Круговорот азота

Пулы азота:

В почве и воде:

- органический N,
- NH_4^+ (NH_3),
- NO_2^-,
- NO_3^-

В атмосфере:

- N_2
- NH_3
- N_2O
- NO
- NO_2
- NO_3^-

Энергетические характеристики основных реакций круговорота азота

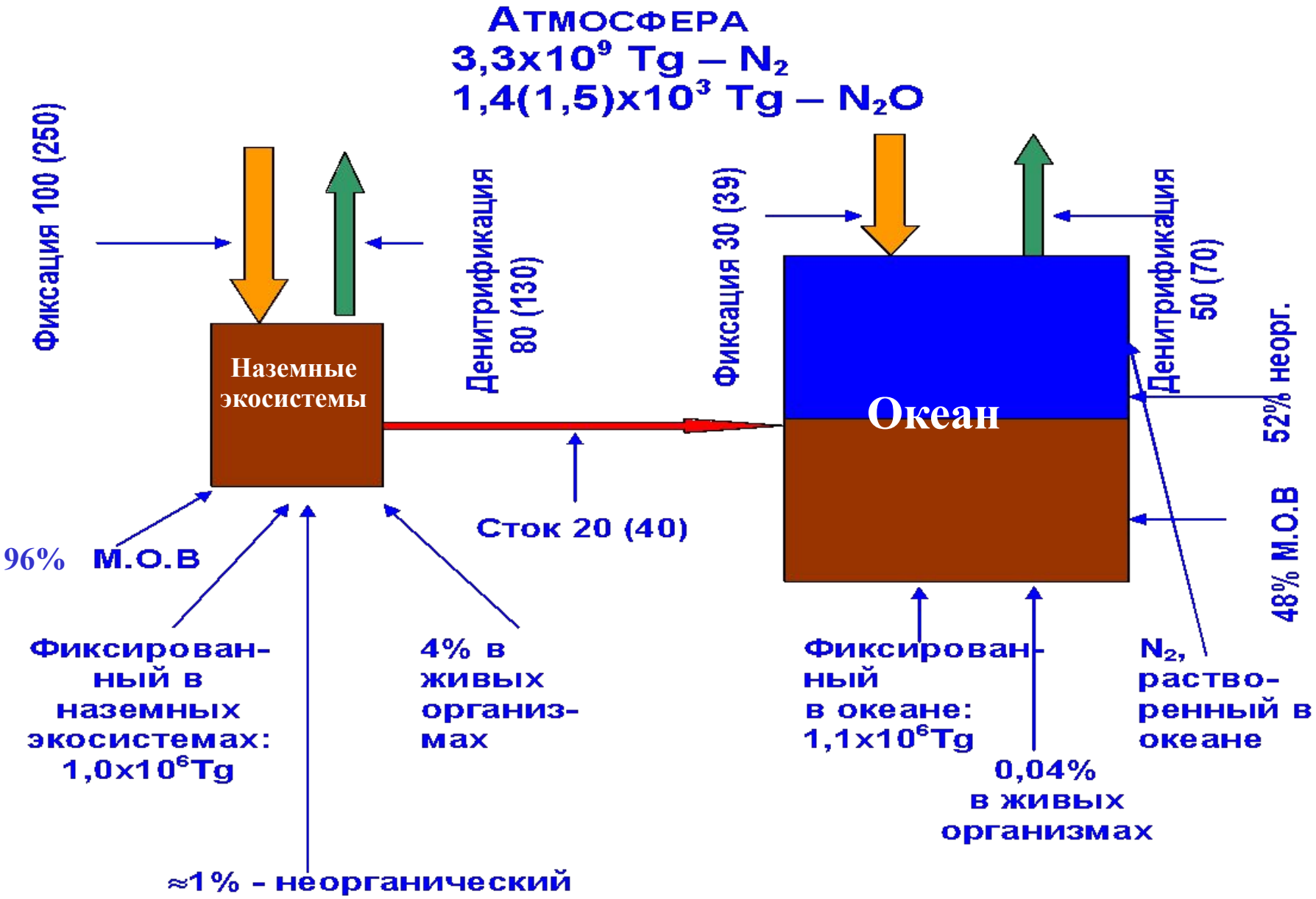
Реакции	Выход энергии, ккал
ДЕНИТРИФИКАЦИЯ	
1. $C_6H_{12}O_6+6KNO_3 \rightarrow 6CO_2+3H_2O+6KOH+\underline{3N_20}$	545 (на 1моль глюкозы)
2. $5C_6H_{12}O_6+24KNO_3 \rightarrow 30CO_2+18H_2O+24KOH+12\underline{N_2}$	570 (на 1моль глюкозы)
3. $5S+6KNO_3+2CaCO_3 \rightarrow 3K_2SO_4+2CaSO_4+ 2CO_2+3\underline{N_2}$	132 (на 1моль серы)
ДЫХАНИЕ	
4. $C_6H_{12}O_6+6O_2 \rightarrow 6CO_2+6H_2O$	686
АММОНИФИКАЦИЯ	
5. $CH_2NH_2COOH+1½O_2 \rightarrow 2CO_2+H_2O+NH_3$ глицин	176
НИТРИФИКАЦИЯ	
6. $NH_3+1½O_2 \rightarrow HNO_2+H_2O$	66
7. $KNO_2+1½O_2 \rightarrow KNO_3$	17,5
ФИКСАЦИЯ АЗОТА	
8. $N_2 \rightarrow 2N$ «активация азота»	-160
9. $2N+3H_2 \rightarrow 2NH_3$	12,8

