Science of the Total Environment 517 (2015) 10–21

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Effects of predicted climatic changes on distribution of organic contaminants in brackish water mesocosms

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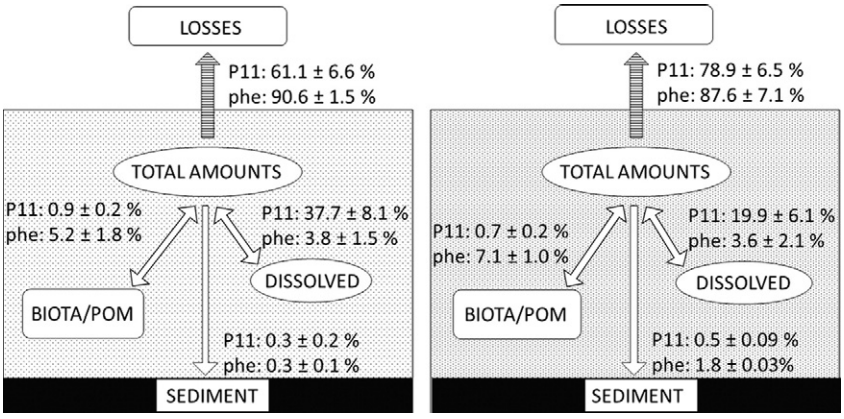
HIGHLIGHTS

- More contaminants remained in the ecosystem at higher organic carbon levels.
- More contaminants were lost in the higher temperature treatments.
- The combined effects are competitive with respect to contaminant cycling.
- The individual properties of each contaminant determine their respective fate.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 November 2014
Received in revised form 10 February 2015
Accepted 13 February 2015
Available online 21 February 2015

Editor: Mark Hanson

Keywords:
Climate change
Temperature
Dissolved organic carbon
Organic contaminants
Environmental distribution
Mesocosms

ABSTRACT

Predicted consequences of future climate change in the northern Baltic Sea include increases in sea surface temperatures and terrestrial dissolved organic carbon (DOC) runoff. These changes are expected to alter environmental distribution of anthropogenic organic contaminants (OCs). To assess likely shifts in their distributions, outdoor mesocosms were employed to mimic pelagic ecosystems at two temperatures and two DOC concentrations, current: 15 °C and 4 mg DOC L^{-1} and, within ranges of predicted increases, 18 °C and 6 mg DOC L^{-1}, respectively. Selected organic contaminants were added to the mesocosms to monitor changes in their distribution induced by the treatments. OC partitioning to particulate matter and sedimentation were enhanced at the higher DOC concentration, at both temperatures, while higher losses and lower partitioning of OCs to DOC were observed at the higher temperature. No combined effects of higher temperature and DOC on partitioning were observed, possibly because of the balancing nature of these processes. Therefore, changes in OCs' fates may largely depend on whether they are most sensitive to temperature or DOC concentration rises. Bromoanilines, phenanthrene, biphenyl and naphthalene were sensitive to the rise in DOC concentration, whereas organophosphates, chlorobenzenes (PCBz) and polychlorinated biphenyls (PCBs) were more sensitive to temperature. Mitotane and diflufenican were sensitive to both temperature and DOC concentration rises individually, but not in combination.

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http://dx.doi.org/10.1016/j.scitotenv.2015.02.051
0048-9697/

1. Introduction

The effects of climate change are widely studied on global and local levels. The Intergovernmental Panel on Climate Change Fifth Assessment Report (IPCC 2013) predicts that mean global temperatures will be 1–1.5 °C higher in 2016–2035 than the 1850–1900 median. Long-term predictions for the period 2081–2100 include mean global warming of 1.4–1.7 °C, with "polar amplification" (2.2 to 2.4 times the global mean increase above latitudes of 67.5° N), resulting in 3.1 to 4.8 °C increases in the northern regions (Anon., 2013). Local climate change models predict increases in sea surface temperatures, of up to 3 °C, and precipitation in the north Baltic Sea region (Neumann, 2010; Schimanke et al., 2012), accompanied by higher runoff of terrestrial dissolved organic carbon (DOC) driven by the anticipated increase in precipitation (Andersson et al., in press; Graham, 2004; Eriksson Hagg et al., 2010).

Climate change is also expected to affect the environmental fates of organic contaminants (OCs), which are thought to be largely governed by temperature (Kallenborn et al., 2012; Macdonald et al., 2003). However, their fates are also influenced by numerous other variables that would be affected by anticipated climate changes, including: wind speed and direction, precipitation patterns, rising sea levels and reductions in ice cover (Kallenborn et al., 2012; Bloomfield et al., 2006; Schiedek et al., 2007; Lamon et al., 2009). Temperature increases can also enhance mobilization of OCs from reservoirs such as natural waters, soils and sediments, and alter rates of OCs' accumulation, sorption and degradation (Macdonald et al., 2003). Indirect effects of climate change on OCs may include increased riverine runoff and changes in long-range transport. Increased runoffs into the northern Baltic Sea are anticipated to result in higher DOC inflows, which may affect the amounts (and possibly profiles) of organic contaminants associated with DOC (Graham, 2004; Eriksson Hagg et al., 2010). The quantity and quality of DOC strongly influence the environmental fate of OCs in brackish water ecosystems (Krop et al., 2001; Uhle et al., 1999), such as the Baltic Sea. For example, changes in partitioning of compounds between water and DOC can affect bioaccumulation pathways in ways that depend on the structure of the food-web (Andersson, 2014). Global climate change is also expected to affect atmospheric long-range transport of OCs (Macdonald et al., 2003) and both their wet and dry deposition patterns. There have been several attempts to predict these changes using multimedia fate modeling (Kallenborn et al., 2012; Bloomfield et al., 2006; Schiedek et al., 2007; Lamon et al., 2009; Noyes et al., 2009; Dalla Valle et al., 2007).

