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Agenda item 3: Methodologies on estimation techniques for releases from non-point sources (catchment runoffs and agriculture) and aquaculture

Guideline on estimation techniques and applied methodologies for non-point source releases from catchment runoffs

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Note by the Secretariat

The LBS Protocol requires in its Article 13 (para 2) the Contracting Parties to submit reports which shall include inter alia: (i) data resulting from pollutants' monitoring and (ii) quantities of pollutants discharged from their territories. For this purpose, the National Baseline Budget of pollutants (NBB) was agreed by the Contracting Parties as "the monitoring tool" to track progress, on a five-yearly basis, of loads of released pollutants. To assist the Countries in this mandate, updated NBB guidelines were developed in 2015 (UNEP(DEPI)/MED WG.404/7). However, these guidelines, do not offer the means by which pollutants from catchment runoffs can be estimated. This issue was the topic of discussion at the Regional Meeting on Reporting of Releases to Marine and Coastal Environment from Land Based Sources and Activities and Related Indicators, which was held in Tirana, Albania on 19-20 March 2019. The meeting recommended the Secretariat to work on supporting countries to develop such guidelines, also considering the increasing importance of pollutants transported by surface runoff impacted by land-based activities into the Mediterranean.

Further to the above, the UNEP/MAP Programme of Work for the biennium 2020-2021, endorsed by COP21 (Napoli, Italy, 2-5 December 2019), mandated the MED POL Programme to develop new National Baseline Budget (NBB) Technical Guidelines to address estimation techniques of pollutants' releases from run-off from catchment areas; thus, strengthening the reporting capacities of the Contracting Parties to Barcelona Convention under LBS Protocol and more particularly under NBB/PRTR.

To this aim, this guidance document was developed. It expands the scope of existing NBB Guidelines by providing specific information on reporting of releases of nutrients, organic carbon and veterinary antibiotics and pharmaceuticals from catchment runoff by applying simple methods from "averaging" to much more complex estimation techniques such as "regression modelling" which require comprehensive data inputs and grid modelling. The estimation techniques about releases to water and land from the above non-point (diffuse) sources are not agreed on the international level. Using the recommended methods would require national inventory data for further testing, calibration and verifying the models which are country specific and pertinent to spatial conditions.

Nevertheless, this guideline can serve in supporting the Contracting Parties to include the runoff from catchment areas in the upcoming 5th NBB Reporting Cycle scheduled for the biennium 2022-2023, as well as to further streamline with PRTR reporting. However, it is to be noted that techniques for estimating releases and discharges are quite complex for nutrients and antibiotics, requiring extensive data and information on nutrients release and organic carbon that can be obtained only through very thorough research requiring the involvement of specialized competent institutions applying regression models which can be only fed with available country specific data.

In this guidance document, in addition to the information provided on the estimation techniques of discharges of nutrients, Total Organic Carbon (TOC) and veterinary antibiotics and pharmaceuticals, additional materials are also provided on accuracy and uncertainty of the estimation methods, and aspects related to quality control/quality assurance relevant to inventories of pollutants releases/discharges. This guideline streamlines these estimation techniques with NBB/PRTR methodologies at process level, where possible, aiming to facilitate the estimations of loads at national level to report certain chemicals to the environment required by NBB and PRTRs.

This Meeting is expected to review this draft guidance document for estimating releases of non-point sources related to catchment runoff taking into consideration the NBB/PRTR methodologies, and to provide its comments and substantive inputs, with the aim of submission of the agreed draft to the MED POL Focal Points Meeting in May 2021 for their approval.

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List of Abbreviations / Acronyms

AMR	Anti-microbial resistance
EC	European Commission
EcAp	Ecosystem Approach
EEA	European Environment Agency
EMEP	European Monitoring and Evaluation Programme
EPA	Environmental Protection Agency
EU	European Union
FAO	Food and Agriculture Organization of the United Nations Rome
HABs	Harmful algal blooms
IACG	The UN Interagency Coordination Group
IPCC	Intergovernmental Panel on Climate Change
JRC	European Commission's Joint Research Centre
LBS	Land Based Sources
MEDPOL	Convention on Protection of the Mediterranean Sea
N	Nitrogen
NAP	National Action Plan
NBB	National Baseline Budget
NBB/PRTR	National Baseline Budget/Pollutant Release and Transfer Registers
NPI	National Pollutant Inventory (Australia)
OECD	Organization for Economic Cooperation and Development
P	Phosphorus
PRTR	Pollutant Release and Transfer Registers
QA/QC	Quality Assurance/Quality Control
TOC	Total Organic Carbon
UNITAR	United Nations Institute for Training and Research
USGS	US Geological Survey
WFD	Water Framework Directive
WHO	World Health Organization

1. Introduction

1. Following the 21st Meeting of the Contracting Parties to the Barcelona Convention COP21 (held in Napoli, Italy, 2-5 December 2019)¹ and the adoption of Decision IG.24/14,² the Programme of Work mandated MEDPOL Programme to develop/update technical guidelines addressing estimation techniques of pollutant releases from diffuse sources (agriculture, catchments runoff and aquaculture).

