1029/2011JG001820, 2012.

Lauerwald, R., Regnier, P., Camino-Serrano, M., Guenet, B., Guimberteau, M., Ducharne, A., Polcher, J. and Ciais, P.: ORCHILEAK (revision 3875): A new model branch to simulate carbon transfers along the terrestrial-aquatic continuum of the Amazon basin, Geosci. Model Dev., 10(10), 3821–3859, doi:10.5194/gmd-10-3821-2017, 2017.

Lavonen, E. E., Gonsior, M., Tranvik, L. J., Schmitt-Kopplin, P. and Köhler, S. J.: Selective chlorination of natural organic matter: Identification of previously unknown disinfection byproducts, Environ. Sci. Technol., doi:10.1021/es304669p, 2013.

Legge, O., Johnson, M., Hicks, N., Jickells, T., Diesing, M., Aldridge, J., Andrews, J., Artioli, Y., Bakker, D. C. E., Burrows, M. T., Carr, N., Cripps, G., Felgate, S. L., Fernand, L., Greenwood, N., Hartman, S., Kröger, S., Lessin, G., Mahaffey, C., Mayor, D. J., Parker, R., Queirós, A. M., Shutler, J. D., Silva, T., Stahl, H., Tinker, J., Underwood, G. J. C., Van Der Molen, J., Wakelin, S., Weston, K. and Williamson, P.: Carbon on the Northwest European Shelf: Contemporary Budget and Future Influences, Front. Mar. Sci., doi:10.3389/fmars.2020.00143, 2020.

Lepistö, A., Futter, M. N. and Kortelainen, P.: Almost 50 years of monitoring shows that climate, not forestry, controls long-term organic carbon fluxes in a large boreal watershed, Glob. Chang. Biol., doi:10.1111/gcb.12491, 2014.

Li, M., Peng, C., Zhou, X., Yang, Y., Guo, Y., Shi, G. and Zhu, Q.: Modeling Global Riverine DOC Flux Dynamics From 1951 to 2015, J. Adv. Model. Earth Syst., doi:10.1029/2018MS001363, 2019.

Lindh, M. V., Lefébure, R., Degerman, R., Lundin, D., Andersson, A. and Pinhassi, J.: Consequences of increased terrestrial dissolved organic matter and temperature on bacterioplankton community composition during a Baltic Sea mesocosm experiment, Ambio, 44, 402–412, doi:10.1007/s13280-015-0659-3, 2015.

Lovelock, C. E., Evans, C., Barros, N., Prairie, Y., Alm, J., Bastviken, D., Beaulieu, J. J., Garneau, M., Harby, A., Harrison, J., Pare, D., Raadal, H. L., Sherman, B., Zhang, C., Ogle, S. M., Grinham, A., Deemer, B., Aurelio dos Santos, M., Kosten, S., Peacock, M., Li, Z. and Stepanenko, V.: 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Volume 4: Agricultura, forestry and other land use (AFOLU). Chapter 7: Wetlands., 2019.

Ludwig, W. and Probst, J. L.: Predicting the oceanic input of organic carbon by continental erosion, Global Biogeochem. Cycles, doi:10.1029/95GB02925, 1996.

Luisetti, T., Jackson, E. L. and Turner, R. K.: Valuing the European "coastal blue carbon" storage benefit., Mar. Pollut. Bull., 71(1–2), 101–6, doi:10.1016/j.marpolbul.2013.03.029, 2013.

Luisetti, T., Turner, R. K., Andrews, J. E., Jickells, T. D., Kröger, S., Diesing, M., Paltriguera, L., Johnson, M. T., Parker, E. R., Bakker, D. C. E. and Weston, K.: Quantifying and valuing carbon flows and stores in coastal and shelf ecosystems in the UK, Ecosyst. Serv., doi:10.1016/j.ecoser.2018.10.013, 2019.

Lupon, A., Denfeld, B. A., Laudon, H., Leach, J., Karlsson, J. and Sponseller, R. A.: Groundwater inflows control patterns and sources of greenhouse gas emissions from streams, Limnol. Oceanogr., doi:10.1002/lno.11134, 2019.

Lyon, S. W., Mörth, M., Humborg, C., Giesler, R. and Destouni, G.: The relationship between subsurface hydrology and dissolved carbon fluxes for a sub-arctic catchment, Hydrol. Earth Syst. Sci., doi:10.5194/hess-14-941-2010, 2010.

Marescaux, A., Thieu, V., Borges, A. V. and Garnier, J.: Seasonal and spatial variability of the partial pressure of carbon dioxide in the human-impacted Seine River in France, Sci. Rep., doi:10.1038/s41598-018-32332-2, 2018.

Marescaux, A., Thieu, V., Gypens, N., Silvestre, M. and Garnier, J.: Modeling inorganic carbon dynamics in the Seine River continuum in France, Hydrol. Earth Syst. Sci. Discuss., doi:10.5194/hess-2019-601, 2019.

Margat, J. and Gun, J. van der: Groundwater around the World., 2013.

Marín-Spiotta, E., Gruley, K. E., Crawford, J., Atkinson, E. E., Miesel, J. R., Greene, S., Cardona-Correa, C. and Spencer, R. G. M.: Paradigm shifts in soil organic matter research affect interpretations of aquatic carbon cycling: Transcending disciplinary and ecosystem boundaries, Biogeochemistry, doi:10.1007/s10533-013-9949-7, 2014.

Marotta, H., Pinho, L., Gudasz, C., Bastviken, D., Tranvik, L. J. and Enrich-Prast, A.: Greenhouse gas production in low-latitude lake sediments responds strongly to warming, Nat. Clim. Chang., doi:10.1038/nclimate2222, 2014.

Mayor, D. J., Thornton, B., Jenkins, H. and Felgate, S. L.: Microbiota: The Living Foundation, in Mudflat Ecology., 2018.

McDonough, L. K., Santos, I. R., Andersen, M. S., O'Carroll, D. M., Rutlidge, H., Meredith, K., Oudone, P., Bridgeman, J., Gooddy, D. C., Sorensen, J. P. R., Lapworth, D. J., MacDonald, A. M., Ward, J. and Baker, A.: Changes in global groundwater organic carbon driven by climate change and urbanization, Nat. Commun., doi:10.1038/s41467-020-14946-1, 2020.

McKinley, G. A., Pilcher, D. J., Fay, A. R., Lindsay, K., Long, M. C. and Lovenduski, N. S.: Timescales for detection of trends in the ocean carbon sink, Nature, doi:10.1038/nature16958, 2016.

McLeod, E., Chmura, G. L., Bouillon, S., Salm, R., Björk, M., Duarte, C. M., Lovelock, C. E., Schlesinger, W. H., Silliman, B. R., Bjork, M., Duarte, C. M., Lovelock, C. E., Schlesinger, W. H. and Silliman, B. R.: A blueprint for blue carbon: Toward an improved understanding of the role of vegetated coastal habitats in sequestering CO2, Front. Ecol. Environ., 9(10), 552–560, doi:10.1890/110004, 2011.

