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Estimating surface water concentrations of "down-the-drain" chemicals in China using a global model

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Abstract

Predictions of surface water exposure to “down-the-drain” chemicals are presented which employ grid-based spatially-referenced data on average monthly runoff, population density, country-specific *per capita* domestic water and substance use rates and sewage treatment provision. Water and chemical load are routed through the landscape using flow directions derived from digital elevation data, accounting for in-stream chemical losses using simple first order kinetics. Although the spatial and temporal resolution of the model are relatively coarse, the model still has advantages over spatially inexplicit “unit-world” approaches, which apply arbitrary dilution factors, in terms of predicting the location of exposure hotspots and the statistical distribution of concentrations. The latter can be employed in probabilistic risk assessments. Here the model was applied to predict surface water exposure to “down-the-drain” chemicals in China for different levels of sewage treatment provision. Predicted spatial patterns of concentration were consistent with observed water quality classes for China.

Key Words: Global, Exposure, Chemical, Model, China

Capsule Abstract

A global-scale model was used to predict spatial patterns of “down-the-drain” chemical concentrations in China. Predictions were consistent with observed water quality classes, demonstrating the potential value of the model.

1. Introduction

"Down-the-drain" chemicals, also referred to as "daily use chemicals", include ingredients used in domestic consumer products (e.g. detergent ingredients such as surfactants, solvents, dyes, perfumes and bleaching agents) and pharmaceuticals, which may be disposed of with household wastewater. In most regions of the world, a significant fraction of household wastewater (either untreated or treated via municipal wastewater treatment plants - WWTPs) will eventually reach surface waters. The impact of such chemicals on receiving water bodies is typically assessed by comparing Predicted Environmental Concentrations (*PECs*) with a Predicted No Effect Concentration (*PNEC*). The latter is generally derived from (mainly laboratory-based) ecotoxicological effects data for a number of different taxonomic groups.

For consumer use of "down-the-drain" chemicals (and neglecting releases during factory production and/or formulation), a crude *PEC* for untreated sewage (PEC_{SEWAGE}) can be calculated by dividing the mass of substance used *per capita* (*U*, mg cap^{-1} day^{-1}) by the domestic *per capita* water use (*W*, L cap^{-1} day^{-1}). For the release of a chemical in a given country or region:

$$PEC_{SEWAGE} = \frac{U}{W} \qquad (1)$$

U can be calculated from tonnage using:

$$U = \frac{T.10^9}{365.P_{COUNTRY}} \quad (2)$$

where $P_{COUNTRY}$ is the population of the country into which the chemical is released and T (tonnes yr^{-1}) is the annual mass of chemical estimated to be used in the study area (country). PEC_{SEWAGE} can be adjusted for removal in WWTPs, if present, and for dilution of the WWTP effluent in the receiving water body to give a surface water *PEC* (PEC_{AQ}) downstream of a WWTP. In the case of a river with an upstream concentration of zero, the concentration immediately after mixing but prior to any in-stream degradation and dilution can be written:

$$PEC_{AQ} = \frac{(1-r).PEC_{SEWAGE}}{DF} \quad (3)$$

where r is the proportion of chemical removed in a WWTP, which ideally should be commensurate with monitoring data (Ort *et al*., 2010) but which can also be estimated from the results of standard laboratory biodegradation tests (e.g. Struijs *et al*., 1991; European Commission, 2003) and DF is the dilution factor which can be defined as:

$$DF = (Q+q)/q \quad (4)$$

in which Q is the discharge of the receiving water body upstream of the effluent (L s^{-1}) and q is the point-source discharge (L s^{-1}) from the WWTP.

This model is limited to assessing *PEC*s in the water column and not concentrations of chemicals sorbed to suspended or settled sediments. In addition, the model makes

the assumption that 100% of the chemical substance is disposed of via household wastewater which, in turn, is treated at WWTPs. It does not consider information on alternative wastewater disposal routes (e.g. discharge to soil or the sea). However, this assumption is supported by a number of studies which demonstrate that predicted concentrations of chemicals commonly used in laundry detergents derived from *per capita* consumption figures agree with monitoring data on chemical concentrations in raw wastewater and in rivers in Europe (e.g. Holt *et al.*, 1998; Whelan *et al.*, 1999; Price *et al*., 2009). Fox *et al.* (2002) showed that boron loads measured at 48 WWTPs across Europe corresponded well with *per capita* inputs predicted from detergent product sales data. Boron has previously been shown to be a good marker for substances contained in detergent products, as it is not biodegraded and is not substantially sorbed in sewers or in WWTPs. Similarly, several studies have reported that predicted linear alkylbenzene sulfonate concentrations generally agree with expectations based on *per capita* use and removal in WWTPs (e.g. Whelan *et al*., 1999; Price *et al*., 2009).

Since both Q and q vary significantly both spatially and temporally, screening-level (comparative) risk assessment models commonly consider a hypothetical "representative" scenario for local scale regulatory exposure assessments, in which the dilution factor is given an arbitrary value (e.g. a value of 10 is recommended in the TGD - European Commission, 2003). This approach is useful for identifying chemicals which may pose significant environmental risks at a given use rate and for facilitating the prioritisation of risk management. However, it is probably a poor predictor of the distribution of *actual* risk which will vary spatially and temporally as a consequence of hydrological variability (Johnson, 2010) and the sizes of point

source loads relative to receiving water discharge. These factors have been accounted for in models such as GREAT-ER (Geography-referenced Regional Exposure Assessment Tool for European Rivers: Feijtel. *et al.*, 1997; Schroeder *et al.*, 2002; Koormann *et al*., 2006; Price *et al.*, 2009), LF2K-WQX (Price *et al*., 2010; Williams *et al*., 2009) QMX (Warren *et al*., 2005; 2007) and PhATE (Cunningham *et al*., 2009; Cunningham *et al*., 2010; Capdevielle *et al*., 2008) which are designed for higher tier risk assessments in specific catchments. However, the application of such models is limited by data requirements (location and sizes of point sources and river discharge statistics). Furthermore, such approaches have mainly been developed in response to, or in anticipation of, regulatory requirements for risk assessment in Europe, North America and Japan and are often inappropriate for data poor areas (Warren *et al*., 2005).