2. To assist countries, updated NBB guidelines were developed in 2015 (UNEP(DEPI)/MED WG.404/7 Annex IV, Appendix B, Page 11). However, these updated NBB guidelines, do not offer means by which pollutants from non-point (diffuse) sources can be estimated. This point was discussed at the Regional Meeting on Reporting of Releases to Marine and Coastal Environment from Land Based Sources and Activities and Related Indicators, which was held in Tirana, Albania on 19-20 March 2019. During the Meeting it was highlighted that reporting of diffuse sources can be only undertaken based on estimation techniques and emission factors which may vary on national and regional levels of each country. Therefore, the recommendation was made to support the Contracting Parties to complement the National Baseline Budget/Pollution Release and Transfer Registers (NBB/PRTRs) methodology with estimation techniques for diffuse sources attributed to catchment runoff).

3. The aim of this guidance document is to provide an overview of estimation techniques and applied methodologies for non-point (diffuse) sources releases to water originating from catchment runoffs focusing on releases of Total Nitrogen (TN), Total Phosphorus (TP) and Total Organic Carbons (TOC) in order to assist the Contracting Parties to the Barcelona Convention on their calculations/estimations under the National Baseline Budget and Pollution Releases and Transfer Registers (NBB/PRTR).

4. Although the review has been made on a global scale, the major focus of this document is on the Mediterranean region.

5. This guidance document has been prepared with the following steps:

- a. **an extensive literature review** (over 80 research papers, documents, and reports) focusing on three key subjects:
 - i. Non-point (diffuse) Discharges to Water (focusing on catchment runoff characteristics and relevant pollutants from agriculture including nutrients, sediment, total organic carbon (TOC) and veterinary antibiotics and pharmaceuticals).
 - ii. Different approaches, methods and techniques recommended for use in current inventories and technical reports to estimate the above pollutant loadings to water from agricultural non-point (diffuse) sources catchment runoffs
 - iii. Peer reviewed research papers describing methodologies and techniques proposed to estimate discharges to water from the above agricultural non-point (diffuse) sources.
 - iv. In addition, we also reviewed potential issues and drawbacks regarding accuracy and uncertainty associated with the proposed calculation methods, techniques and approaches.
- b. **streamline the most appropriate methodologies and techniques** to estimate nutrients, sediment, TOC and veterinary antibiotics and pharmaceuticals discharges agricultural non-point (diffuse) sources to water via catchments runoff.

¹ <https://www.unenvironment.org/unepmap/events/meeting/21st-meeting-contracting-parties-convention-protection-marine-environment-and>

² https://wedocs.unep.org/bitstream/handle/20.500.11822/31712/19ig24_22_2414_eng.pdf

- c. **integrate this new information to create a guidance** of the methods and techniques to assist contracting parties in estimations of the pollutants emissions to air and discharges to water and land originating from farming of animals and agriculture non-point (diffuse) sources.

6. These guidelines will facilitate the monitoring of implementation of the Regional Plans for Agriculture and Stormwater Management, which will be developed in the biennium 2022-2023. Thus, the newly proposed techniques for estimation of pollution loads will enable the generation of compatible data to evaluate the effectiveness of the adopted measures in the framework of the National Action Plans and the new Regional Plans for Agriculture and Stormwater Runoff Management.

2. Non-point (diffuse) Discharges to Water

2.1 Runoff Characteristics

7. Runoff is the water consisting of surface and subsurface flows which occur when rainfall exceeds the soil infiltration rate (Box 1.1). Depending on the speed of appearance after rainfall or melting snow (a), and the source (b), the US Geological Survey (USGS) [2] classifies runoff as: *Direct or Base runoff (a) and Surface runoff, Storm interflow, or Groundwater (subsurface) runoff (b)*.

Box 1.1: Definitions of runoff. Source USGS [1].

1. The part of the precipitation, snow melt, or irrigation water that appears in uncontrolled (not regulated by a dam upstream) surface streams, rivers, drains or sewers.
2. The sum of total discharges described in (1), above, during a specified time period.
3. The depth to which a watershed (drainage area) would be covered if the entire runoff for a given period of time were uniformly distributed over it.

8. Factors affecting the runoff are summarized in Table 1:

Table 1: Meteorological and Physical factors influencing runoff (adapted from [2]).

Meteorological factors	Physical characteristics
<ul style="list-style-type: none"> • Type of precipitation (rain, snow, sleet, etc.) • Rainfall intensity • Rainfall amount • Rainfall duration • Distribution of rainfall over the watersheds • Direction of storm movement • Antecedent precipitation and resulting soil moisture • Other meteorological and climatic conditions that affect evapotranspiration, such as temperature, wind, relative humidity, and season. 	<ul style="list-style-type: none"> • Land use • Vegetation • Soil type (e.g., infiltration) • Drainage area • Basin/catchment shape • Elevation • Slope • Topography • Direction of orientation • Drainage network patterns

2.2 Catchment Runoff

9. As the goal of this document is to provide guidance to estimate pollution (nutrients, total organic carbon, pathogens, emerging contaminants) loads originating from the agricultural activities carried by catchments runoff, it is important to distinguish between catchment and watershed areas. Catchment area is defined as an area from which water drains into a particular lake, river, etc.; for example, the catchment area of a large river with its tributaries (Figure 1). Watershed (or a drainage basin) is defined as the topographical boundary dividing two adjacent catchment