Medeiros, P. M., Seidel, M., Niggemann, J., Spencer, R. G. M., Hernes, P. J., Yager, P. L., Miller, W. L., Dittmar, T. and Hansell, D. A.: A novel molecular approach for tracing terrigenous dissolved organic matter into the deep ocean, Global Biogeochem. Cycles, doi:10.1002/2015GB005320, 2016.

Mendonça, R., Müller, R. A., Clow, D., Verpoorter, C., Raymond, P., Tranvik, L. J. and Sobek, S.: Organic carbon burial in global lakes and reservoirs, Nat. Commun., doi:10.1038/s41467-017-01789-6, 2017.

Metcalfe, D. B., Hermans, T. D. G., Ahlstrand, J., Becker, M., Berggren, M., Björk, R. G., Björkman, M. P., Blok, D., Chaudhary, N., Chisholm, C., Classen, A. T., Hasselquist, N. J., Jonsson, M., Kristensen, J. A., Kumordzi, B. B., Lee, H., Mayor, J. R., Prevéy, J., Pantazatou, K., Rousk, J., Sponseller, R. A., Sundqvist, M. K., Tang, J., Uddling, J., Wallin, G., Zhang, W., Ahlström, A., Tenenbaum, D. E. and Abdi, A. M.: Patchy field sampling biases understanding of climate change impacts across the Arctic, Nat. Ecol. Evol., doi:10.1038/s41559-018-0612-5, 2018.

Milliman, J. D. and Syvitski, J. P. M.: Geomorphic/tectonic control of sediment discharge to the ocean: the importance of small mountainous rivers, J. Geol., doi:10.1086/629606, 1992.

Monteith, D. T., Stoddard, J. L., Evans, C. D., De Wit, H. A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopécek, J. and Vesely, J.: Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry, Nature, doi:10.1038/nature06316, 2007.

Morris, A. W., Mantoura, R. F. C., Bale, A. J. and Howland, R. J. M.: Very low salinity regions of estuaries: important sites for chemical and biological reactions [10], Nature, doi:10.1038/274678a0, 1978.

Mulholland, P. J.: Large-Scale Patterns in Dissolved Organic Carbon Concentration, Flux, and Sources, in Aquatic Ecosystems., 2003.

Müller, R. A., Futter, M. N., Sobek, S., Nisell, J., Bishop, K. and Weyhenmeyer, G. A.: Water renewal along the aquatic continuum offsets cumulative retention by lakes: Implications for the character of organic carbon in boreal lakes, Aquat. Sci., doi:10.1007/s00027-013-0298-3, 2013.

Myhre, G., Shindell, D., Breon, F.-M., Collins, W., Fuglestvedt, J., Huang, J., Koch, D., Lamarque, J.-F., Lee, D., Mendoza, B., Nakajima, T., Robock, A., Stephens, G., Takemura, T. and Zhang, H.: Anthropogenic and Natural Radiative Forcing, in Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, vol. 9781107057, edited by T. F. Stocker, D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, and P. M. Midgley, pp. 659–739, Cambridge University Press, Cambridge, United Kingdom, and New York, NY, USA., 2013.

Natchimuthu, S., Panneer Selvam, B. and Bastviken, D.: Influence of weather variables on methane and carbon dioxide flux from a shallow pond, Biogeochemistry, doi:10.1007/s10533-014-9976-z, 2014.

Natchimuthu, S., Sundgren, I., Gålfalk, M., Klemedtsson, L., Crill, P., Danielsson, Å. and Bastviken, D.: Spatio-temporal variability of lake CH4 fluxes and its influence on annual whole lake emission estimates, Limnol. Oceanogr., doi:10.1002/lno.10222, 2016.

Nedwell, D. B., Jickells, T. D., Trimmer, M. and Sanders, R.: Nutrients in Estuaries, in Advances in Ecological Research., 1999.

Nellemann, C., Corcoran, E., Duarte, C. M., Valdés, L., De Young, C., Fonseca, L. and Grimsditch, G.: Blue Carbon - The Role of Healthy Oceans in Binding Carbon. [online] Available from: http://books.google.com/books?id=onCVCHQl4RoC, 2009.

Nydahl, A. C., Wallin, M. B. and Weyhenmeyer, G. A.: No long-term trends in pCO2 despite increasing organic carbon concentrations in boreal lakes, streams, and rivers, Global Biogeochem. Cycles, doi:10.1002/2016GB005539, 2017.

Ollivier, Q. R., Maher, D. T., Pitfield, C. and Macreadie, P. I.: Punching above their weight: Large release of greenhouse gases from small agricultural dams, Glob. Chang. Biol., doi:10.1111/gcb.14477, 2019.

Opsahl, S. and Benner, R.: Distribution and cycling of terrigenous dissolved organic matter in the ocean, Nature, doi:10.1038/386480a0, 1997.

Painter, S. C., Lapworth, D. J., Woodward, E. M. S., Kroeger, S., Evans, C. D., Mayor, D. J. and Sanders, R. J.: Terrestrial dissolved organic matter distribution in the North Sea, Sci. Total Environ., 630, 630–647, doi:10.1016/j.scitotenv.2018.02.237, 2018.

Panneer Selvam, B., Natchimuthu, S., Arunachalam, L. and Bastviken, D.: Methane and carbon dioxide emissions from inland waters in India - implications for large scale greenhouse gas balances, Glob. Chang. Biol., doi:10.1111/gcb.12575, 2014.

Parr, T. B., Cronan, C. S., Ohno, T., Findlay, S. E. G., Smith, S. M. C. and Simon, K. S.: Urbanization changes the composition and bioavailability of dissolved organic matter in headwater streams, Limnol. Oceanogr., doi:10.1002/lno.10060, 2015.

Peacock, M., Ridley, L. M., Evans, C. D. and Gauci, V.: Management effects on greenhouse gas dynamics in fen ditches, Sci. Total Environ., doi:10.1016/j.scitotenv.2016.11.005, 2017.

Peacock, M., Audet, J., Jordan, S., Smeds, J. and Wallin, M. B.: Greenhouse gas emissions from urban ponds are driven by nutrient status and hydrology, Ecosphere, doi:10.1002/ecs2.2643, 2019.

Pickard, A. E., Monteith, D., Evans, C., Williamson, J., Spears, B. M., Gilbert, P. and Leith, F.: Coniferous forestry increases aquatic dissolved organic carbon in Europe’s largest blanket bog, Prep, n.d.

Polimene, L., Allen, J. I. and Zavatarelli, M.: Model of interactions between dissolved organic carbon and bacteria in marine systems, Aquat. Microb. Ecol., doi:10.3354/ame043127, 2006.

Pumpanen, J., Lindén, A., Miettinen, H., Kolari, P., Ilvesniemi, H., Mammarella, I., Hari, P., Nikinmaa, E., Heinonsalo, J., Bäck, J., Ojala, A., Berninger, F. and Vesala, T.: Precipitation and net ecosystem exchange are the most important drivers of DOC flux in upland boreal catchments, J. Geophys. Res. Biogeosciences, doi:10.1002/2014JG002705, 2014.