Распределение азота в различных резервуарах Земли

Резервуары	Млн. т
РАСТИТЕЛЬНАЯ БИОМАССА (наземная)	$1,1\text{-}1,4 \times 10^4$
ЖИВОТНАЯ БИОМАССА (наземная)	2×10^2
ОПАД (наземный)	$1,9\text{-}3,3 \times 10^3$
ПОЧВА	
-органическое вещество	$3,0 \times 10^5$
-нерастворимый неорганический	$1,6 \times 10^4$
-микроорганизмы	$5,0 \times 10^2$
ПОРОДЫ	$1,9 \times 10^{11}$ (1)
ОСАДКИ	$4,0 \times 10^8$ (3)
УГОЛЬНЫЕ ОТЛОЖЕНИЯ	$1,2 \times 10^5$
ОКЕАН	
растительная биомасса	$3,0 \times 10^2$
животная биомасса	$1,7 \times 10^2$
мертвое органическое вещество	$5,3 \times 10^5$
N_2 (растворенный)	$2,2 \times 10^7$ (4)
NO_3^-	$5,7 \times 10^5$
NH_4^+	$7,0 \times 10^3$
АТМОСФЕРА	
N_2	$3,9 \times 10^9$ (2)
N_2O	$1,3 \times 10^3$
NH_3, NO_x, NO_3^-, органический N	3-4

(Tamm, 1991)

Глобальный биогеохимический цикл азота



Динамика численности населения Мира за последние 50 лет и прогноз до 2100 г.