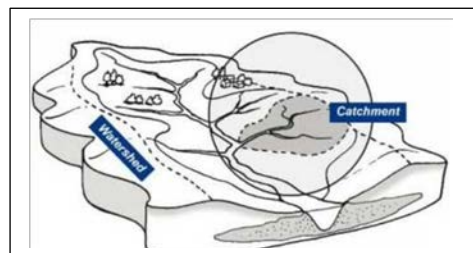


Figure 1: Catchment and watershed areas

basins, such as a ridge or a crest. It is a region of land within which water flows down into a specified body, such as a river, lake, sea, or an ocean.

2.2.1 Nature of the source and relevant pollutants from agriculture

10. Catchments in rural areas are influenced by direct anthropogenic impacts from both point and non-point nutrient sources. Catchment runoff originating from agricultural non-point (diffuse) sources includes surface and subsurface flows from animal farm and feeding operations, cropping systems, their field level interactions (both temporal and spatial) and climate (storm frequency and hydrology, temperature). Estimating pollution loadings and controlling this type of contamination is highly complex and requires integration of scientific, technological, socio-economical and educational factors [7-10].

11. Nutrients (total nitrogen and phosphorus) contained in catchment runoff from non-point (diffuse) agricultural sources are of the greatest concern and thus the most typically estimated [1] [8-11] [13-19]. These pollutants are also included in Annex (I) of the LBS Protocol and listed in the Annex IV of the NBB/PRTR Guidance (UNEP(DEPI)/MED WG.404/7)⁵. Other pollutants include total organic carbon [20-23] and veterinary antibiotics and pharmaceuticals [24-29].

Nutrients

12. Catchment runoff from non-point (diffuse) agricultural sources contains excessive quantities of nutrients which results in nutrient enrichment (eutrophication) of lakes and coastal waters [7-10] [13-15]. The European Environment Agency (EEA) declared eutrophication as a pan-European problem of a major concern 25 years ago [30-31]. Despite all the efforts and vast investments, it remains a major threat to achieving the good status of waters required by the WFD [4-6][31].

13. Eutrophication has numerous detrimental impacts on the environment, health (animal and human) and the economy. These are summarized in Table 2:

Table 2: *Impacts of Eutrophication (Source: Drizo [31]).*

Impact	Reference
Intensified growth and production of algae, cyanobacteria (blue-green algae) and aquatic plants usually appearing as algal scums or floating mats of plants and commonly referred to as “algal blooms”. This excessive abundance in vegetation and bacteria increases respiration rates causing significant fluctuations in dissolved oxygen (DO) concentrations and water transparency, eventually leading to hypoxia.	e.g. Corell, 1998 [32]; Smith and Schindler, 2009 [33]; Ansari et al, 2011 [34].
Fish kills and reduced biodiversity. Low DO causes loss of invertebrates and fish and through their decay, algae and bacteria proliferation, further reducing oxygen content of water and loss of biodiversity.	Corell, 1998 [32]; Ansari et al, 2011 [34]; Hautier et al, 2009 [35].
Toxins excretion. Certain algal species, including cyanobacteria, produce toxins that may seriously affect the health of fish, birds and mammals. This can occur either through the food chain, or direct contact or ingestion of the algae. Recent studies revealed that most cyanobacteria produce the neurotoxin beta-N-methylamino-L-alanine (BMAA) which had been linked with the development of neurodegenerative diseases (Alzheimer's and Parkinson's diseases, and Amyotrophic Lateral Sclerosis (ALS)).	Briand et al, 2003 [36]; Banack et al, 2010 [37]; Brand et al, 2010 [38].
Aesthetics. Eutrophication causes increased turbidity, unpleasant odours, slimes and foam formation diminishing aesthetic value of waters.	e.g. Corell, 1998 [32]; Ansari et al, 2011 [34];
Considerable economic losses. Algal blooms reduce potable water supplies, property values, tourism and recreation. The losses of local economies due to eutrophication were estimated at \$2.2 billion per year in the USA in 2009, and between £75 to £114.3 million per year for England and Wales in 2003.	Dodds, 2009 [39]; Pretty et al, 2003 [40].

14. Global Climate Change will promote cyanobacterial growth and exacerbate algal blooms at much larger scales, further diminishing water availability and potable water supplies [41-42] [31].

Total Organic Carbon (TOC)

15. The chemical composition and concentration of organic matter influence many critical biogeochemical processes in rivers. Human activities in agricultural catchments may alter the quantity and composition of organic matter delivered to rivers resulting in adverse effects on ecosystems and society [21-23][47]. For example, riverine dissolved organic carbon (DOC) contributes energy to aquatic food webs through uptake by microbes and abiotic processes that produce bioavailable particulate organic carbon (POC) from DOC (flocculation and sediment adsorption). TOC (DOC plus POC) influences light attenuation in rivers with effects on primary productivity and autochthonous DOC production. An elevated organic content promotes increase in the growth of microorganisms which contribute to the depletion of oxygen supplies and water transparency [21-23][47]. Decreased dissolved oxygen (DO) concentrations can cause loss of invertebrates and fish and loss of biodiversity.