Queimaliños, C., Reissig, M., Pérez, G. L., Soto Cárdenas, C., Gerea, M., Garcia, P. E., García, D. and Diéguez, M. C.: Linking landscape heterogeneity with lake dissolved organic matter properties assessed through absorbance and fluorescence spectroscopy: Spatial and seasonal patterns in temperate lakes of Southern Andes (Patagonia, Argentina), Sci. Total Environ., 686, 223–235, doi:10.1016/j.scitotenv.2019.05.396, 2019.

Quéré, C. Le, Moriarty, R., Andrew, R. M., Peters, G. P. and Ciais, P.: Global carbon budget 2014, Earth Syst. Sci. Data Discuss., 6, 1–90, doi:10.5194/essdd-6-1-2014, 2014.

Rawlins, B. G., Palumbo-Roe, B., Gooddy, D. C., Worrall, F. and Smith, H.: A model of potential carbon dioxide efflux from surface water across England and Wales using headwater stream survey data and landscape predictors, Biogeosciences, doi:10.5194/bg-11-1911-2014, 2014.

Raymond, P. A. and Bauer, J. E.: Use of 14C and 13C natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: A review and synthesis, Org. Geochem., 32(4), 469–485, doi:10.1016/S0146-6380(00)00190-X, 2001.

Raymond, P. A. and Spencer, R. G. M.: Riverine DOM, in Biogeochemistry of Marine Dissolved Organic Matter: Second Edition., 2015.

Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P. and Guth, P.: Global carbon dioxide emissions from inland waters, Nature, doi:10.1038/nature12760, 2013.

Raymond, P. A., Saiers, J. E. and Sobczak, W. V.: Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse- shunt concept, Ecology, doi:10.1890/14-1684.1, 2016.

Regan, S., Hynds, P. and Flynn, R.: An overview of dissolved organic carbon in groundwater and implications for drinking water safety, Hydrogeol. J., doi:10.1007/s10040-017-1583-3, 2017.

Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, I. A., Laruelle, G. G., Lauerwald, R., Luyssaert, S., Andersson, A. J., Arndt, S., Arnosti, C., Borges, A. V., Dale, A. W., Gallego-Sala, A., Goddéris, Y., Goossens, N., Hartmann, J., Heinze, C., Ilyina, T., Joos, F., Larowe, D. E., Leifeld, J., Meysman, F. J. R., Munhoven, G., Raymond, P. A., Spahni, R., Suntharalingam, P. and Thullner, M.: Anthropogenic perturbation of the carbon fluxes from land to ocean, Nat. Geosci., 6(8), 597–607, doi:10.1038/ngeo1830, 2013.

Rodellas, V., Garcia-Orellana, J., Masqué, P., Feldman, M., Weinstein, Y. and Boyle, E. A.: Submarine groundwater discharge as a major source of nutrients to the Mediterranean Sea, Proc. Natl. Acad. Sci. U. S. A., doi:10.1073/pnas.1419049112, 2015.

Rowe, E. C., Tipping, E., Posch, M., Oulehle, F., Cooper, D. M., Jones, T. G., Burden, A., Hall, J. and Evans, C. D.: Predicting nitrogen and acidity effects on long-term dynamics of dissolved organic matter, Environ. Pollut., doi:10.1016/j.envpol.2013.08.023, 2014.

Royer, T. V. and David, M. B.: Export of dissolved organic carbon from agricultural streams in Illinois, USA, Aquat. Sci., doi:10.1007/s00027-005-0781-6, 2005.

Sabine, C. L. and Feely, R. A.: The oceanic sink for carbon dioxide, Greenh. gas Sink., 31–49, doi:10.1079/9781845931896.0000, 2004.

Sandberg, J., Andersson, A., Johansson, S. and Wikner, J.: Pelagic food web structure and carbon budget in the northern Baltic Sea: Potential importance of terrigenous carbon, Mar. Ecol. Prog. Ser., 268, 13–29, doi:10.3354/meps268013, 2004.

Santín, C., Doerr, S. H., Preston, C. M. and González-Rodríguez, G.: Pyrogenic organic matter production from wildfires: a missing sink in the global carbon cycle, Glob. Chang. Biol., doi:10.1111/gcb.12800, 2015.

Saunois, M., Bousquet, P., Poulter, B., Peregon, A., Ciais, P., Canadell, J. G., Dlugokencky, E. J., Etiope, G., Bastviken, D., Houweling, S., Janssens-Maenhout, G., Tubiello, F. N., Castaldi, S., Jackson, R. B., Alexe, M., Arora, V. K., Beerling, D. J., Bergamaschi, P., Blake, D. R., Brailsford, G., Brovkin, V., Bruhwiler, L., Crevoisier, C., Crill, P., Covey, K., Curry, C., Frankenberg, C., Gedney, N., Höglund-Isaksson, L., Ishizawa, M., Ito, A., Joos, F., Kim, H. S., Kleinen, T., Krummel, P., Lamarque, J. F., Langenfelds, R., Locatelli, R., Machida, T., Maksyutov, S., McDonald, K. C., Marshall, J., Melton, J. R., Morino, I., Naik, V., O'Doherty, S., Parmentier, F. J. W., Patra, P. K., Peng, C., Peng, S., Peters, G. P., Pison, I., Prigent, C., Prinn, R., Ramonet, M., Riley, W. J., Saito, M., Santini, M., Schroeder, R., Simpson, I. J., Spahni, R., Steele, P., Takizawa, A., Thornton, B. F., Tian, H., Tohjima, Y., Viovy, N., Voulgarakis, A., Van Weele, M., Van Der Werf, G. R., Weiss, R., Wiedinmyer, C., Wilton, D. J., Wiltshire, A., Worthy, D., Wunch, D., Xu, X., Yoshida, Y., Zhang, B., Zhang, Z. and Zhu, Q.: The global methane budget 2000-2012, Earth Syst. Sci. Data, doi:10.5194/essd-8-697-2016, 2016.