In this paper, we explore the possibilities for improving predictions of point-source pollutant concentrations in surface waters using spatially-referenced global data sets of predicted runoff (derived from water balance model calculations using long-term global climate data) and population density. We extend the grid-based global estimation of dilution (Keller *et al.*, 2006) and national-scale load estimation for non-degradable chemicals, such as boron (Keller *et al.*, 2007) by introducing the potential for in-stream chemical degradation during routing. As an illustration, the model is applied to predict aquatic exposure to "down-the-drain" chemicals in China. These predictions will inevitably be crude estimates of local conditions, which will vary significantly spatially between and within water bodies and temporally, but may provide a reasonable initial estimate which can be refined locally if required. The greatest value of the proposed model is for better definition of overall risk to surface

fresh waters for a whole country or region as a viable alternative to standard scenario-based predictions, anywhere in the world.

2. Modelling Approach

2.1 Conceptual model and implementation

At a coarse level of spatial resolution point-source chemical loadings and river-reach specific discharge cannot be accurately estimated. However, a proxy for exposure estimates (PEC_{AQ}) based on population density and predicted runoff in a given region (e.g. catchment or country) has previously been developed (Keller *et al.*, 2007). In this approach, runoff is estimated by hydrologically effective rainfall, i.e. all water transfer from the land to surface waters via all major hydrological pathways (overland flow, throughflow and baseflow). River discharge (Q) is the product of the catchment area and the estimated mean runoff. Domestic wastewater discharge (q) can be expressed as the product of catchment area, population density and domestic *per capita* water use.

Cell-specific concentrations in a global grid-based model can be calculated from a combination of load estimations and the water balance via simple mass balance concepts. Load is routed through the flow direction network, discounting for degradation, which is assumed to take place according to first order kinetics. Concentration in each cell (C_i) is calculated from:

$$C_i = \frac{(1-F).P_i.U_i + F.(1-r).P_i.U_i + \sum L_{IN}}{Q_i} = \frac{P_i.U_i.(1-F.r) + \sum L_{IN}}{Q_i} \qquad (5)$$

where P_i and U_i are, respectively, the population and the *per capita* chemical consumption (g cap^{-1} day^{-1}) of cell *i*, *F* is the fraction of the population served by (at least) secondary sewage treatment, Q_i is total discharge (derived by a cumulative routing of discharge through the grid using the flow direction vectors) and L_{IN} is the influent load from an upstream cell (which may be many). L_{IN}, itself, is derived from an accumulation through the network with degradation in parallel. If Q_i is expressed in m^3 day^{-1} then C_i is in g m^{-3} i.e. mg L^{-1}. For each cell, load L_i is passed to the adjacent downslope cell with the lowest altitude:

$$L_i = [P_i.U_i.(1 - F.r) + \sum L_{INF}].\exp(-\gamma) \quad (6)$$

where γ is a dimensionless degradation term i.e.:

$$\gamma = \tau.k \quad (7)$$

in which *k* is the first order rate constant (h^{-1}) and τ is travel time (h). The special cases of chemicals which degrade so rapidly that insignificant chemical loads are passed to downstream cells and those which are perfectly conservative, such as boron (with no in-river loss: Keller *et al*., 2007) are captured by setting *k* to infinity and zero, respectively. Travel time is calculated as the quotient of the stream path length, *x* (m), and a nominal water velocity, *v* (m s^{-1}), allowing for stream channel sinuosity described by a factor, *S* (the ratio of the talweg distance to straightline distance):

$$\tau. = \frac{x.S}{v.3600} \quad (8)$$

The model was implemented in a Visual BASIC for Applications (VBA) program which invoked an iterative algorithm to calculate water and chemical load transfers between grid cells. Iteration is required because cells are visited sequentially by row and column order which means that they may receive inputs from cells which occur later in the sequence which, in turn, need to be cascaded through the network. In each iteration, chemical load is passed to downslope cells, discounting transfers for degradation. Cells may receive inputs from more than one upslope cell but only deliver water and chemical to one downslope cell (e.g. O'Callaghan and Mark, 1984). Note that although flow accumulation calculations can be performed in many commercial GIS software packages, routing chemical loads with decay is more challenging and requires the construction of a customised routine.

2.2 Hydrological data

2.2.1 Runoff Data

Long-term average monthly and annual runoff can be predicted using macroscale hydrological models. Macroscale models are those which are capable of being applied, without calibration, at the catchment scale over a large geographical domain (Arnell, 1999b). They have been used to define land-surface parameterization schemes in general circulation models (e.g. Kite *et al.*, 1994; Abdulla & Lettenmaier, 1997*a*; Nijssen *et al.*, 1997, Wood *et al.*, 1992; Arnell, 1999a) and for estimating water resource availability at global, continental or regional scales (e.g. Vorosmarty *et al.*, 1989; Abdulla & Lettenmaier, 1997*b*; Fekete *et al.*, 1999; Oki, 2001; Alcamo *et al.*, 2003). They are often based on a division of the global land surface into a grid, commonly with a spatial resolution of 0.5º latitude by 0.5º longditude (30 arc minutes). The actual dimensions of each grid cell will vary with latitude. At the equator cells are over 3000 km^2 but are less than 100 km^2 at very high latitudes. Typically, each cell is approximately 2000 km^2 in mid latitudes (Arnell, 1999c).