в 1960 — 3 млрд,

в 1993 — 5,65 млрд,

12 октября 1999 года население Земли составило 6 млрд человек

в 2003 — 6,3 млрд,

в 2006 — 6,5 млрд,

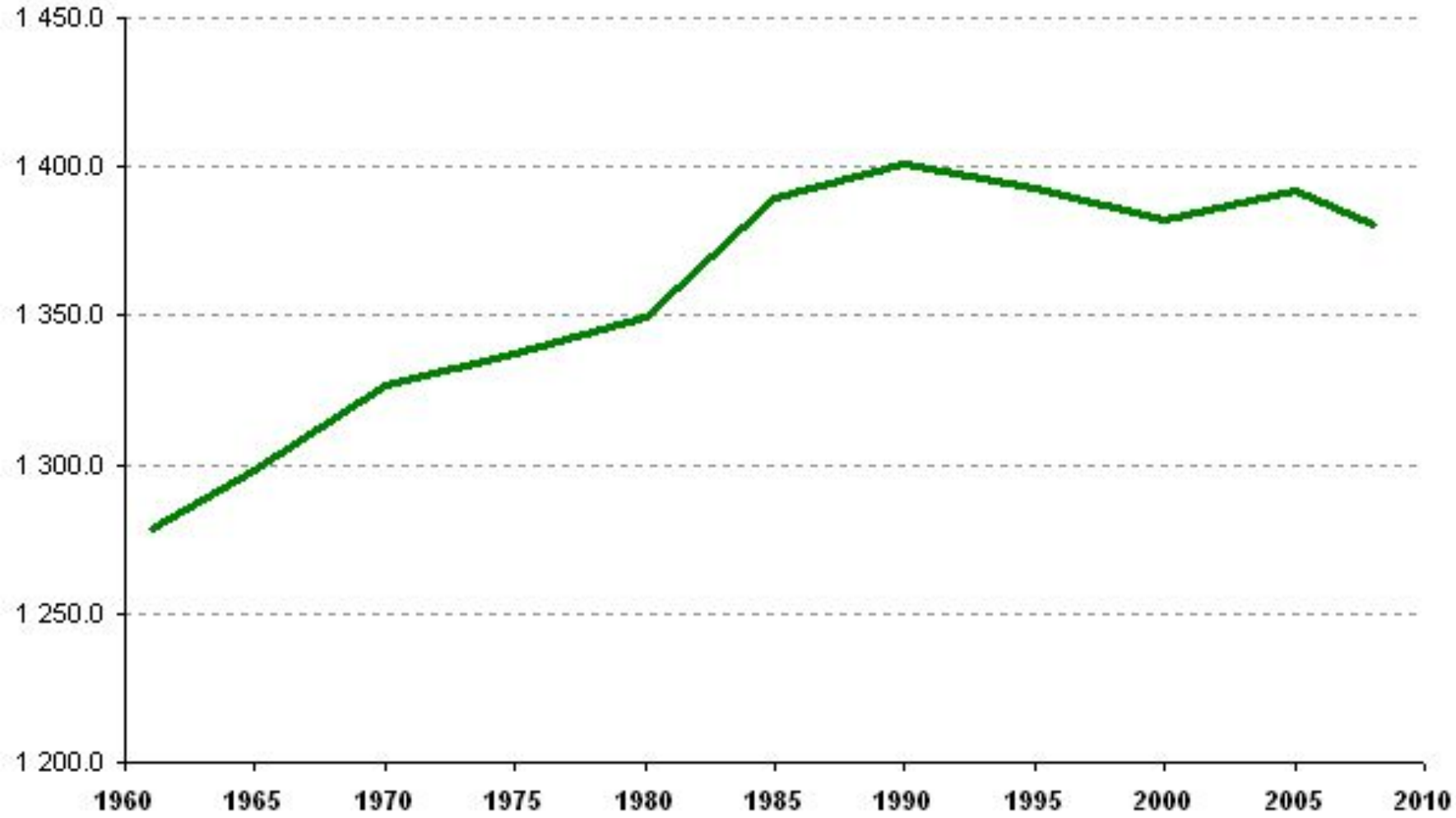
в 2010 — 6,8 млрд,

1 ноября 2011 — 7,0 млрд человек[1][2],

прогноз на 2050 год — 9 миллиардов человек[3][4], на 2100 год — 10 млрд

https://ru.wikipedia.org/wiki/%CD%E0%F1%E5%EB%E5%ED%E8%E5_%C7%E5%EC%EB%E8

Изменение площади пахотных земель в Мире за последние 50 лет (млн. га)



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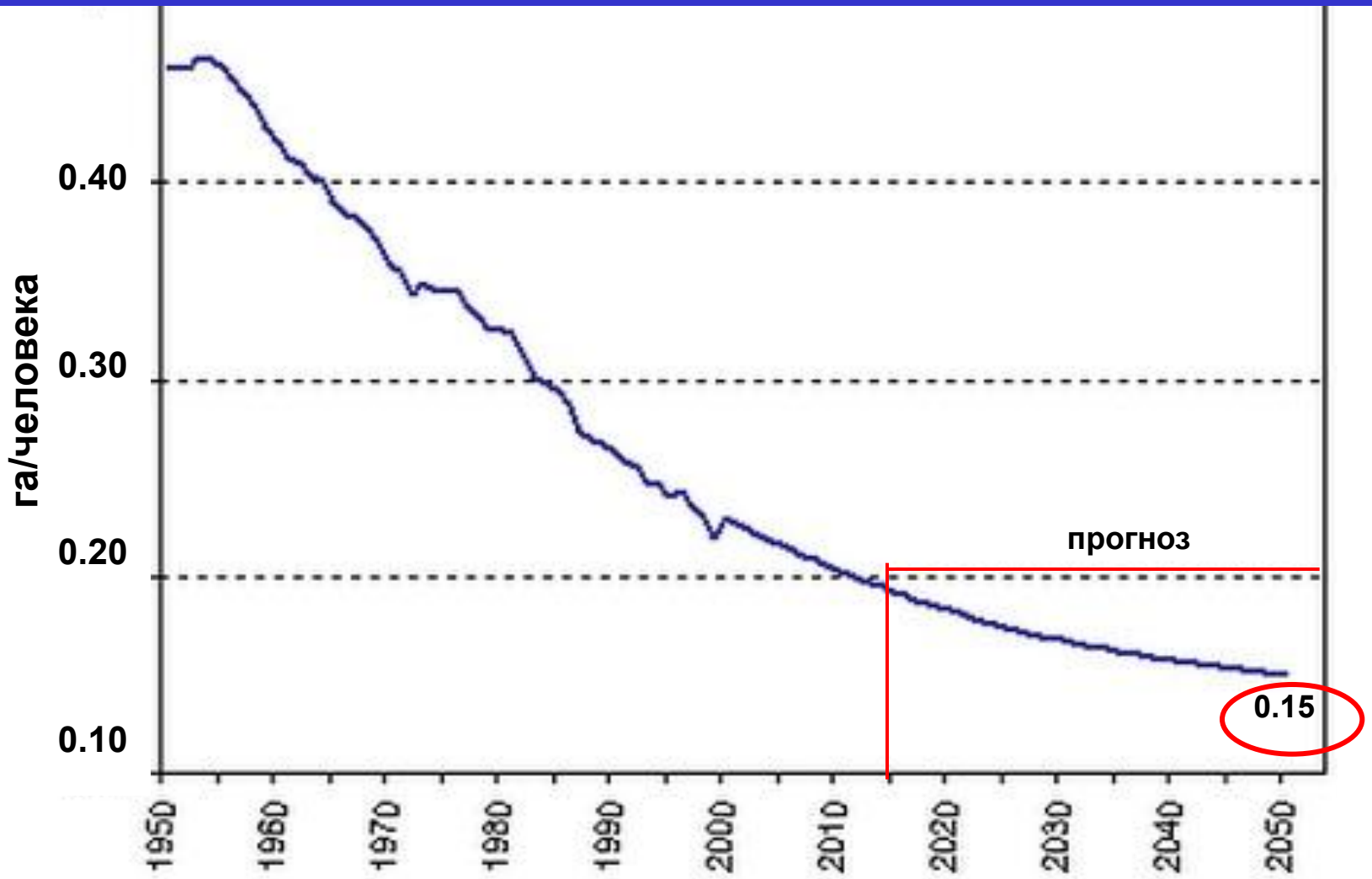
Динамика площади пашни в Мире в расчёте на 1 чел.