Saunois, M., Stavert, A. R., Poulter, B., Bousquet, P., Canadell, J. G., Jackson, R. B., Raymond, P. A., Dlugokencky, E. J., Houweling, S., Patra, P. K., Ciais, P., Arora, V. K., Bastviken, D., Bergamaschi, P., Blake, D. R., Brailsford, G., Bruhwiler, L., Carlson, K. M., Carrol, M., Castaldi, S., Chandra, N., Crevoisier, C., Crill, P. M., Covey, K., Curry, C. L., Etiope, G., Frankenberg, C., Gedney, N., Hegglin, M. I., Höglund-Isakson, L., Hugelius, G., Ishizawa, M., Ito, A., Janssens-Maenhout, G., Jensen, K. M., Joos, F., Kleinen, T., Krummel, P. B., Langenfelds, R. L., Laruelle, G. G., Liu, L., Machida, T., Maksyutov, S., McDonald, K. C., McNorton, J., Miller, P. A., Melton, J. R., Morino, I., Müller, J., Murgia-Flores, F., Naik, V., Niwa, Y., Noce, S., O'Doherty, S., Parker, R. J., Peng, C., Peng, S., Peters, G. P., Prigent, C., Prinn, R., Ramonet, M., Regnier, P., Riley, W. J., Rosentreter, J. A., Segers, A., Simpson, I. J., Shi, H., Smith, S. J., Steele, P. L., Thornton, B. F., Tian, H., Tohjima, Y., Tubiello, F. N., Tsuruta, A., Viovy, N., Voulgarakis, A., Weber, T. S., van Weele, M., van der Werf, G. R., Weiss, R. F., Worthy, D., Wunch, D., Yin, Y., Yoshida, Y., Zhang, W., Zhang, Z., Zhao, Y., Zheng, B., Zhu, Q., Zhu, Q. and Zhuang, Q.: The Global Methane Budget 2000–2017, Earth Syst. Sci. Data Discuss., doi:10.5194/essd-2019-128, 2019.

Sawakuchi, H. O., Neu, V., Ward, N. D., Barros, M. de L. C., Valerio, A. M., Gagne-Maynard, W., Cunha, A. C., Less, D. F. S., Diniz, J. E. M., Brito, D. C., Krusche, A. V. and Richey, J. E.: Carbon dioxide emissions along the lower Amazon River, Front. Mar. Sci., 4(MAR), 1–12, doi:10.3389/fmars.2017.00076, 2017.

von Schiller, D., Bernal, S., Dahm, C. N. and Martí, E.: Nutrient and Organic Matter Dynamics in Intermittent Rivers and Ephemeral Streams, in Intermittent Rivers and Ephemeral Streams: Ecology and Management., 2017.

von Schiller, D., Datry, T., Corti, R., Foulquier, A., Tockner, K., Marcé, R., García-Baquero, G., Odriozola, I., Obrador, B., Elosegi, A., Mendoza-Lera, C., Gessner, M. O., Stubbington, R., Albariño, R., Allen, D. C., Altermatt, F., Arce, M. I., Arnon, S., Banas, D., Banegas-Medina, A., Beller, E., Blanchette, M. L., Blanco-Libreros, J. F., Blessing, J., Boëchat, I. G., Boersma, K. S., Bogan, M. T., Bonada, N., Bond, N. R., Brintrup, K., Bruder, A., Burrows, R. M., Cancellario, T., Carlson, S. M., Cauvy-Fraunié, S., Cid, N., Danger, M., de Freitas Terra, B., Dehedin, A., De Girolamo, A. M., del Campo, R., Díaz-Villanueva, V., Duerdoth, C. P., Dyer, F., Faye, E., Febria, C., Figueroa, R., Four, B., Gafny, S., Gómez, R., Gómez-Gener, L., Graça, M. A. S., Guareschi, S., Gücker, B., Hoppeler, F., Hwan, J. L., Kubheka, S., Laini, A., Langhans, S. D., Leigh, C., Little, C. J., Lorenz, S., Marshall, J., Martín, E. J., McIntosh, A., Meyer, E. I., Miliša, M., Mlambo, M. C., Moleón, M., Morais, M., Negus, P., Niyogi, D., Papatheodoulou, A., Pardo, I., Pařil, P., Pešić, V., Piscart, C., Polášek, M., Rodríguez-Lozano, P., Rolls, R. J., Sánchez-Montoya, M. M., Savić, A., Shumilova, O., Steward, A., Taleb, A., Uzan, A., Vander Vorste, R., Waltham, N., Woelfle-Erskine, C., Zak, D., Zarfl, C. and Zoppini, A.: Sediment Respiration Pulses in Intermittent Rivers and Ephemeral Streams, Global Biogeochem. Cycles, doi:10.1029/2019GB006276, 2019.

Schlitzer, R.: Carbon export fluxes in the Southern Ocean: Results from inverse modeling and comparison with satellite-based estimates, Deep. Res. Part II Top. Stud. Oceanogr., doi:10.1016/S0967-0645(02)00004-8, 2002.

Schmidt, M. W. I., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D. A. C., Nannipieri, P., Rasse, D. P., Weiner, S. and Trumbore, S. E.: Persistence of soil organic matter as an ecosystem property, Nature, doi:10.1038/nature10386, 2011.

Shen, Y., Chapelle, F. H., Strom, E. W. and Benner, R.: Origins and bioavailability of dissolved organic matter in groundwater, Biogeochemistry, doi:10.1007/s10533-014-0029-4, 2015.

Shin, W. J., Chung, G. S., Lee, D. and Lee, K. S.: Dissolved inorganic carbon export from carbonate and silicate catchments estimated from carbonate chemistry and δ 13C DIC, Hydrol. Earth Syst. Sci., doi:10.5194/hess-15-2551-2011, 2011.

Siebert, S., Burke, J., Faures, J. M., Frenken, K., Hoogeveen, J., Döll, P. and Portmann, F. T.: Groundwater use for irrigation - A global inventory, Hydrol. Earth Syst. Sci., doi:10.5194/hess-14-1863-2010, 2010.

Škerlep, M., Steiner, E., Axelsson, A. and Kritzberg, E. S.: Afforestation driving long-term surface water browning, Glob. Chang. Biol., doi:10.1111/gcb.14891, 2019.

Slomp, C. P. and Van Cappellen, P.: Nutrient inputs to the coastal ocean through submarine groundwater discharge: Controls and potential impact, J. Hydrol., doi:10.1016/j.jhydrol.2004.02.018, 2004.

Smeaton, C. and Austin, W. E. N.: Sources, Sinks, and Subsidies: Terrestrial Carbon Storage in Mid-latitude Fjords, J. Geophys. Res. Biogeosciences, doi:10.1002/2017JG003952, 2017.

Sobek, S., Tranvik, L. J., Prairie, Y. T., Kortelainen, P. and Cole, J. J.: Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes, Limnol. Oceanogr., doi:10.4319/lo.2007.52.3.1208, 2007.

Stallard, R. F.: Terrestrial sedimentation and the carbon cycle: Coupling weathering and erosion to carbon burial, Global Biogeochem. Cycles, doi:10.1029/98GB00741, 1998.

Stepanenko, V., Mammarella, I., Ojala, A., Miettinen, H., Lykosov, V. and Vesala, T.: LAKE 2.0: A model for temperature, methane, carbon dioxide and oxygen dynamics in lakes, Geosci. Model Dev., doi:10.5194/gmd-9-1977-2016, 2016.

Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V. and Midgley, P. M.: IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, IPCC, AR5, 1535, 2013.

Stuart, M. E. and Lapworth, D. J.: Macronutrient status of UK groundwater: Nitrogen, phosphorus and organic carbon, Sci. Total Environ., doi:10.1016/j.scitotenv.2016.02.181, 2016.