In this paper, we have used the runoff predictions (Figure 1) produced by Fekete *et al.* (1999) (see also Vorosmarty *et al.*, 1989 and Vorosmarty *et al.*, 1998). These data were generated by combining a simple water balance model with observed river discharge data. The gauged discharge data used were collated by the Global Runoff Data Centre (GRDC) from 1348 gauging stations with tributaries larger than 2500 km^2 and with time series exceeding 12 years with < 10% missing data. The water balance model uses the data set of Legates and Willmott (1990a) for global precipitation, the formula of Hamon (1963) to calculate evapotranspiration on the basis of temperature (using the data set of Legates and Willmott, 1990b), soil type

data from the FAO/UNESCO soil data bank (FAO/UNESCO, 1986), topographic data from the ETOPO5 global elevation data set (Edwards, 1989) and a contemporary land cover classification derived from the Terrestrial Ecosystem Model (Melillo *et al.*, 1993) with Olson's land use classification (Olson, 1991).

2.2.2 Flow direction

River discharge generally accumulates downstream with increasing catchment area. The mean annual runoff at any point in the channel network is the mean annual discharge divided by the total catchment area contributing to that point and, thus, represents an area-weighted average of spatial variations in runoff therein. For large catchments, upstream contributing cells in the runoff grid can be identified using topographic data derived from a Digital Terrain Model (DTM). An appropriate data set identified for the purposes of this study is that described by Graham *et al.*, (1999). This data set consists of flow direction and flow accumulation grids derived from the National Geophysical Data Center TerrainBase 5' Global DTM (Row *et al.*, 1995) at 5', 1/2° and 1° resolutions. The flow direction and accumulation data were derived from a filled DTM using a single direction algorthim (flow only in the direction of the steepest downslope cell – e.g. O'Callaghan and Mark, 1984), with manual corrections for discrepancies between model coastlines. Note that flow is accumulated across the entire land surface and is not influenced by national boundaries. It should also be noted that this data set was selected here because we have used it for earlier work but more recent alternative data sets may provide better flow direction representation. These include DDM30 (Doll and Lehner, 2002), Hydro1k (USGS, 2000) and HydroSHEDS (**Hydro**logical data and maps based on **SH**uttle **E**levation **D**erivatives at multiple **S**cales: USGS: http://hydrosheds.cr.usgs.gov/).

Cell areas were calculated using:

$$A_{CELL} = k_{AREA}.(\sin(\phi_1) - \sin(\phi_2)) \quad (9)$$

where A_{CELL} is the area (km^2) of a grid cell with minimum latitude ϕ_1 and maximum latitude ϕ_2 (both in radians) and k_{AREA} is a constant defined as:

$$k_{AREA} = 0.5.\frac{\pi}{180}6371^2 \quad (10)$$

Whilst we recognise that determining flow direction from elevation data can be problematic, particularly for flat areas and at such a coarse level of resolution, discussion of such problems is beyond the scope of this paper. The predicted spatial distribution of discharge clearly shows the location of large river systems and confirms, qualitatively, the validity of the area-accumulation routines.

2.3 Population data and household water use estimates

2.3.1 Population data

There are a number of data sets for the global distribution of population (e.g. UNEP / Environment Canada Global Population Distribution 1° x 1° Database and the Gridded Population of the World (GPW): CIESIN, 2000). The GPW v.2 data set for 1995 was used in the work described this paper. This data set comes as population counts or population density (cap km^{-2}) and has been adjusted to correspond with

national-level population estimates issued by the United Nations for 2005. The original (2.5 arc minute) grid was amalgamated to a 0.5° x 0.5° resolution.

2.3.2 Domestic Water Use Rates

Daily per capita domestic water use (*W*) varies widely from country to country and even within countries as a consequence of water availability, infrastructure, wealth and habits. Individual values for each country were taken from a range of public domain sources (e.g. Gleick *et al*., 2010). If a country-specific estimate could not be found then a value from a neighbouring country was used provided that the socio-economic status of that country was considered to be similar. If multiple values were available then the value from the most reliable source was used.

3. Application to China

The model was applied to estimate the spatial variation of surface water concentrations of Linear Alkylbenzene Sulfonate (LAS) in China in order to explore the potential of the model as a risk assessment tool in a large and relatively data-poor country. LAS is a commonly used anionic surfactant used in a range of domestic products – predominantly for laundry. It was selected here as an example "down-the-drain" chemical because a number of studies have been published on its behaviour in sewage treatment works (e.g. Holt *et al*., 1995; Holt *et al*., 1998; Waters and Feijtel, 1995) and in rivers (e.g. McAvoy *et al*., 1993; McAvoy *et al*., 2003; Whelan *et al*., 1999; Fox *et al*., 2000; Eichhorn *et al*., 2001; Eichhorn *et al*., 2002; Whelan *et al*., 2007). We assumed the current national average *per capita* water use of 200 L cap^{-1} day^{-1} (personal communication, Zheng Xingcan, Chief Engineer of State Urban Water