Veterinary antibiotics and pharmaceuticals

16. The widespread use of large quantities of veterinary antibiotics and pharmaceuticals (tetracyclines, elfamycins, macrolides, lincosamides, polyethers, beta-lactams, quinolones, streptogramins, and sulfonamides, carbadox, amprolium, carbadox) in agricultural animal operations has become an issue of a global public health concern [24-29] [48-51].

17. In Europe, one-third of antibiotics consumption is related to veterinary use in livestock production for disease prevention, and for subtherapeutic use as a feed supplement for a growth promotion [27]. These antibiotics and supplements can make selective pressure on bacteria and boost growth of bacteria resistant to the effects of antimicrobials in the gastrointestinal tract of livestock. Manure from antibiotic treated livestock also contain unmetabolized antibiotics that facilitate development of the anti-microbial resistance (AMR). AMR is a natural mechanism in bacteria which prevents antibiotic bactericidal properties, thus rendering treatments ineffective [27-29][49]. Moreover, it can pass to pathogenic bacteria and potentially cause an incurable infection. In 2019, the UN Interagency Coordination Group (IACG) on Antimicrobial Resistance released a report highlighting that drug-resistant diseases already cause at least 700,000 deaths globally a year, and that number of deaths could increase to 10 million per year globally by 2050. The IACG also underlined that the economic damage of uncontrolled antimicrobial resistance could be comparable to those experienced during the 2008-2009 global financial crisis and result in dramatically increased health care expenditures, adverse impacts on food and feed production, trade and livelihoods, and increased poverty and inequality [51].

3. Description of techniques for estimating discharges from agricultural non-point (diffuse) sources releases to water via catchment runoffs

18. Several researchers investigated, modelled and attempted to estimate diffuse pollution loads and the effects of policy and mitigation measures at the catchment scales [12-23] [64-71]. However, models' accuracy is dependent on data input, whose collection for non-point (diffuse) sources is highly complex and expensive [70] [55-56][1][11]. Richards [70], NSW EPA National Pollutant Inventory [54] and US EPA National Management Measures to Control Nonpoint Source Pollution from Agriculture [56-57] provide comprehensive descriptions of load estimation techniques and problems associated with the fact that pollutant concentrations are generally sampled infrequently, often at routine intervals (i.e., daily, weekly, monthly, or seasonally). Additional information on "Non-point/diffuse Sources Pollution Inventories" are provided in Annex I.

19. These aforementioned documents highlight the fact that there are many different techniques used for calculating load estimates, varying in complexity, accuracy and bias. Factors affecting the choice of technique may depend on the data resolution, the operator's skills and mathematical ability, the computer technology available, and data collection methods employed.

3.1 Pollutant Load Estimation Methods and Techniques

3.1.1 Averaging

20. Averaging methods are generally considered to be the simplest available techniques for pollutant load (PL) estimation and are often applied because of an absence of more appropriate techniques. Estimates of PL over a time period are made by multiplying the average concentration (in that time period) by mean daily flow for each day in the time period to obtain a succession of estimated daily (unit) loads. Another approach involves multiplying the average observed concentration by the average flow based on all days of the year to obtain an "average" daily load, which is then converted to the total load [54][70]. The NSW EPA provides information on 14 different averaging techniques and equations used for the determination of annual riverine loads [54].

3.1.2 Ratio estimators

21. Ratio estimators determine the average daily load for the days with concentration observations, adjust it proportionally by reference to some parameter which is more thoroughly sampled and then calculate the total annual load by multiplying the adjusted daily load by 365 [54][70]. The most common parameter used for adjustment is discharge data, with ratio estimate calculated as:

$$Y_R = (y/x) X \quad \text{(Equation 3.1)}$$

where:

- y and x are the sample means of y_i (load data) and x_i (discharge data)
- YR is the ratio estimate of a load and
- X is the discharge.

22. Richards pointed out that while multivariate ratio estimators involving more than one adjustment parameter have been described in the statistical literature, the mathematics are very complex, and consequently such estimators have not been applied to load estimation problems [70].

23. Ratio estimators assume that there is a linear relationship between the daily loads and the adjustment parameter, which passes through the origin. As these conditions will not be met in the field, ratio estimators are often biased [54][70]. Several researchers developed estimators which include correction terms which eliminate or greatly reduce the bias (e.g. [72] (p. 150-186)).

3.1.3 Regression estimators

24. Regression estimators, commonly referred to as rating curves, are based on extrapolating a limited number of concentration measurements over the entire period of interest by developing a relationship between pollutant concentration or load and stream discharge, and applying this relationship to the entire discharge record [54][70]. Most regression estimators are based on a linear regression model, however, log transformation is frequently used, because many environmental parameters are approximately log-normally distributed and the log of pollutant load or concentration is assumed to be a linear relationship of the log of stream discharge.

25. However, a number of studies have shown that the regression curve estimates based on such log-log relationship are biased, in particular in predicting sediment loads [54].

26. The problems most encountered with regression estimators and attempts to overcome them have been discussed in detail in [54] and [70].