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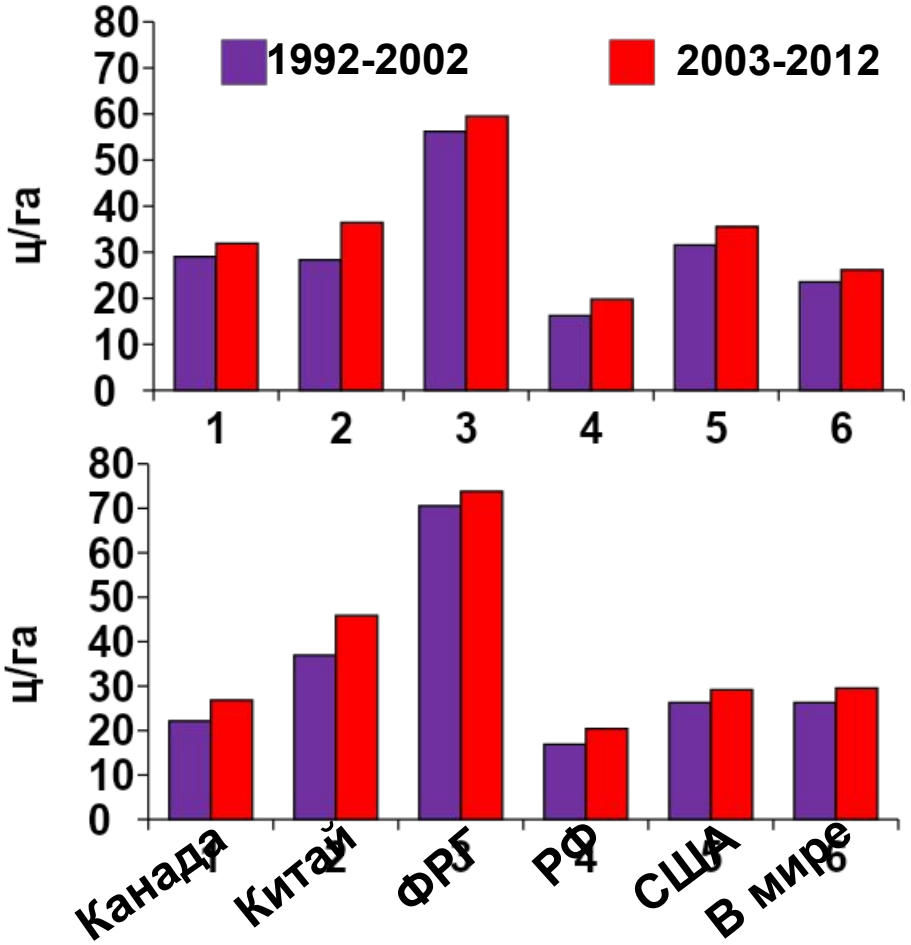
Население и удельная площадь пашни на 1 человека

Регионы, страны	Население, млн. чел.	Пашня, млн. га	Удельная площадь, га/чел.
США	315	186	0.6
Западная Европа	380	95	0.25
Россия	140	85	0.6
Весь мир	7000	1400	0.2

Без минеральных удобрений в Нечерноземье можно прокормить только 1 чел./га пашни

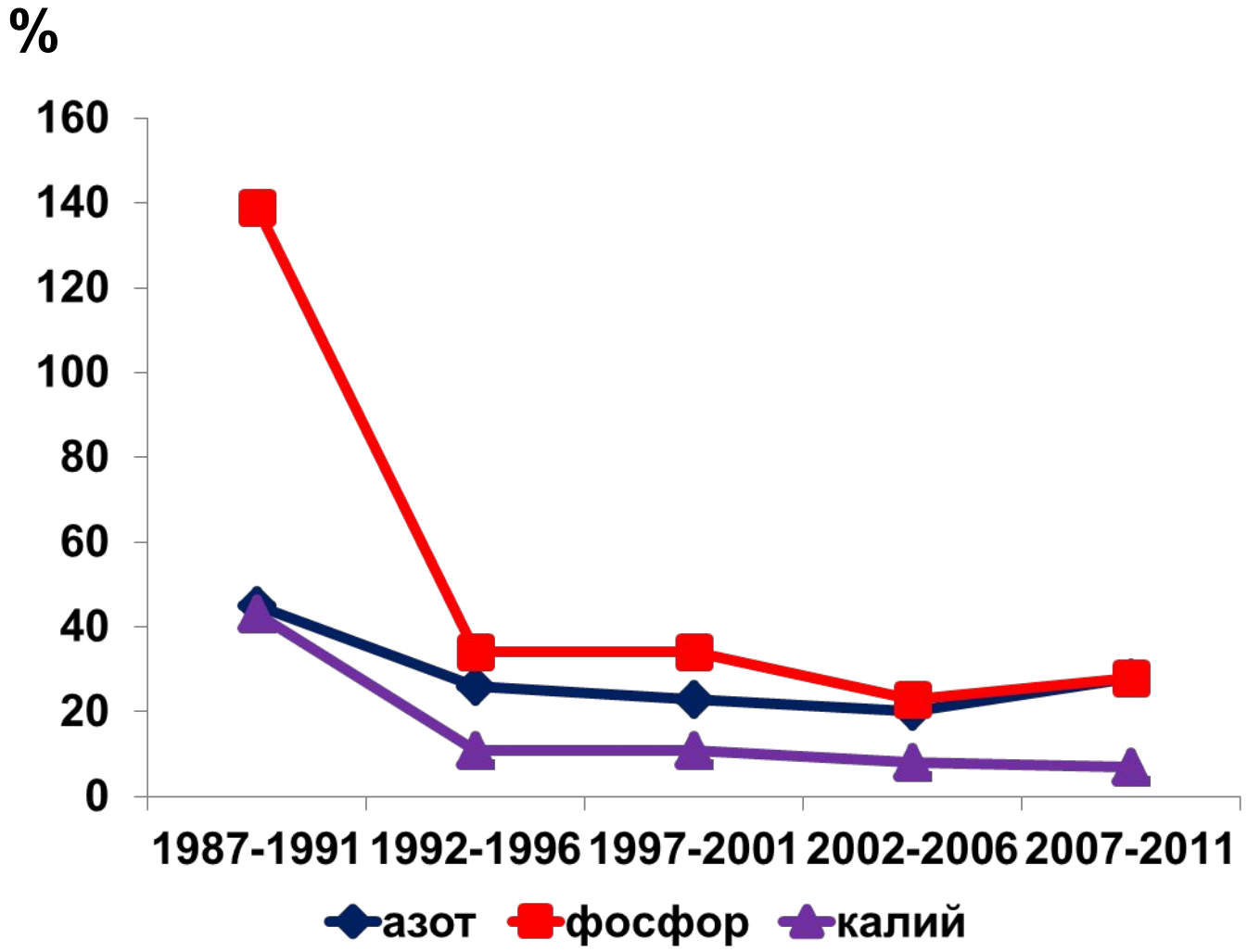
Урожайность зерновых в некоторых странах и мире