Stutter, M. I., Graeber, D., Evans, C. D., Wade, A. J. and Withers, P. J. A.: Balancing macronutrient stoichiometry to alleviate eutrophication, Sci. Total Environ., doi:10.1016/j.scitotenv.2018.03.298, 2018.

Sugimura, Y. and Suzuki, Y.: A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample, Mar. Chem., doi:10.1016/0304-4203(88)90043-6, 1988.

Tang, J., Yurova, A. Y., Schurgers, G., Miller, P. A., Olin, S., Smith, B., Siewert, M. B., Olefeldt, D., Pilesjö, P. and Poska, A.: Drivers of dissolved organic carbon export in a subarctic catchment: Importance of microbial decomposition, sorption-desorption, peatland and lateral flow, Sci. Total Environ., doi:10.1016/j.scitotenv.2017.11.252, 2018.

Taylor, S., Gilbert, P. J., Cooke, D. A., Deary, M. E. and Jeffries, M. J.: High carbon burial rates by small ponds in the landscape, Front. Ecol. Environ., doi:10.1002/fee.1988, 2019.

Tesi, T., Langone, L., Giani, M., Ravaioli, M. and Miserocchi, S.: Source, diagenesis, and fluxes of particulate organic carbon along the western adriatic Sea (mediterranean Sea), Mar. Geol., doi:10.1016/j.margeo.2013.03.001, 2013.

Tian, H., Yang, Q., Najjar, R. G., Ren, W., Friedrichs, M. A. M., Hopkinson, C. S. and Pan, S.: Anthropogenic and climatic influences on carbon fluxes from eastern North America to the Atlantic Ocean: A process-based modeling study, J. Geophys. Res. Biogeosciences, doi:10.1002/2014JG002760, 2015.

Tiegs, S. D., Costello, D. M., Isken, M. W., Woodward, G., McIntyre, P. B., Gessner, M. O., Chauvet, E., Griffiths, N. A., Flecker, A. S., Acuña, V., Albariño, R., Allen, D. C., Alonso, C., Andino, P., Arango, C., Aroviita, J., Barbosa, M. V. M., Barmuta, L. A., Baxter, C. V., Bell, T. D. C., Bellinger, B., Boyero, L., Brown, L. E., Bruder, A., Bruesewitz, D. A., Burdon, F. J., Callisto, M., Canhoto, C., Capps, K. A., Castillo, M. M., Clapcott, J., Colas, F., Colón-Gaud, C., Cornut, J., Crespo-Pérez, V., Cross, W. F., Culp, J. M., Danger, M., Dangles, O., De Eyto, E., Derry, A. M., Villanueva, V. D., Douglas, M. M., Elosegi, A., Encalada, A. C., Entrekin, S., Espinosa, R., Ethaiya, D., Ferreira, V., Ferriol, C., Flanagan, K. M., Fleituch, T., Shah, J. J. F., Barbosa, A. F., Friberg, N., Frost, P. C., Garcia, E. A., Lago, L. G., Soto, P. E. G., Ghate, S., Giling, D. P., Gilmer, A., Gonçalves, J. F., Gonzales, R. K., Graça, M. A. S., Grace, M., Grossart, H. P., Guérold, F., Gulis, V., Hepp, L. U., Higgins, S., Hishi, T., Huddart, J., Hudson, J., Imberger, S., Iñiguez-Armijos, C., Iwata, T., Janetski, D. J., Jennings, E., Kirkwood, A. E., Koning, A. A., Kosten, S., Kuehn, K. A., Laudon, H., Leavitt, P. R., Da Silva, A. L. L., Leroux, S. J., LeRoy, C. J., Lisi, P. J., MacKenzie, R., Marcarelli, A. M., Masese, F. O., McKie, B. G., Medeiros, A. O., Meissner, K., Miliša, M., Mishra, S., Miyake, Y., Moerke, A., et al.: Global patterns and drivers of ecosystem functioning in rivers and riparian zones, Sci. Adv., doi:10.1126/sciadv.aav0486, 2019.

Tipping, E., Boyle, J. F., Schillereff, D. N., Spears, B. M. and Phillips, G.: Macronutrient processing by temperate lakes: A dynamic model for long-term, large-scale application, Sci. Total Environ., doi:10.1016/j.scitotenv.2015.09.129, 2016.

Tóth, J.: A theoretical analysis of groundwater flow in small drainage basins, J. Geophys. Res., doi:10.1029/jz068i016p04795, 1963.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dillon, P., Finlay, K., Fortino, K., Knoll, L. B., Kortelainen, P. L., Kutser, T., Larsen, S., Laurion, I., Leech, D. M., Leigh McCallister, S., McKnight, D. M., Melack, J. M., Overholt, E., Porter, J. A., Prairie, Y., Renwick, W. H., Roland, F., Sherman, B. S., Schindler, D. W., Sobek, S., Tremblay, A., Vanni, M. J., Verschoor, A. M., Von Wachenfeldt, E. and Weyhenmeyer, G. A.: Lakes and reservoirs as regulators of carbon cycling and climate, Limnol. Oceanogr., 54(6 PART 2), 2298–2314, doi:10.4319/lo.2009.54.6_part_2.2298, 2009.

Tye, A. M. and Lapworth, D. J.: Characterising changes in fluorescence properties of dissolved organic matter and links to N cycling in agricultural floodplains, Agric. Ecosyst. Environ., doi:10.1016/j.agee.2016.01.033, 2016.

Verdonschot, R. C. M., Keizer-vlek, H. E. and Verdonschot, P. F. M.: Biodiversity value of agricultural drainage ditches: A comparative analysis of the aquatic invertebrate fauna of ditches and small lakes, Aquat. Conserv. Mar. Freshw.

Ecosyst., doi:10.1002/aqc.1220, 2011.

Vodacek, A., Hogel, F. E., Swift, R. N., Yungel, J. K., Peltzer, E. T. and Blough, N. V.: The use of in situ and airborne fluorescence measurements to determine UV absorption coefficients and DOC concentrations in surface waters, Limnol. Oceanogr., doi:10.4319/lo.1995.40.2.0411, 1995.

Wallin, M., Buffam, I., Öquist, M., Laudon, H. and Bishop, K.: Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: Concentrations and downstream fluxes, J. Geophys. Res. Biogeosciences, doi:10.1029/2009jg001100, 2010.

Wallin, M. B., Campeau, A., Audet, J., Bastviken, D., Bishop, K., Kokic, J., Laudon, H., Lundin, E., Löfgren, S., Natchimuthu, S., Sobek, S., Teutschbein, C., Weyhenmeyer, G. A. and Grabs, T.: Carbon dioxide and methane emissions of Swedish low-order streams-a national estimate and lessons learnt from more than a decade of observations, Limnol. Oceanogr. Lett., doi:10.1002/lol2.10061, 2018.

Wang, Z. A. and Cai, W. J.: Carbon dioxide degassing and inorganic carbon export from a marsh-dominated estuary (the Duplin River): A marsh CO2 pump, Limnol. Oceanogr., doi:10.4319/lo.2004.49.2.0341, 2004.