3.2 Nutrients

27. As stated earlier, documents on inventories on discharges to water provided by national governments and international agencies for countries to use are currently lacking. MED POL will thus use techniques proposed in peer reviewed scientific literature.

28. Malve et al. [69] developed an export coefficient model of diffuse pollution at large scales with the aim to provide reasonable estimates across the whole of Europe based on readily accessible datasets, and that would be agreeable to application within a gridded model of water quality loadings to surface waters. They used a linear export coefficient model and data from a set of observed river basins to estimate terrestrial diffuse non-point pollution loads. Total annual load transported out of observed catchments was calculated by summing up the loads from all land uses together with estimated losses from scattered settlement and point sources, by multiplying it with a retention coefficient and by subtracting the resulting amount with retention in lakes, as following:

$$L_j = r_1 * \left\{ \sum_{i=1}^n (e_i * C_{i,j}) + (S_j + P_j) \right\} - r_2 * lake_j \quad (\text{Equation 3.2})$$

where:

- L_j = total load from terrestrial sources ($\text{kg km}^{-2} \text{y}^{-1}$)
- r_1 = retention coefficient within the catchment and in streams, excluding lakes
- e_i = export coefficient for I ($\text{kg y}^{-1} C_{i,j}$)
- $C_{i,j}$ = characteristic (i) of catchment (j)
- S_j = load from scattered settlement in a catchment j ($\text{kg km}^{-2} \text{y}^{-1}$)
- P_j = load from point sources in a catchment j ($\text{kg km}^{-2} \text{y}^{-1}$)
- r_2 = retention per lake percentage ($\text{kg km}^{-2} \text{y}^{-1} \%^{-1}$)
- $lake_j$ = lake percentage of catchment j (%)

29. Detailed calculations of the linear export coefficient model for parameters required for NBB Reporting i.e., biochemical oxygen demand (BOD), total nitrogen (TN) and total phosphors (TP) can be found in [69]. The coefficients were fitted to data from European Union European Environment Agency databases of 79–106 selected river basins around Europe. The study showed that estimated export coefficients were on a reasonable level with estimates made by other methods within Europe. The main findings were that

- i) runoff, number of livestock and point load were common factors for BOD, TP and TN loads with runoff as the most important factor;
- ii) cropland area also contributed to diffuse TN load;
- iii) average slope steepness and runoff, as a combined factor, had a negative effect on diffuse TP load and iv) lake area reduced diffuse loads.

30. The authors pointed out that a larger set of data with higher spatial and temporal resolution and partitioning of the data based on, e.g., climate or spatial patterns would further improve the precision of the export coefficient estimates. Moreover, that when applied at the catchment scale, the parameters should be updated with local data. Finally, that an integration of data from the administrative monitoring, modelling and management of river basins would bring an improvement in data availability, model predictions and cost efficiency of management measures and policies.

31. Zhang et al. [65] used the ADAS Agricultural Pollutant Transfer (APT) framework to generate nitrogen, total phosphorus and sediment loading from non-point (diffuse) agricultural sources in England and Wales. The ADAS APT framework was developed for national scale modelling for policy support [73]. The framework predicts pollutant losses from agricultural land and woodland at field scale and includes pollutant loadings delivered to watercourses. A waterbody is represented as a great number of fields which are then subject to landscape scale retention to estimate delivery of pollution from agricultural land to rivers. Both surface and subsurface (land drainage) are included as delivery pathways. The framework requires three core types of data: daily weather information,

physical attributes of the land, and crop and livestock management data. Detailed information can be found in [65] and [73].

32. More recently, Malago et al. [14] developed a conceptual statistical regression model (GREEN-Rgrid), to estimate nutrient fluxes into the Mediterranean Sea. The major benefit of this model is that that links nutrient inputs to water quality measurements. It runs on an annual basis on a routing grid cell structure to establish the emitting-receiving grid cell relationship, where the upstream nutrient load is added as an additional point source to the receiving downstream grid cell. This model can be used to estimate total nitrogen (TN) and phosphorus (TP), nitrate (N-NO₃) and orthophosphate (P-PO₄) from both non-point (diffuse) and point sources.

33. The load at the outlet of a grid cell is expressed as:

$$L_i = [SUR_i S_i R_i + (PS_i + UL_i) R_i] * (1-RES_i) \quad (\text{Equation 3.3})$$

where:

i represents the grid cell

L = is the annual nutrient load (ton y⁻¹)

SUR= the nutrient (nitrogen and phosphorus) surplus in the grid cell (ton y⁻¹)

PS = the point sources (ton y⁻¹)

UL = the upstream load (ton y⁻¹)

S and R = the soil and river reduction factors in each grid cell (dimensionless)

RES = the nutrient retention in lakes/reservoirs (dimensionless)

3.3 Total Organic Carbon (TOC)

34. Andrén and Kätterer [75] developed the Introductory Carbon Balance Model, ICBM as an instrument for predicting soil carbon balances in Swedish agricultural land. However, the authors pointed out that the model could also be used for other estimates of soil carbon dynamics, and that the Swedish regions could be replaced with any number of regions anywhere in the world. A detailed description of model assumptions and parameterization are described in detail in [75]. The authors also highlighted that for the general application of the model it is crucial to find ways to obtain good parameter values when available data are less complete and proposed a few strategies.