Supply & Drainage Engineering, see also Zheng, 2010) and the government target for national urban connection to WWTPs of 70% (personal communication, Zheng Xingcan). Clearly, using this target urban connection rate is illustrative only and is not appropriate for a current risk assessment since the actual connection rate will be much lower in some urban areas. The latest official estimate for the urban population of China is 47% (China Statistical Yearbook, 2010). A consumption rate for LAS was estimated by combining detergent sales data for China from Euromonitor (www.euromonitor.com) for 2009 for four key detergent products: powders, liquids, bars and fine fabric detergents with expected inclusion levels of LAS per product format to give an overall LAS tonnage for China in 2009. Although this is inconsistent with the population data used (2005), the errors are assumed to be tolerable, given the uncertainties which exist in per capita usage and sewage treatment provision. A value for *U* was calculated as 1.8 g cap^{-1} day^{-1} using the CEISIN 1995 (CEISIN, 2000) estimate for the total population of China (1.28 billion). This compares with estimates of 1.34 g cap^{-1} day^{-1} for Germany reported by Schroeder *et al*. (2002) and 4 g cap^{-1} day^{-1} for the UK (Holt *et al.*, 1995). A removal rate for LAS in WWTPs was assumed to be 98% which is appropriate for activated sludge type plants (Holt *et al*., 1995), the dominant type of treatment technology currently being deployed across China (e.g. U.S. Department of Commerce, 2005). A riverine LAS degradation rate constant of 0.05 h^{-1} was assumed, which is equivalent to a 14 hour half life (Whelan *et al*., 1999). This is appropriate for moderate sized temperate rivers. However, more rapid degradation rates for LAS have been reported for tropical systems (e.g. McAvoy *et al*., 2003; Whelan *et al*., 2007) and for shallow streams in the UK (e.g. Fox *et al*., 2000). In all river reaches, the mean river velocity was assumed to be 0.25 m s^{-1} and the sinuosity was assumed to be 1.5 (after Richards,

1982). Clearly, in reality, different river reaches will have very different mean velocity and sinuosity but representation of these is currently beyond the scope of the modelling approach presented here, particularly at such a coarse spatial resolution.

Maps of predicted mean annual LAS concentration in surface waters across China is presented in Figure 2 for two scenarios. In the first, current estimated sewage treatment provision (70%) was assumed, with 30% of waste water generated in each cell assumed to be discharged to surface waters untreated (Figure 2a). In the second scenario, 100% of the Chinese population was assumed to be connected to secondary WWTPs (Figure 2b). This represents the potential reduction in exposure (and, by extension, risk) resulting from large scale investment in wastewater treatment technologies. It is estimated that approximately 1900 large WWTPs were operating in China in 2010 with targets of 7000 and 12000 set for 2015 and 2020, respectively (personal communication, Zheng Xingcan). The target national design capacity for 2020 is 200 M m^3 day^{-1} which is equivalent to 1 billion people equivalents using 200 L cap^{-1} day^{-1}. The additional treatment provision is predicted to decrease expected concentrations of LAS (and, by extension, other point-source chemicals) significantly in most Chinese rivers. This implies that a significant reduction in ecotoxicological risks associated with such chemicals can be expected in the near future.

Cumulative frequency distributions of *PEC* values across China are shown in Figure 3 for each treatment provision scenario. The *PNEC* proposed by Dyer *et al.* (2003) for LAS (245 μg L^{-1}) derived from a species sensitivity distribution approach is also shown. These data suggest that LAS concentrations may exceed the *PNEC* in a significant number of cells, when connectivity to WWTPs is 70%. This is not unexpected since it is well recognised that even relatively minor and intermittent untreated discharge can exert a dominant influence on pollutant concentrations in receiving systems (see Whelan *et al*., 1999). Derivation of a statistical distribution of *PEC*s allows probabilistic risk (*sensu* Cardwell *et al*., 1999) to quantified by integrating the product of the exposure probability density function (essentially the relative frequency distribution of PECs) and the species sensitivity distribution (representing the effect vs concentration relationship). That said, the extent to which conventional risk assessment for "down-the-drain" chemicals is a useful indicator of ecological impact is questionable in systems receiving significant volumes of untreated waste water (direct discharge) because the ecosystem is often so impacted by high concentrations of sanitary determinands, such as BOD, ammonia and nitrite (McAvoy *et al*., 2003; Whelan *et al*., 2007; Finnegan *et al*., 2009). In such cases, an alternative risk assessment model has been proposed in which i) chemical concentrations are compared to the PNEC at the point where the receiving system has recovered from conventional waste water pollution, and ii) chemical concentrations in the impact zone are assessed for potential inhibition of natural recovery processes such as nitrification and respiration (McAvoy *et al*., 2003). It should also be noted

that large areas of China are arid or semi-arid (FAO, 1997) and have low predicted mean annual runoff. This means that many surface waters draining urbanised catchments are likely to be effluent-dominated (i.e. most of the flow is derived from wastewater, especially under low flow conditions). This explains the vertical lines in Figure 3 which represent the mean concentrations of LAS in treated and untreated waste water for the two scenarios considered.

In the scenario in which 100% provision of secondary sewage treatment was assumed, surface water exposure to LAS is significantly reduced (Figure 2b). In this scenario, predicted LAS concentrations approach the PNEC only in those river reaches where there is no dilution (vertical sections in the cumulative distributions shown in Figure 3). Ecotoxicological risk assessment in effluent-dominated systems is philosophically interesting since the fluvial ecology exists essentially as a consequence of the effluent discharge (i.e. few aquatic organisms live in naturally ephemeral rivers and streams in dry periods). Thus, although high concentrations of many pollutants may be observed, the ecosystem has developed to tolerate this exposure, including commonly-occurring “down-the-drain” chemicals.