Ячмень

Пшеница

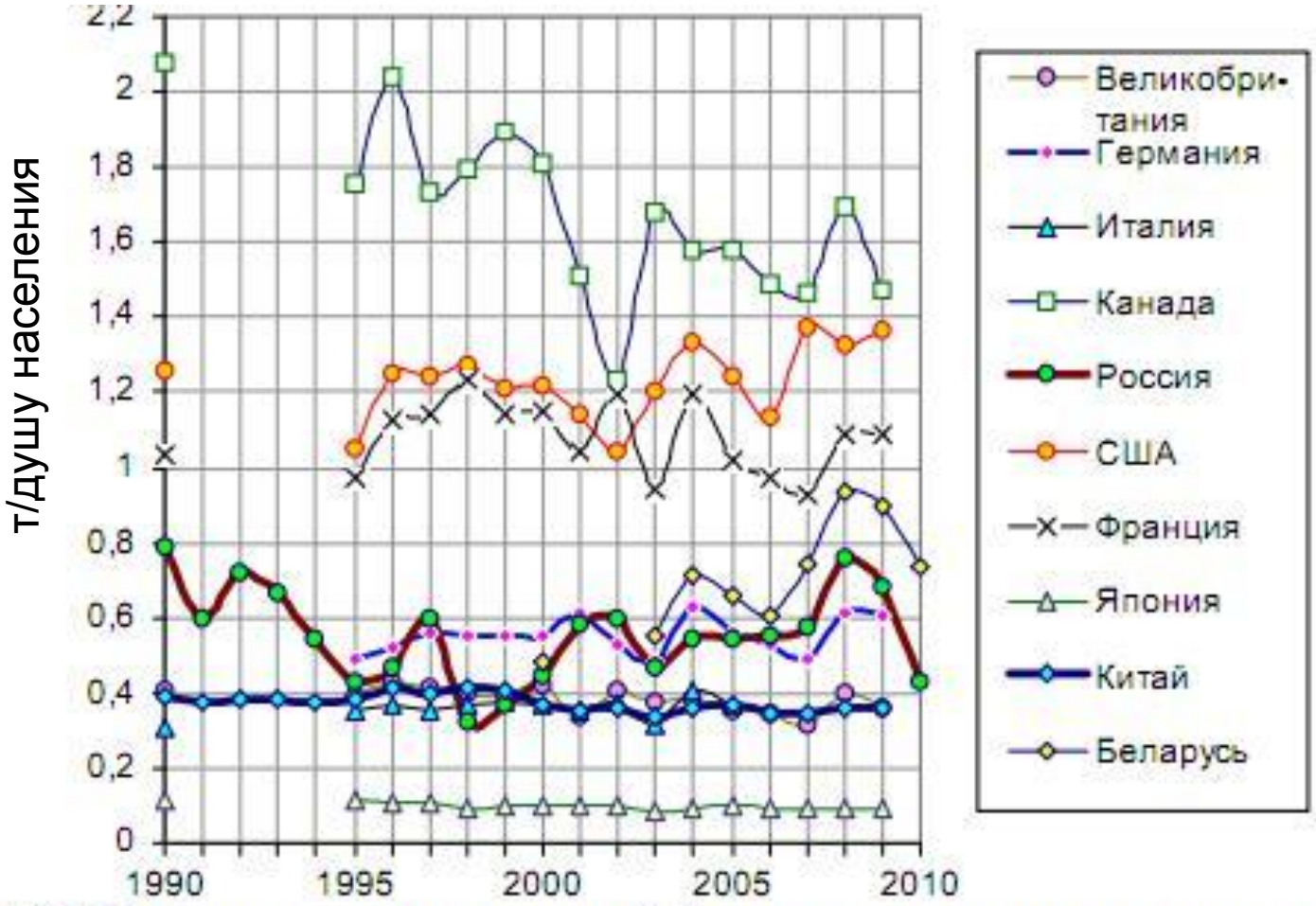
Компенсация выноса питательных веществ с урожаями внесением минеральных удобрений на территории России (%)



Ведущие потребители минеральных удобрений в мире (2010 г.)