35. Nadeu [76] conducted a thorough review of models attempting to simulate erosion-induced C fluxes at the catchment or regional scale. The author pointed out that the only model that considers the effect of tillage erosion on soil and C redistribution is the SPEROS-C model [77] and highlighted that this model has been applied successfully in small agricultural catchments allowing to quantify C exported and redistributed at each site and its associated vertical fluxes [75][77]. The SPEROS-C model consists of a soil redistribution component based on the SPEROS model [77] and a soil organic carbon (SOC) dynamics component based on the ICBM model [75]. The importance of SPEROS-C model is that simulates redistribution of sediments and the associated C both laterally, i.e., spatially between soil profiles, and vertically, i.e., within the soil profiles due to burial and erosion. It therefore integrates the soil erosion component in the evolution of the SOC at the slope or catchment scale and it does this through a multiple-layer approach.

36. More recently, Boix Fayos et al [21] used Nadeu's approach to estimate the total organic carbon (TOC) redistributed TOC_{red} by lateral flows at the catchment scale:

$$TOC_{red} = 0.26 \times TOC_{red} + 0.20 \times TOC_{red} + \sum TOC_{CD} + \sum TOC_{exp} \quad (\text{Equation 3.4})$$

where:

0.26 = the fraction of sediment that it is redeposited at the hillslopes after initial erosion extracted from modelling exercises at the sub-catchment level in the Rogativa catchment, Spain [75]

0.20 = the fraction of soil organic carbon that is mineralized during transport and deposition processes, extracted from literature review

TOC_{red} = redistributed total organic carbon
 TOC_{CD} = total organic carbon stored in alluvial wedges behind check-dams
 TOC_{exp} = represents organic carbon exported downstream check-dams, being both estimated from the volume and the density of sediments retained by check-dams and their trap efficiency

3.4 Veterinary antibiotics and pharmaceuticals

37. Wöhler et al [29] recently assessed pharmaceutical water pollution from both human and veterinary pharmaceuticals at three geographical levels: global, national (considering Germany and the Netherlands) and catchment level.

38. For veterinary pharmaceutical loads, they made separate estimates per animal type (beef cattle, dairy cattle, pigs, broiler and laying hens) for Germany and the Netherlands as a whole and for the for Vecht catchment, which is shared between the two countries. The main emission pathways via direct (excretion of grazing animals) and indirect (manure collection and application) emissions were taken into consideration.

39. Aggregated loads per pharmaceutical and livestock type were defined as:

$$L_t[i] = L_d[i] + \sum_m L_{in}[i, m] \quad (\text{Equation 3.5})$$

where:

$L_t[i]$ = the total load of a specific veterinary pharmaceutical from livestock type i (kg y^{-1})
 $L_d[i]$ = the load from manure directly emitted to pastureland (kg y^{-1})
 $L_{in}[i,m]$ = the indirect load from manure type m (liquid or solid) applied to fields after temporary storage.

40. Direct loads were estimated according to the method developed by Boxal et al. [78] as following:

$$L_d[i] = 365 \times a[i] \times f_e \times f_d[i] \quad (\text{Equation 3.6})$$

where:

a = the administered substance per day (kg d^{-1})
 f_e = the excreted fraction
 f_d = the fraction directly emitted to pastureland.

41. The pharmaceutical load from manure that has been stored before application to fields was estimated per livestock type i and manure type m (liquid or solid) using a first-order degradation model, assuming constant production of manure over time.

$$L_{in}[i, m] = \frac{365}{T[i, m]} \times \left(\frac{a[i] \times f_e \times (1 - f_d[i]) \times f_{man}[i, m]}{k[i, m]} \times (1 - e^{-k[i, m] \times T[i, m]}) \right) \quad (\text{Equation 3.7})$$

where:

$365/T$ = the number of storage periods per year
 a = the administered substance per day (kg d^{-1})
 f_e = the excreted fraction
 $(1-f_d)^{[i]}$ = the fraction of the daily production that is stored
 $f_{man}^{[i,m]}$ = the fraction of manure type m
 k = the degradation rate (day^{-1}); By definition, $k = \ln(2)$ divided by the half-life of the substance (which differs per type of manure and livestock type).
 T = duration of one storage period (days)

42. The quantities of administered substances (separately for beef cattle, dairy cattle, pigs, broilers and laying hens) were estimated from the veterinary pharmaceutical sales data. Data on

pharmaceutical degradation during manure storage were obtained from literature. Due to the lack of livestock-specific data, the authors assumed the same excretion fractions as in human metabolism.

43. Data sources and assumptions for the model can be found in the Supplemental Information³ of the research paper.

44. The researchers pointed out that while pharmaceutical transport to water through leaching and runoff has been investigated in experimental trials, modelling attempts and risk assessment methods, a comprehensive method is lacking.

45. Annex II provides overview information of “Release Estimation Techniques and Applied Methodologies for Estimation of Releases of Pollution from Catchments Runoff.”