4. Evaluation of the model

Long-term measurements of specific “down-the-drain” chemical concentrations in rivers are rare which makes validation of the proposed model difficult. The results presented here for China are qualitatively consistent with other spatial assessments of water quality (Tang and Bi, 1996) in which water pollution was identified as being most serious in the north and north east of the country, particularly around Beijing,

Yinchuan and Shanghai. In the absence of spatially-resolved data for measured LAS concentrations, the *PECs* presented in Figure 2 were compared in relative terms with water quality classes assigned to specific reaches of several major rivers from across China. According to Chen and Xia (2000) there are over 3000 water quality monitoring stations in China. Rivers are assigned a class from I (excellent) to "worse than V" (very poor) on the basis of monitoring data for a range of water quality determinands. Some of these criteria may be related to point sources (such as domestic waste water or industrial effluent), although some may be the result of diffuse-source pollution. Caution should, therefore, be applied to their interpretation in the context of this study. It should be remembered that the main objective was to identify the quality of spatial patterns predicted, rather than to validate absolute concentration values. River water quality classes were digitised manually from maps published by the Ministry of Environmental Protection (2009) onto an existing digital river network in ArcGIS (Figure 4). Spatially coincident values of predicted LAS concentrations and assigned river water quality class were then extracted using an intersection function in the GIS, following the raster to vector conversion of predicted concentration data. This procedure resulted in river reaches of different lengths assigned different classes, with differing numbers of intersected cells containing predicted LAS concentrations (i.e. the number of sampled cells for each class was not the same). There were a total of 1907 paired values of water quality class and predicted LAS concentration, with between 96 (Class V) and 498 (Class II) pairs in each class. Figure 5 shows the average LAS concentration predicted for each river water quality class (assuming 70% connection to secondary waste water treatment), along with upper and lower quartiles and the 90^{th} and 10^{th} percentile concentrations to indicate the variability of predicted concentrations in each class. Although the

variability of predicted LAS concentrations in each class is very high, there is a consistent increase in average concentration with water quality class, suggesting that predicted concentrations are in approximate agreement with observed water quality. This probably reflects a deterioration of water quality in densely populated areas (where wastewater generation and industrial activity are likely to be higher) or areas where dilution of wastewater effluent is low. The fact that the mean concentration exceeds the 75^{th} percentile for four of the six water quality classes is due simply to the fact that the predicted concentrations are highly skewed positively. The 90^{th} percentile concentration predicted for Class VI river reaches is lower than the maximal (undiluted) concentration predicted for arid zones, with 70% connection to waste water treatment (2.83 mg L^{-1}), in part reflecting a paucity of sampled surface waters in these areas. Further work should be done to validate the model predictions for specific pollutants.

5. Conclusions

The model described here allows consistent, spatially explicit, hydrologically-based environmental risk assessments for "down-the-drain" chemicals discharged to freshwaters to be performed in any country in the world. The method represents an intermediate level between generic (and crude) multi-media models or "back-of-the-envelope" exposure calculations and detailed (but rather data hungry) process-based models, such as GREAT-ER (Feijtel *et al.*, 1997; Koormann *et al*., 2006; Price *et al.*, 2009). A key output from this approach is the ability to identify particular regions in which concentrations of certain chemicals may be a cause for concern. In this way, it provides a means of targeting more detailed local-scale risk assessments and risk management measures (such as improving sewage treatment provision or even changing product formulations). It represents a step-change in thinking about risk assessment of chemicals which, up to now, has focussed on environmental protection in the developed world using generic scenarios to indicate relative risk. In addition to improving environmental risk assessments for "down-the-drain" chemicals by better-predicting the spatial variability in exposure, combining information on runoff and socio-economic factors (such as population density and *per capita* water consumption) can be used to predict potential water stress and associated threats (e.g. Vorosmarty et al., 2010).

Given the critical importance of dilution and conveyance for the predicted exposure of "down-the-drain" chemicals discussed in this paper, further work is required to evaluate the quality of the hydrological predictions, with respect to gauged flows. In

addition, the influence of flow seasonality (along with any mitigating influence of groundwater) and of major artificial influences (e.g. reservoirs and abstractions) on patterns of associated risk should be further evaluated. Whilst the use of mean flow is useful for predicting the spatial pattern of expected exposure to pollutants, it does not capture seasonal and episodic variations in concentration resulting from temporal flow variations (Johnson, 2010). Seasonality is likely to be particularly pronounced in those parts of China which have a strong monsoon climate, where 70% of precipitation can fall in just four months of the year (Jiang, 2009). Actual concentrations and loads will vary greatly spatially (in relation to dilution, upstream loads and, importantly in China, spatial differences in sewage treatment provision), even in relatively small geographical areas (Johnson 2010). It is likely that it will only be possible to validate hydrological and pollution predictions rigorously in a few key catchments where data are available on *per capita* "down-the-drain" chemical and water use, wastewater disposal routes, hydrology and observed water quality. As a consequence of this analysis, it may be necessary to refine both the hydrological model and the assumed spatial pattern of emission in some key areas, to calibrate some key model parameters or to increase spatial and temporal resolution.