N		P_2O_5		K_2O	
Страна	Млн. т.	Страна	Млн.т.	Страна	Млн.т.
1. Китай	26.1	1. Китай	8.60	1. США	4.47
2. Индия	10.9	2. Индия	4.21	2. Китай	3.47
3. США	10.5	3. США	3.86	3. Бразилия	2.56
4. Франция	2.32	4. Бразилия	2.34	4. Индия	1.57
5. Пакистан	2.26	5. Австралия	1.10	5. Франция	1.03
6. Индонезия	1.96	6. Франция	0.80	6. Малайзия	0.64
……..	……	……..	……	……..	…..
17. Россия	0.96	19. Россия	0.28	21. Россия	0.18

Производство зерновых и зернобобовых на душу населения в некоторых странах



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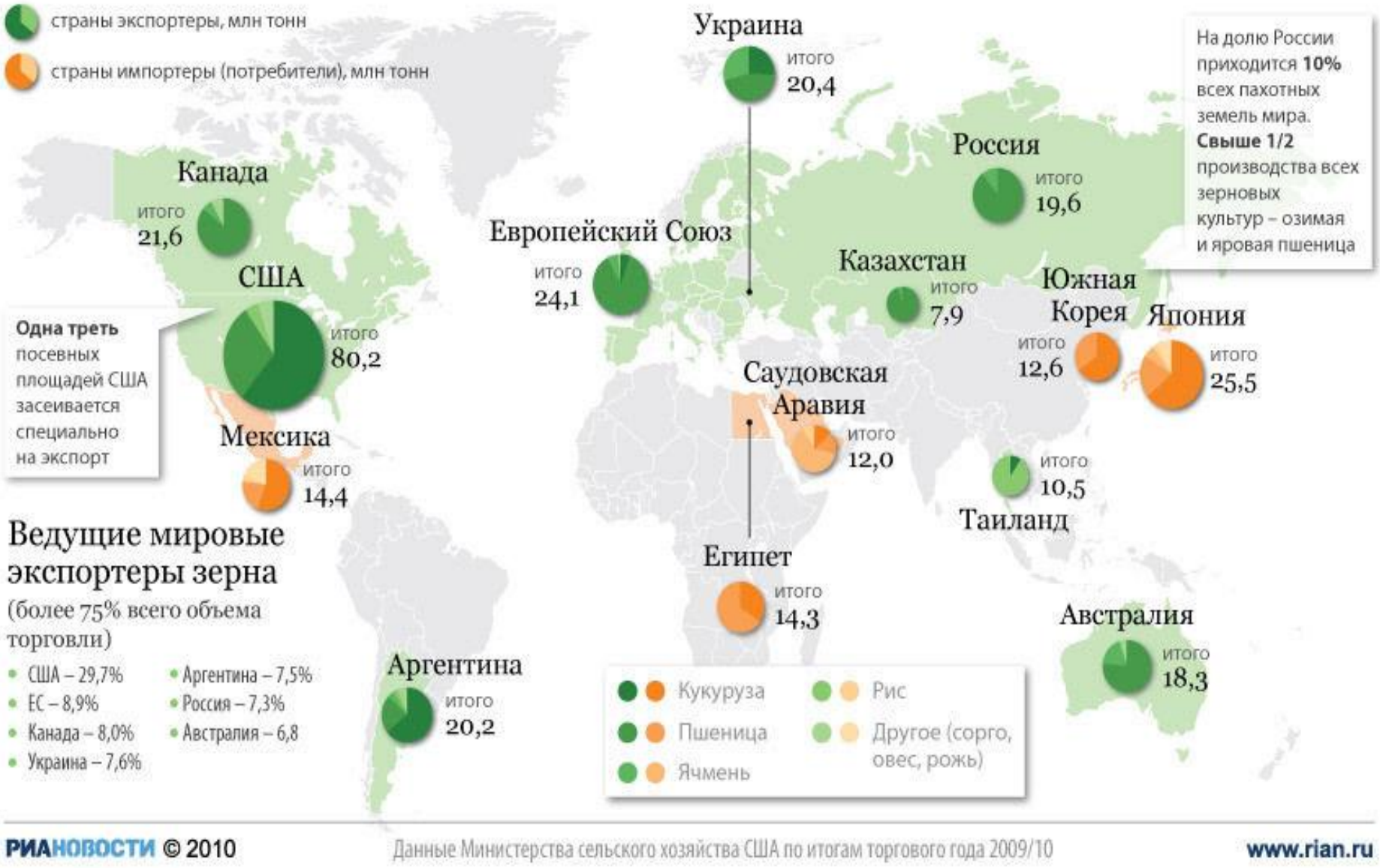
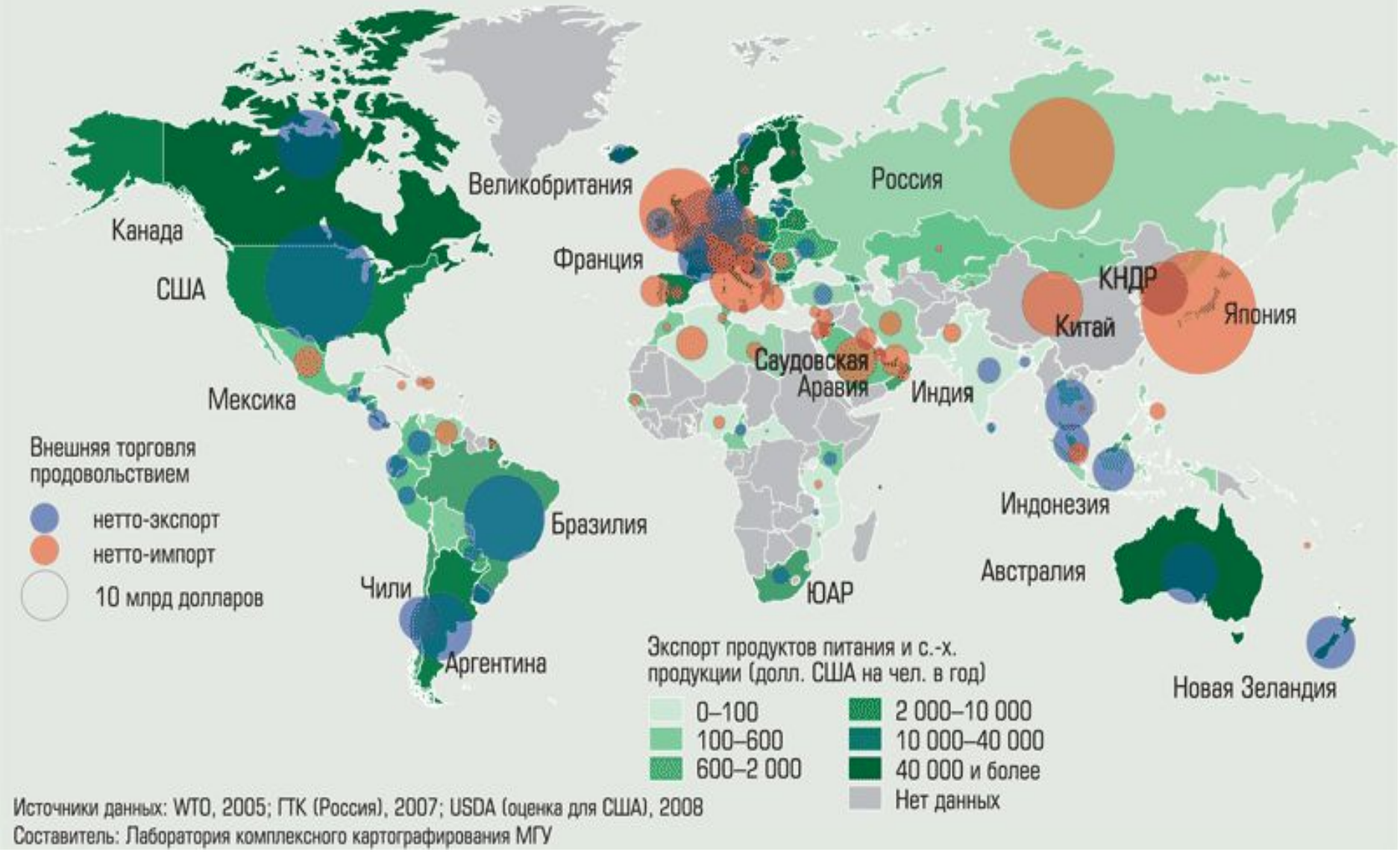
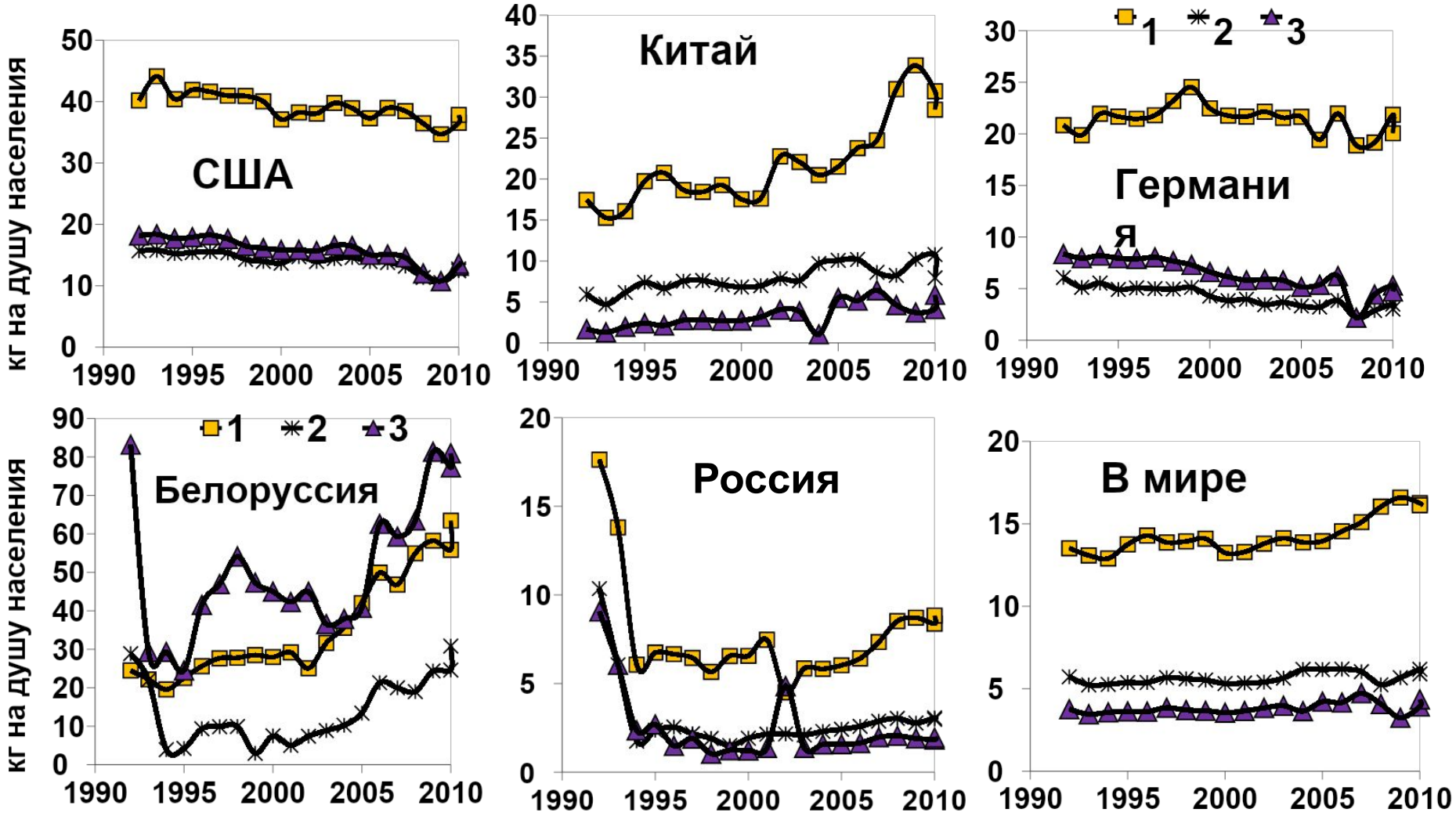
Мировые экспортёры и импортёры зерна