3.5 Comments on reliability Accuracy and uncertainty in calculations

46. The reviewed studies and inventories underline that there are often large differences between measured and estimated loads computed using different methods. The reasons reported include a variety of factors including the lack of consideration of topography and soil erosion, climatic factors and the inaccurate interpretation/categorisation of land use classes, lack of reliable data [1][11] [52][54][64] [69-70]. The OECD Compendiums [1][11] recommend that in situation when data are poor or lacking, it is preferable not to rely on a single estimation technique and that in such cases, all the assumptions and the uncertainty limits of the outcomes should be clearly specified.

4. Conclusions

47. This document provides a comprehensive review of techniques and applied methodologies for estimation of non- point (diffuse) sources releases to water (i.e., catchment runoffs) focusing on releases of TN, TP, sediments, TOC, and veterinary antibiotics and pharmaceuticals.

48. During the process of desktop research and compilation of information (provided in Annex III), it became apparent that:

- a) The estimations should be considered at catchment level than the watershed level, where possible;
- b) unlike the air emissions inventory area, there are no extensive guidance documents on inventories on discharges to water provided by national governments and international agencies for countries to use.
- c) The estimation techniques about releases to water and land from the above non-point (diffuse) sources is often not available.
- d) Appropriate information on discharges to water from non-point (diffuse) sources is essential part of the catchment modelling process. However, it is a complex area of scientific research which requires a greater depth of expert knowledge.

³ Appendix II. Supplementary data. <https://www.sciencedirect.com/science/article/pii/S2589914720300049#appsec1>

Annex I
Non-point/diffuse Sources Pollution Inventories

Brief Overview

49. The need for reliable estimation and prediction of non-point (diffuse) pollutant exports on a catchment scale has been discussed in several Inventories and Guidance documents [1][8] [52-55].

50. The first proposal of a European Inventory of Emissions to Inland Waters focused on four main issues:

- i) the substances to report;
- ii) the sources generating emissions/releases;
- iii) the spatial; and
- iv) time scales for reporting [52].

51. For the purposes of the EEA, only the topographic surface catchments were considered. The European Commission's Joint Research Centre (JRC) developed the River and Catchment Database as the first comprehensive database of river networks and catchment boundaries for the entire European continent. This Database enabled linking between river and area drained, and together with the hierarchical structure from small catchments to large river basins, allowed the study of relevant processes at a variety of scales and independent of national and/or administrative boundaries [53]. These data are available to the European Environment Agency, DG Eurostat, DG Environment and others for use within the European institutional framework and for supporting the Water Information System for Europe [53].

52. The Australian Inventory [54] is a comprehensive compilation of techniques which can be used to estimate catchment exports. It also provides information on categorisation of catchment models including the assumptions, inputs required, complexity, ease of use, availability and application to Australian catchments, model acceptance criteria and the uncertainty associated with model outputs. It also describes and discusses methods for pollutant load estimation based on direct observation and provides an inventory of nutrient generation rates and modelling groups in Australia. The authors concluded that physics-based models and the more complex conceptual models are not appropriate for estimating catchment exports across most Australian catchments. However, that empirical and conceptual approaches can be combined to provide models that enable i) event responsiveness and sensitivity to climate variability; ii) allow investigation of catchment source strengths and iii) general physical interpretability of modelling result [54]. Additionally, it was also concluded that there is no single optimal sediment and nutrient (direct) load estimation technique. The selection of an appropriate load estimation technique depends not only on the availability of concentration and discharge data, but also on the hydrological characteristics of the catchment being analyzed, the expected accuracy of estimates and the preferred complexity of the load estimation technique. All techniques considered were found to have disadvantages in certain situations [54].

53. The UNITAR Guidance [55] suggested linking of pollution factors with source parameters that are known or easily obtained. For example, in the case of agriculture, the parameters could include the size and composition of cultivated area, the quantity of pesticide or fertilizer use and the locations where these chemicals are applied. In this manner, one could perform a reasonable estimate of aggregate emissions arising from non-point (diffuse) sources of certain pollutants starting from simple, known parameters that are readily measured or obtained for each source type.

54. The OECD Resource Compendiums of PRTR release estimation techniques provide updated description of aims and uses of emissions inventories [1][11]. The documents underlined that

55. The preparation of non-point inventories on discharges to water represents an essential part of the catchment modelling process. They also acknowledged that it is also a complex area of scientific research which requires a greater depth of expert knowledge. Moreover, both Compendiums (2003 and more recent, 2020) highlighted that unlike the air emissions inventory area, there are no extensive guidance documents on inventories on discharges to water provided by national governments and international agencies for countries to use [1][11].