It is recognised that in many countries, particularly in the developing world, consumer habits and overall consumption of household products containing the types of chemicals discussed here will vary spatially (perhaps most dramatically between urban and rural areas: Hodges *et al*., 2011). This variability has not been taken into account here, although it is likely to be lower for "essential" household products like laundry detergents than for some "luxury" products. Other factors were also not considered explicitly, which may be important for PEC_{AQ} locally, including

alternative wastewater disposal routes (e.g. septic tanks, cesspits, use of grey-water in irrigation and disposal to the marine environment). For example, in some areas clothes may be washed directly in-stream or on river banks (e.g. Gordon et al., 2009). Alternatively waste laundry liquor from manual laundry operations may be disposed of to soil, rather than to a sewer. Nevertheless, we maintain that the predominant factors influencing surface water exposure to "down-the-drain" chemicals will be population density (as a surrogate for loading), wastewater treatment facilities and river discharge (providing dilution and conveyance). The method of exposure assessment described here provides a practicable means of identifying the gross spatial patterns of concentration regionally, including highlighting likely exposure "hotspots". However, the extent to which it can generate accurate absolute predictions of chemical concentrations is currently uncertain. Should further work show that the model does provide a good predictor of absolute exposure it has great potential for predicting the statistical distribution of concentrations as an input to regional scale probabilistic risk assessments.

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Figure Captions

Figure 1. Predicted mean annual river discharge ($m^3 s^{-1}$) using runoff data generated by Fekete *et al.* (1999) for (a) The land surface of the world excluding Antarctica, Greenland and small islands and (b) China.

Figure 2. Predicted mean annual LAS concentration in surface waters across China given a target sewage treatment provision for urban areas of 70% (a) and 100% connection to secondary WWTPs (b).

Figure 3. Cumulative frequency distributions of predicted mean annual LAS concentrations in surface waters across China for 70% and 100% connection to secondary sewage treatment. Also shown is the LAS *PNEC* (Dyer et al., 2003).

Figure 4. River water quality Classes for major Chinese river reaches (Red designates poor water quality "worse than Class V"; Green designates good water quality at Class I). Derived from the Chinese Ministry of Environmental Protection (2010).

Figure 5. Average annual predicted LAS concentrations in Chinese river reaches (Ministry of Environmental Protection, 2010) with different water quality classes. Error bars show the 90^{th} and 10^{th} percentile concentrations, boxes show the 75^{th} and 25^{th} percentile concentrations.