Climate change and other slow processes are difficult to study in the field. Thus, mesocosms are often used to elucidate likely responses of specific modeled ecosystems to such processes and various stressors. Notably, mesocosms have been frequently used to investigate the toxicity and physiological effects of various herbicides, insecticides, fungicides and pharmaceuticals on either single species or specific food webs (Pablo and Hyne, 2009; Nietch et al., 2013; Mohr et al., 2008; Maltby et al., 2005; Lizotte et al., 2013; Bakke, 1988). They have also been used to assess the transport and fate of dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), chlorpyrifos and PAHs (Gohil et al., 2014; Zhou et al., 2013; Pablo et al., 2008; Yamada et al., 2003), but not potential effects of climate change on the distribution and fate of OCs in (model) ecosystems.

Thus, in the study presented here we investigated effects of two climatic changes (temperature and DOC rises) predicted by local climate change scenarios on the environmental distribution of OCs in Baltic Sea water mesocosms. Effects of increases in temperature (3 °C) and DOC levels (2 mg L^{-1}) were studied both separately and in combination. These values are based on the highest predicted increase of the respective parameter (Neumann, 2010; Meier, 2006). Organic compounds were added as a mixture at sub-acute toxicity levels (0.1 μg L^{-1}). The mixture included some legacy persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated benzenes (PCBz), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), which are bioaccumulative and have well known adverse effects on living organisms including humans (Schwarzenbach, 2003; Nacci et al., 2002; Baron, 1981; Binelli and Provini, 2004). We also included emerging contaminants, including anthropogenic organophosphates (used as plasticizers and flame retardants) and biogenic low molecular weight brominated compounds (Bidleman et al., 2014). The compounds were selected to represent diverse classes of environmental contaminants, including polar and non-polar compounds and numerous functional groups.

2. Materials

A DOC extract was prepared for addition to the mesocosms from soil collected from a bank of the river Öreälven located west from Norrbyn, Sweden using a spade. Its drainage basin is dominated by forested areas and is essentially undisturbed by anthropogenic activities (besides forestry and some small scale farming). The river has high concentrations of humic substances, during the spring period the river humic concentrations are >100 μg L^{-1}. The detailed properties of the river are described elsewhere (Andersson et al., 2013). MilliQ water was added to the soil, which consisted mainly of peat material, together with Amberlite IRC748I ion-exchange resin to remove metal ions. The resulting suspension was filtered through a 90 μm filter and the DOC content of the filtrate was determined gravimetrically following filtration through a 0.2 μm filter. Appropriate amounts of the 90 μm filtrate were added to the mesocosms (described below) to give the desired DOC concentrations. Dichloromethane, acetone, methanol, cyclohexane, toluene, and ethyl acetate (GC–MS grade) were purchased from Merck and Fischer Scientific. Whatman glass fiber filters (GF/A and Fs, 1.0 and 0.7 μm, 47 mm, 20 mm and 150 mm diameter), Eppendorf tubes and Falcon tubes were obtained from VWR International AB (Stockholm, Sweden). Spiking solutions of OCs were prepared from individual certified standard materials purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Isotope labeled (deuterated or ^{13}C) internal standards were obtained from QMx laboratories Ltd. (Essex, United Kingdom) and Cambridge Isotope Laboratories Inc. (Tewksbury, MA, USA). Information about the individual OCs can be found in Tables 1 and S1 (Supplementary Information, SI). Solid-phase microextraction (SPME) assemblies including fused silica polydimethylsiloxane (FS-PDMS) fibers with a 100 μm coating mounted in a manual SPME holder were purchased from Supelco, Sigma-Aldrich AB (Stockholm, Sweden). TurboVap (Biotage EU, Uppsala, Sweden) and Heidolph (Schwabach, Germany) evaporation systems were used to concentrate samples. For size exclusion chromatography a 150 mm internal diameter Omnifit glass column (Diba Industries Ltd. Cambridge, United Kingdom) was used. It was packed in-house with 27 g of SX-3 polystyrene-divinylbenzene (PS-DVB) copolymer Bio-Beads (Bio-Rad Laboratories AB, Sundbyberg, Sweden) according to the producer's instructions (Bio-Rad Bio-Gel, 2000).

3. Methods

3.1. Experimental design

Sets of brackish water mesocosms, prepared as described below, were used in a 2 × 2 full factorial experiment. The treatments were incubation at two temperatures (15 °C and 18 °C), with two DOC concentrations (ca. 4 mg L^{-1}, the initial concentration in the brackish water, and 6 mg L^{-1} DOC). OCs were added to all of these systems. In addition, control mesocosms (with no added OCs) were subjected to each treatment to track changes resulting from the added compounds. All treatments were applied in triplicate, thus there 24 mesocosms in total (Fig. 1).

The mesocosms were established in brand new 1 m^3 polypropylene tanks (Allembalage AB, Jordbro, Sweden), which were thoroughly rinsed with high pressure hot and cold water before filling. The selected