Annex II
Overview of Approaches, Accuracy and uncertainty and Quality control and quality assurance
Associated with Techniques and Applied Methodologies for Estimation of Pollution Releases
from Catchments Runoff

Overview of available approaches

56. The OECD Resource Compendium highlights that there is a wide variety of models and techniques to estimate the pollutant loads from catchment areas. These techniques are generally incorporated into empirical, conceptual and/or physics-based catchment models [1][11]. The US EPA National Management Measures to Control Nonpoint Source Pollution from Agriculture provides a detailed guide of load estimation techniques through monitoring and modelling of pollutant load [56] and on management measures to prevent and solve non-point source problems in watersheds [57]. It highlights the importance of site and catchment hydrology, and analysis of on-site treatment needs in understanding nonpoint source problems and the impacts of management measures on pollutant sources and delivery patterns [57]. The Chapter on Loading techniques [56] describes different loading models designed to predict pollutant movement from the land surface to waterbodies which are categorized as watershed loading models, field-scale models, and receiving-water models. Of these, field-scale models are most frequently used in agricultural systems [56]. Chapter 5 [57] provides a very good summary of models that have been evaluated for a relatively wide range of conditions and have been shown to be appropriate for the farm or field including GLEAMS [58], EPIC [59], DRAINMOD [60], REMM (Riparian Ecosystem Management Model) [61] and others.

57. The Australian National Pollutant Inventory [54] provides a thorough overview of techniques for pollutant loads estimates and the response of a catchment to rainfall events, the implementation of different modelling approaches including calibration acceptance criteria, and the factors affecting the predictive capacity of models.

58. In Europe, the European Pollutant Release and Transfer Register (E-PRTR) promulgated by the Regulation No 166/2006⁴ stipulates that E-PRTR database must include releases of pollutants from diffuse sources where available [62]. When such data are not available, the European Commission is required to take actions to initiate reporting on these sources. In the last 15 years a number of international activities were initiated by the Commission and the European Environmental Agency (EEA) to stimulate and facilitate reporting on diffuse sources. One of these projects was “Diffuse water emissions in E-PRTR Project” completed in 2013 is of particular relevance as the researchers 1) gathered available data on diffuse releases to surface water with data sets available up to 2009; 2) proposed alternative estimation methods where emission data are not available on the European scale; 3) developed a methodology to derive disaggregated spatial data to obtain geographical information system layers; 4) derived gridded emission map layers covering all EU27 Member States and the EFTA countries (Switzerland, Liechtenstein, Norway and Iceland) for the selected sectors and pollutants with the highest resolution possible [62].

59. However, despite these efforts, currently there are no extensive guidance documents on inventories on discharges to water provided by national governments and international agencies for countries to use [1][11].

Accuracy and uncertainty

60. The OECD Compendium summarizes factors that influence the quality of inventories. These include accuracy (the measure of ‘truth’ of a measure or estimate); comparability (between different methods or datasets); completeness (the proportion of all emissions sources that are covered by the inventory); and representativeness (in relation to the study region and sources of emissions) [1][11]. For non-point (diffuse) source emissions sources the feasibility and level of accuracy are determined by the types and quality of available information [1]. The UNITAR Guidelines highlights that the availability of information needed varies greatly between countries and for different regions within a country. Therefore, the evaluation of availability and accuracy of information is a key when considering types of non-point (diffuse) to be included in the national PRTR system [55]. The USEPA highlighted that prediction uncertainty is caused by natural process variability, and bias and error in sampling, measurement, and modeling [56].

⁴ <https://eur-lex.europa.eu/eli/reg/2006/166/2009-08-07>

61. According to the OECD Compendium [1][11], errors or uncertainty in the preparation of the inventories may include: 1) Emission factors (which do not reflect real life conditions); 2) Activity data that do not adequately reflect the study region (scaling down national or state activity data to smaller regions always results in decreased accuracy); 3) Spatial and temporal disaggregation may introduce errors that are difficult to quantify; 4) Sample surveys may be subject to sampling errors.

Quality control and quality assurance

62. The IPCC Guidelines for National Greenhouse Gas Inventories provides a comprehensive description of the quality assurance/quality control (QA/QC) and verification which are also relevant to inventories of non-point (diffuse) sources to water [63]. Well-developed and established QA/QC contributes to the transparency, consistency, comparability, completeness, and accuracy of inventories (Box A.1):

Box A.1.: Definitions of QA/QC and Verification

Quality Control (QC) is a system of routine technical activities and procedures to assess and maintain the quality of the inventory. The QC system is compiled by the inventory team and is designed to: (i) Provide routine and consistent checks to ensure data integrity, correctness, and completeness; (ii) Identify and address errors and omissions; and (iii) Document and archive inventory material and record all activities. QC activities comprise general methods such as accuracy checks on data acquisition and calculations, and the use of approved standardised procedures. QC activities also include technical reviews of categories, activity data, emission factors, other estimation parameters, and methods.

Quality Assurance (QA) is a system of review procedures conducted by independent third parties. The purpose of reviews is to verify that measurable objectives (data quality objectives) are met, and to ensure that the inventory represents the best possible estimates of emissions and removals given the current state of scientific knowledge and data availability, and support the effectiveness of the QC programme.

Verification refers to the collection of activities and procedures conducted during the planning and development stage, or after the completion of an inventory that can help to establish its reliability for the intended applications of the inventory.

The OECD Compendium [1][11] also provide summary of QA/QC. They highlight the importance of proper documentation, which ensures reproducibility, transparency and assists future inventory updates. Documentation should include all raw data used, assumptions, steps in calculations, and communications with data providers and QA/QC processes. Moreover, the important missing data (e.g., missing pollutants, missing source types) also need to be acknowledged and documented [1][11].

Annex III
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