Figure 1

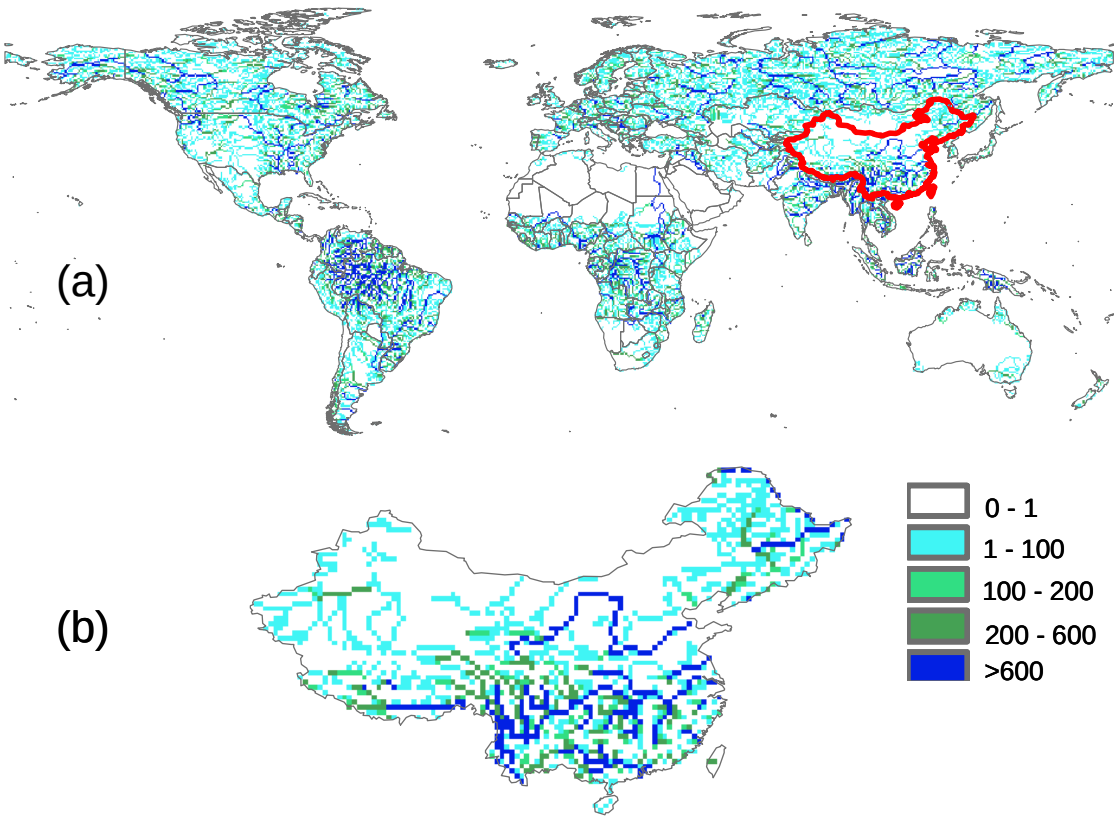


Figure 2

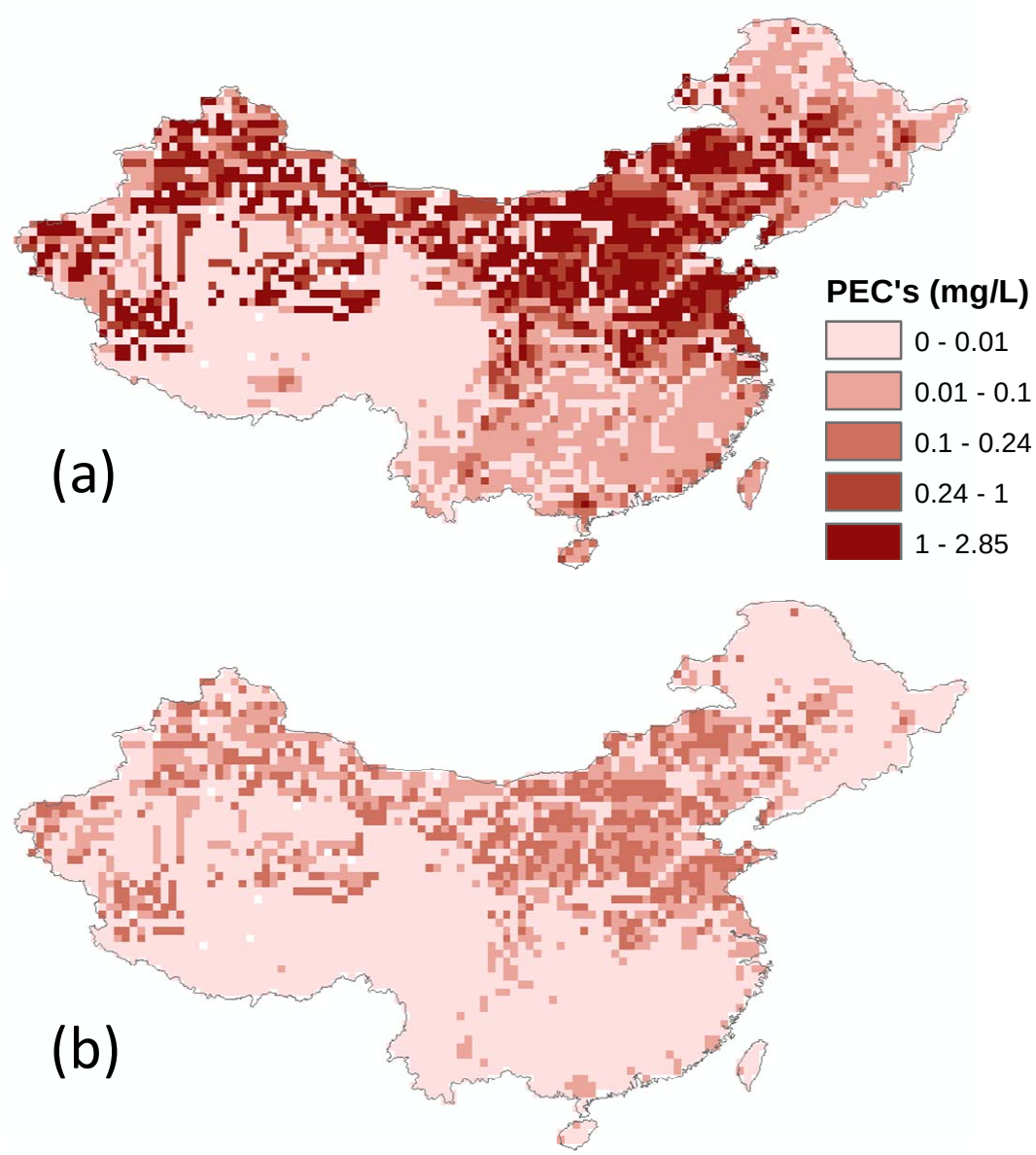


Figure 3

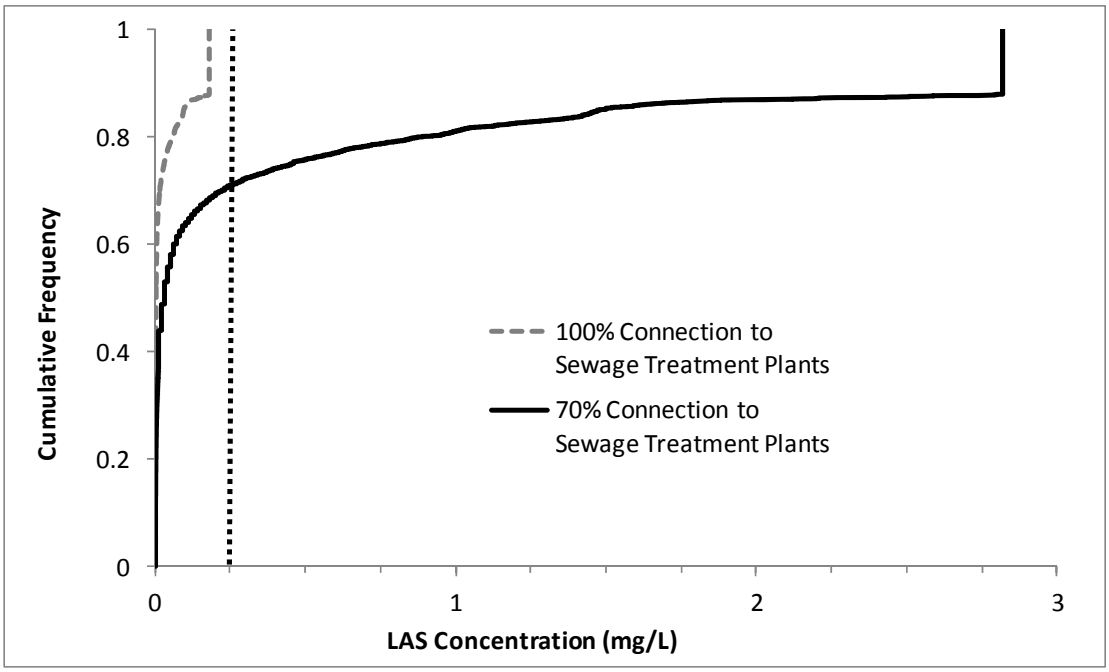

1
0.8
0.6
0.4
0.2
0
Cumulative Frequency
0
1
2
3
LAS Concentration (mg/L)
100% Connection to Sewage Treatment Plants
70% Connection to Sewage Treatment Plants