Wassenaara, L. I., Aravena, R., Fritz, P. and Barker, J. F.: Controls on the transport and carbon isotopic composition of dissolved organic carbon in a shallow groundwater system, Central Ontario, Canada, Chem. Geol. Isot. Geosci. Sect., doi:10.1016/0168-9622(91)90032-R, 1991.

Webb, J. R., Leavitt, P. R., Simpson, G. L., Baulch, H. M., Haig, H. A., Hodder, K. R. and Finlay, K.: Regulation of carbon dioxide and methane in small agricultural reservoirs: Optimizing potential for greenhouse gas uptake, Biogeosciences, doi:10.5194/bg-16-4211-2019, 2019.

Wiegner, T. N. and Seitzinger, S. P.: Photochemical and microbial degradation of external dissolved organic matter inputs to rivers, Aquat. Microb. Ecol., doi:10.3354/ame024027, 2001.

Wik, M., Varner, R. K., Anthony, K. W., MacIntyre, S. and Bastviken, D.: Climate-sensitive northern lakes and ponds are critical components of methane release, Nat. Geosci., doi:10.1038/ngeo2578, 2016.

Williams, J. R.: Sediment routing for agricultural watersheds, JAWRA J. Am. Water Resour. Assoc., doi:10.1111/j.1752-1688.1975.tb01817.x, 1975.

Williamson, J., Tye, A., Lapworth, D., Monteith, D., Sanders, R., Mayor, D. J., Barry, C., Bowes, M., Burden, A., Callaghan, N., Farr, G., Felgate, S.L., Gilbert, P., Hargreaves, G., Keenan, P., Kitidis, V., Juergens, M., Martin, A., Mounteney, I., Nightingale, P., Pereira, G., Olszewska, J., Pickard, A., Rees, A., Spears, B., Stinchcombe, M., White, D., Williams, P., Worrall, F., and Evans. C. Landscape inflences on the riverine export of DOC in Great Britain (Submitted).

Wilson, H. F. and Xenopoulos, M. A.: Effects of agricultural land use on the composition of fluvial dissolved organic matter, Nat. Geosci., doi:10.1038/ngeo391, 2009.

Winterdahl, M., Wallin, M. B., Karlsen, R. H., Laudon, H., Öquist, M. and Lyon, S. W.: Decoupling of carbon dioxide and dissolved organic carbon in boreal headwater streams, J. Geophys. Res. Biogeosciences, doi:10.1002/2016JG003420, 2016.

Worrall, F., Davies, H., Bhogal, A., Lilly, A., Evans, M., Turner, K., Burt, T., Barraclough, D., Smith, P. and Merrington, G.: The flux of DOC from the UK - Predicting the role of soils, land use and net watershed losses, J. Hydrol., doi:10.1016/j.jhydrol.2012.04.053, 2012.

Worrall, F., Howden, N. J. K., Burt, T. P. and Bartlett, R.: Declines in the dissolved organic carbon (DOC) concentration and flux from the UK, J. Hydrol., doi:10.1016/j.jhydrol.2017.12.001, 2018.

Yamanaka, Y. and Tajika, E.: Role of dissolved organic matter in the marine biogeochemical cycle: Studies using an ocean biogeochemical general circulation model, Global Biogeochem. Cycles, doi:10.1029/97GB02301, 1997.

Yan, J., Manelski, R., Vasilas, B. and Jin, Y.: Mobile colloidal organic carbon: An underestimated carbon pool in global carbon cycles?, Front. Environ. Sci., doi:10.3389/fenvs.2018.00148, 2018.

Yool, A., Popova, E. E. and Anderson, T. R.: MEDUSA-2.0: An intermediate complexity biogeochemical model of the marine carbon cycle for climate change and ocean acidification studies, Geosci. Model Dev., doi:10.5194/gmd-6-1767-2013, 2013.

Yvon-Durocher, G., Allen, A. P., Bastviken, D., Conrad, R., Gudasz, C., St-Pierre, A., Thanh-Duc, N. and Del Giorgio, P. A.: Methane fluxes show consistent temperature dependence across microbial to ecosystem scales, Nature, doi:10.1038/nature13164, 2014.

Zhang, H., Lauerwald, R., Regnier, P., Ciais, P., Yuan, W., Naipal, V., Guenet, B., Van Oost, K. and Camino-Serrano, M.: An effective upscaling scheme for implementing the lateral soil and carbon movement processes into large-scale a land surface model, J. Adv. Model. Earth Syst., n.d.

Zhou, J. L., Rowland, S., Fauzi, R., Mantoura, C. and Braven, J.: The formation of humic coatings on mineral particles under simulated estuarine conditions-A mechanistic study, Water Res., doi:10.1016/0043-1354(94)90008-6, 1994.

Appendix 1 – Activities of the working group

The above objectives were met through a series of three sequential workshops (WS) which were held in areas with existing infrastructure to maximise the exchange of information on monitoring techniques.

1.3.1 Workshop 1: Skogaryd, Sweden (11th – 14th January 2018)

Figure 1: WS1 participants during a field visit to a forested monitoring station near the Skogaryd research station which hosted our stay.

WS1 was held at the Skogaryd Research Station, Sweden and hosted by the University of Gothenburg. Day 1 included presentations from many workshop participants (Table 1) covering a range of subjects and methodologies relating to measuring C fluxes across the land-ocean continuum. These presentations prompted discussions about national differences in the extent to which land-ocean C fluxes are measured and understood. The workshop included field visits to various sites within the Skogaryd research catchment to observe the installation of Eddy Covariance Flux Towers and SkyGas systems in both terrestrial and lake environments, and a demonstration of low-cost, automated floating gas flux chambers developed by David Bastviken and colleagues.

Table 1: Authors and titles of presentations made at RINGO 1.4 WS1

Name	Title
Daniel Mayor	LOCATE: measuring GB-scale land-ocean C fluxes
Chris Evans	Integrating gaseous and aquatic C fluxes
Annalea Lohila and Ivan Mammarella	An overview of recent research activities in Finland related to lake-atmosphere GHG exchange and (to some extent) C transport from land to Baltic sea
Anna Luchetta	Monthly variations of pCO_2 in the coastal waters of the Gulf of Trieste (northern Adriatic Sea) and estimates of air-sea exchanges
Michele Giani	Seasonal variability of CO_2 system in the coastal waters of the Trieste Gulf (Marine Protected Area of Miramare)
David Bastviken	Observation systems for aquatic greenhouse gas exchange – challenges, alternatives, and experiences from e.g. the Skögaryd Research Catchment
Marcus Wallin	Source and fate of C in low-order streams
Antonine Verlet-Banide	High-frequency water- and air-side methane (CH_4) measurements
Adam Hastie	C cascades from land to ocean in the Anthropocene: data driven models - data validated earth system models

1.3.2 Workshop 2: Southampton, UK (19th – 21st November 2018)

WS2 was held in Southampton, UK at the U. K. National Oceanography Centre. As with WS1, Day 1 included presentations from a range of participants and a number of invited speakers (Table 2) covering a broad range of relevant subjects. Delegates took part in a field trip aboard the University of Southampton's research vessel, *R.V. Callista*, where they were introduced to a range of oceanographic tools including the deployment of a CTD (Conductivity, Temperature and Depth) and sampling rosette, the underway sampling system and the on-board Acoustic Doppler Current Profiler (ADCP). A tour of the NOCS marine robotics facility gave delegates the opportunity to observe a wide range of autonomous vehicles, and underwater sampling technologies. Discussion was driven by breakout sessions covering the following topics: What is the status of European land-ocean carbon flux measurements? What parameters are required for future monitoring best practice? What methodologies are currently used to make these measurements? Are these methodologies optimal? What are the associated uncertainties in these measurements?

Figure 2: WS2 participants during a tour of the Marine Autonomous Robotics Systems (MARS) facility, National Oceanography Centre (NOC), Southampton, UK.

Table 2: Authors and titles of presentations made at RINGO 1.4 WS2. (= invited non-delegate presentation).*

Name	Title
Stacey Felgate	Progress made since WP1
Anders Lindroth	A new headspace system for semi-continuous measurements of CO2 and CH4 surface water concentrations.
Michael Peacock	GHG emissions from ditches and artificial ponds
Ronny Lauerwald	Statistical and process-based modelling of inland water C fluxes
Chris Evans	GB scale river monitoring via the LOCATE project
Vas Kitidis	C fluxes on the NW European shelf
Tom Anderson*	Discussion of the LOCATE UniDOM land-ocean C flux model
Geoff Hargreves*	Presentation of the LOCATE sensor pods
Matt Mowlem*	Presentation of the NOC biogeochemical sensor development facility

Figure 3: WS3 participants following a successful three-day meeting in Hyytiälä, Finland.

1.3.3 Workshop 3: Hyytiälä, Finland (5^{th} – 8^{th} November 2019)

The final WS (WS3) was held at the Hyytiälä Research Station in Finland, hosted by the University of Helsinki. Day 1 opened with a series of presentations on relevant subject areas (Table 3), with the rest of the WS being spent constructing this report. Field visits allowed delegates the opportunity to observe Eddy Covariance systems across a number of ecosystem types (wetland, Lake (Lake Kuivajärvi) and forest (ICOS SMEAR II station). A breakout session led by Ivan Mammarella took place on Day 2 to discuss the parameters which must be measured in order to fulfil the minimum and ideal requirements of a European LOAC C flux monitoring network (e.g. Table 6). Several delegates joined this breakout session via Skype.

Table 3: Authors and titles of presentations made at RINGO 1.4 WS3.

Name	Title
Dan Mayor	What are the minimum and ideal requirements for a land-ocean C monitoring network?
Amy Piccard	Aquatic C from Peatlands - Impacts of land use and extreme events
Vas Kitidis	CDOM Spectral Slopes in the Land-Ocean Continuum
Annalea Lohila	Recharge from peatland influencing groundwater patterns in river side esker - ICOS Class I site FI-Sod
Stacey Felgate	Outline of the draft report for agreement

Appendix 2 – Examples of Autonomy

Here we present two examples of autonomy currently in use to study land-ocean C fluxes. The inclusion of these examples is not endorsement, but rather is intended to give a flavor of what is available. Advances are rapid in this field, and thus any decision on autonomous technology most appropriate to pan-European flux monitoring is best taken as and when funding becomes likely.

1. LOCATE Sensor Pods

The UK's Land Ocean Carbon Transfer (LOCATE) project (www.locate.ac.uk) developed a package of autonomous sensor packages designed to be deployed from a river or estuary bank for periods of months to years (Figure 7). These 'sensor pods' carry a customisable suite of sensors aimed at characterising land-ocean C fluxes, including a spectrolyser which measures an optical fingerprint over multiple wavelengths to provide proxy values for DOC, a fluorimeter which are selectable from a range of options and LOCATE specified: Conductivity and temperature, Total Algae (chlorophyll and Blue/Green Algae), Dissolved Oxygen, Turbidity, pH/ORP Sensor and fDOM Sensor. The S::Can Spectro::lyser measures an optical fingerprint of the water over a range of wavelengths. The peaks in the return signal determine the concentration of different parameters, according to the calibration used. The data from the Spectro::lyser are stored on the device and downloaded manually.

Figure 8: An example set up for the LOCATE sensor pod components. The submersible sensors pictured consist of the Xylem EXO2 multi-parameter sonde, an S::Can Spectro::lyser and a Vaisala CO2 sensor. The atmospheric sensors (not pictured) consist of a Vaisala met station and a Skue Instruments PAR sensor.

These submersible sensors are mounted to a framework to prevent damage, and that framework can host atmospheric sensors that connect to a central logger, powered by rechargeable batteries. The logger uses the 3G, GPRS network to transmit data to the remote server where the data can be viewed and downloaded. The batteries are charged by mains electricity, or by renewable energy sources. Deployment has been most successful when undertaken at key locations where auxiliary data is already measured (i.e. co-located with a discharge station and/or weather station) and within easy reach of the maintaining institute. Data are transmitted in real time, but maintenance visits are required on a monthly basis, mostly to de-foul the sensors. Location must be secure (i.e. private land). Data are produced at high temporal resolution, allowing ephemeral events to be captured that are ordinarily missed via manual sampling (see Table 7) .

Pictured are two deployments, one in a remote catchment using solar panels and a 'trolley' system to maintain surface position with changing tides and one destined for an urban marina where mains power and a floating jetty were provided (figure 8).