Figure 4

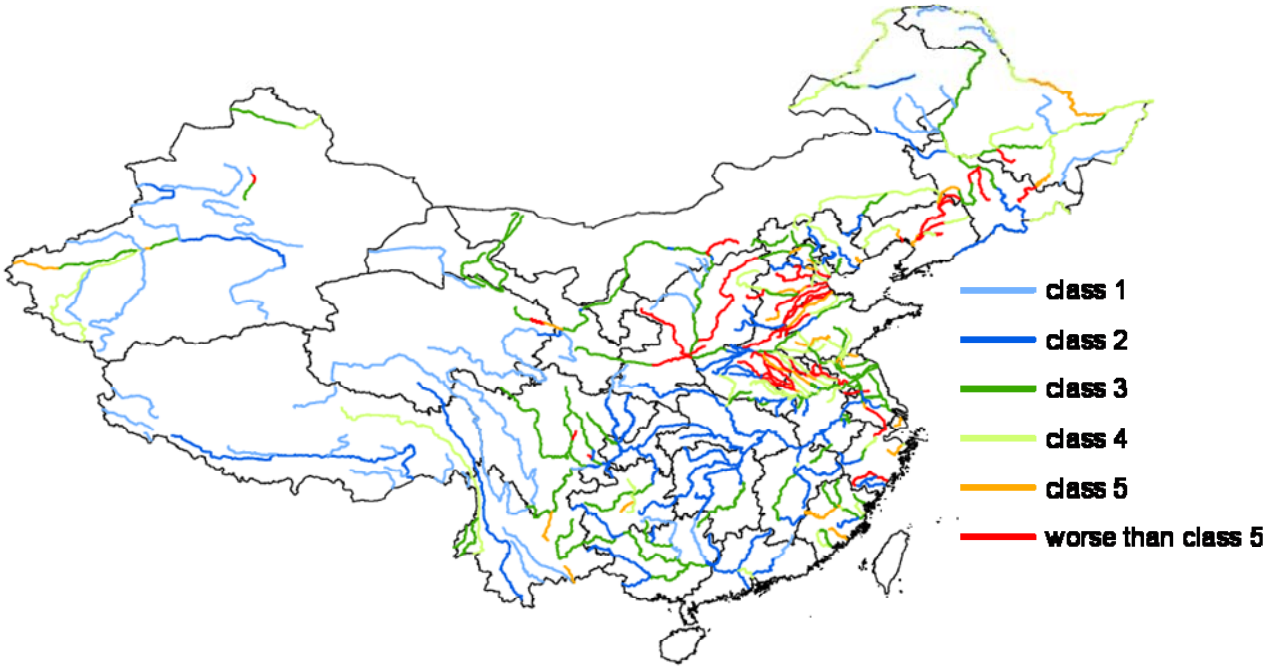
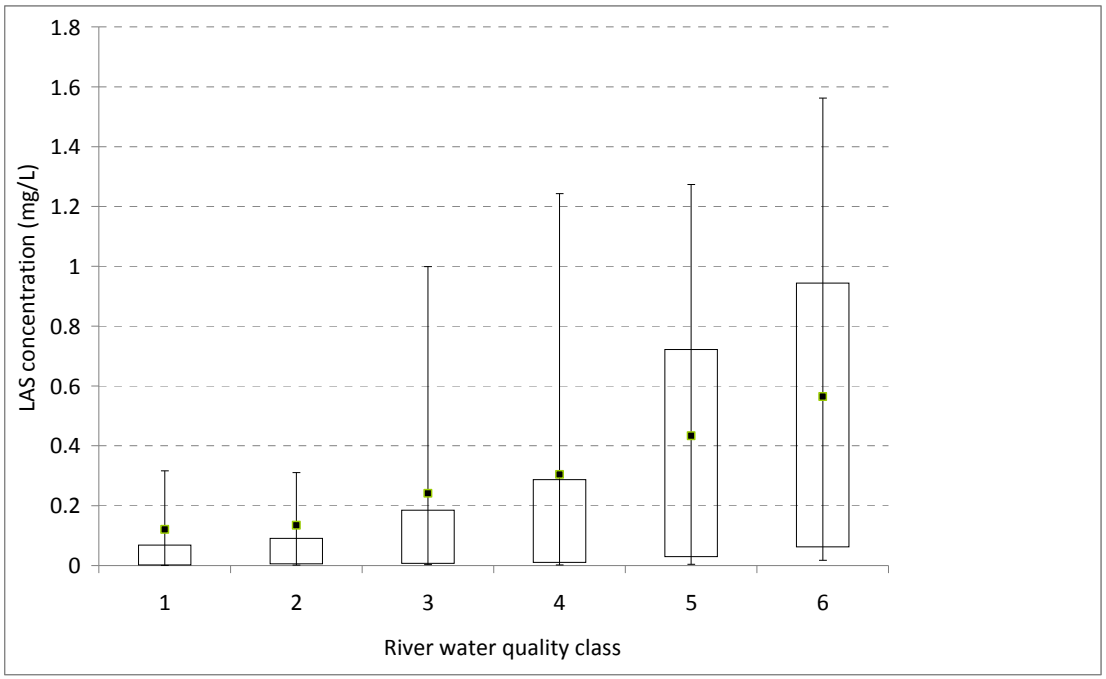


Figure 5


1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
LAS concentration (mg/L)
1
2
3
4
5
6
River water quality class