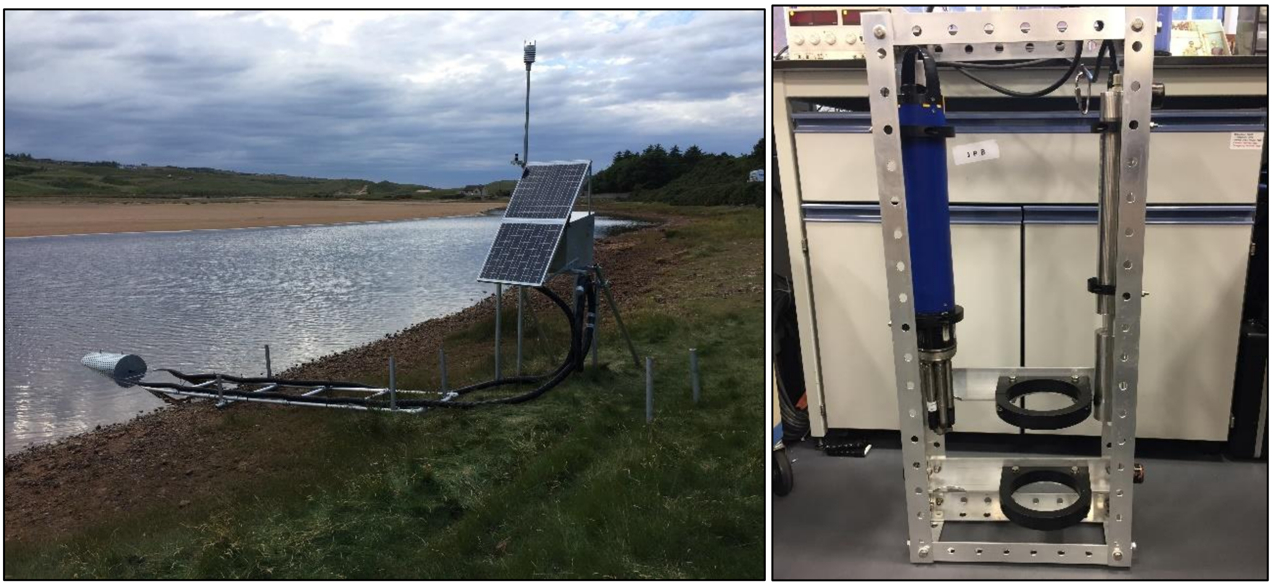

Figure 9: Deployment of a LOCATE sensor pod in the Halladale River, N. Scotland. This deployment included solar panels to power the instruments in lieu of a mains hook-up, and a buoyant trolley system to allow for changes in water height. Bespoke cage de

2. The CAMEL

The Containerised Autonomous Marine Environmental Laboratory (CAMEL; Figure 9) is a fully containerised research facility developed by the National Oceanography Centre's Marine Autonomy and Robotic Systems (MARS; https://mars.noc.ac.uk) and operated by the UK's National Marine Equipment Pool. The system can be shipped to any port and deployed from a quayside, beach, riverbank, or vessel. The concept is simple, yet highly innovative: two shipping containers act as a self-contained research laboratory, workshop, and control centre, complete with an autonomous surface vehicle called the C-Worker 4. The facility is housed in two fully transportable ISO containers which are insulated, air-conditioned, and can be powered via mains hook-up or their own diesel generators. A workshop is well equipped to service and repair the instrumentation, whilst an Operations Room holds all required communications equipment to run autonomous surveys and collect data. The CAMEL holds sensors securely during campaigns and transportation, and carries a range of operational equipment including a weather station, wave-measuring buoy with GPS, a sound velocity profiler, a micro Remotely Operated Vehicle (ROV), and an inflatable boat with an outboard motor.

The facility as a whole was designed to map and monitor marine environments in Small Island Developing States (SIDS), the autonomous systems which the CAMEL houses have broad applicability to other environments. In particular, the C-Worker 4 was recently successfully deployed in a mid-sized estuary across the full salinity gradient, adding confidence in its suitability for both marine and freshwater monitoring activities. A bespoke facility such as the one described above could be produced, with the basic facility (excluding the C-Worker) costing ~£200k.

Figure 10: CAMEL containers ready to deploy from a quay in Central America, and the C-Worker 4 in action.

At a cost of ~£350k, the C-worker 4 can be purchased as a stand-alone item (www.asvglobal.com), and it is this product (or a similar one) which we would foresee being of most use in the high-resolution spatial monitoring of European waters, particularly with regards the monitoring of estuaries and larger fluvial systems and lakes. The NOC vehicle carries three easily exchangeable scientific payloads, each being lowered remotely through the hull of the USV after launch:

(1) A **hydrographic** payload equipped with a high-resolution multibeam echo sounder (cost = ~£170k).

(2) A **geophysical** payload equipped with a high-grade side-scan sonar, with interferometric bathymetry and a sub-bottom profiler system (cost = ~£170k).

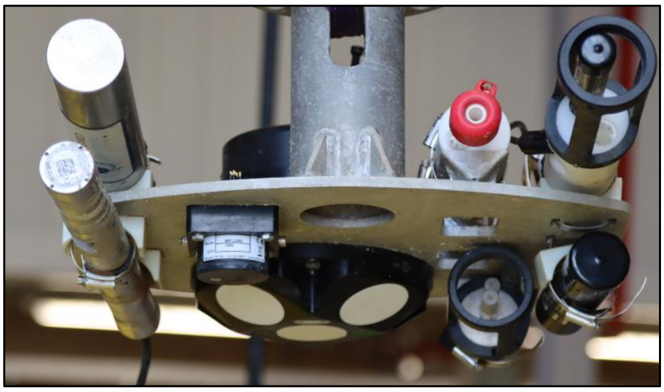

Figure 11: The C-worker 4's Oceanographic Payload suspended from under the surface vehicle.

(3) An **oceanographic** payload equipped with a suite of sensors including an Acoustic Doppler Current Profiler (ADCP), a CTD (conductivity, temperature, and depth sensor), a fluorimeter that allows for proxy measurements of i.e. nutrients, chlorophyll, and organic matter, and sensors capable of quantifying pH, DO, and pCO_2 (cost = ~£120k; Figure 11).

Subject to space and power requirements, other sensors can be added as required and according to deployment requirements. Land-ocean fluxes could be monitored using only the oceanographic payload or some derivation thereof, but the purchase of the additional payloads would ensure maximum value from any investment and the ability to utilise the resource across multiple projects. The C-Worker 4 has a fully contained, self-righting hull (figure x), is road transportable on a trailer and easily launched/recovered from an A-frame set-up, has a 24-48 hour endurance period, a maximum weight of about 900kg, and a maximum speed of 7 knots. Of note is the shallow draft (~ 60cm), high level of manoeuvrability, and excellent track-holding, making the C-Worker 4 (or similar vehicle) particularly suitable for accessing estuaries and fluvial waters which might be problematic for i.e. ribs and small manned vessels, and especially where there is a need to repeat the same trajectory.

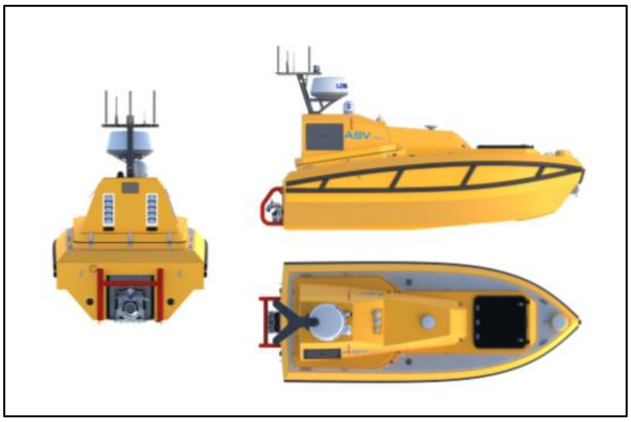

Figure 12: The C-Worker 4 (image provided by ASV; for more info see www.asvglobal.com).

To purchase the C-Worker and oceanographic package would cost ~£500k, and we would forsee one unit being shared by multiple states. However, bulk purchase would attract a discount, and other makes and models are on the market with a lower spec and more economical price-point. Direct quotes should be obtained from manufacturers as and when purchase of such a unit becomes a possibility.