Международная торговля сельскохозяйственной продукцией

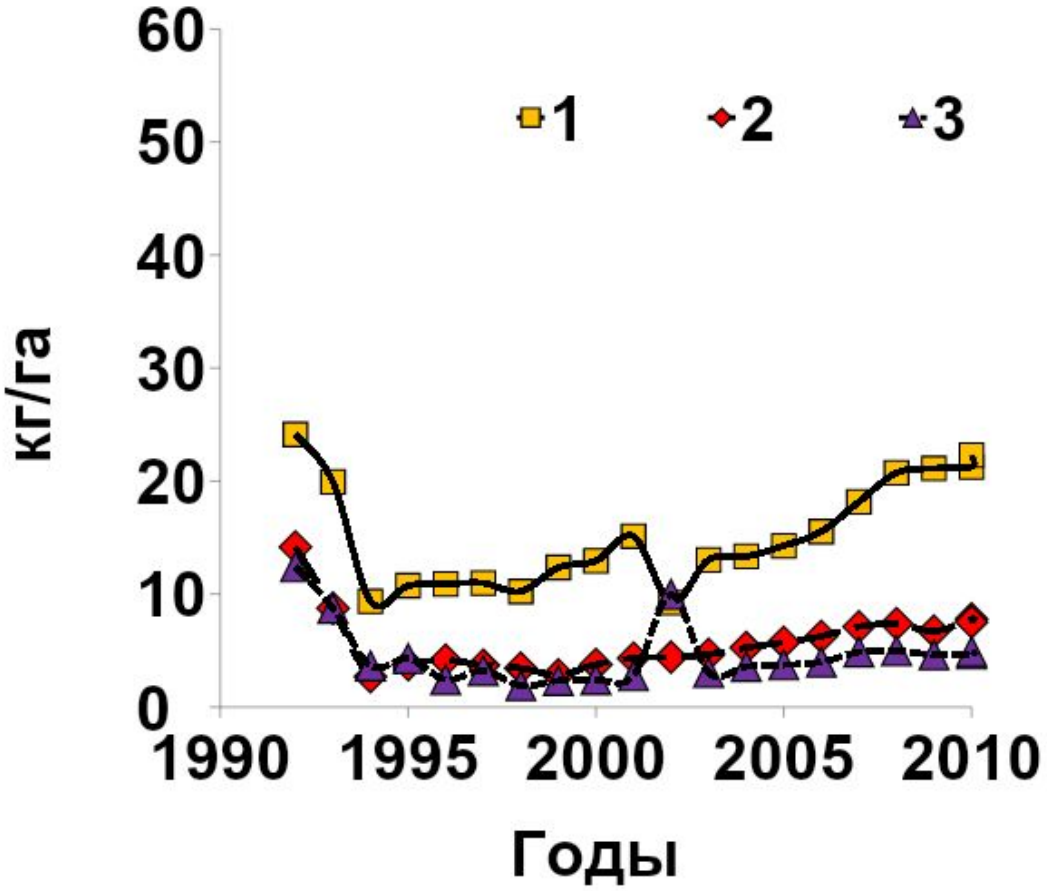


Применение минеральных удобрений в земледелии некоторых стран и в мире
(в действующем веществе, кг/душу населения)



1 – азот (N), 2 – фосфор (P_2O_5), 3 – калий (K_2O)

Средние дозы минеральных удобрений (N,P,K) на посевах с/х культур в РФ



1 – азот, 2 – фосфор, 3 – калий

Потребность в азоте

Потребность населения в протеине
60-70 г/чел./день или 4 кг *N*/чел./год

Потребность в *N*уд. рассчитывается исходя из равного количества потребляемого протеина (животного и растительного)
***50% и 15%* - коэффициенты усвоения, соответственно.**

***N*уд. – потребность = 17 кг *N*/чел./год**

Для населения 140 млн. человек – 2,4 млн.т *N* уд.

Каждый гектар пашни России должен получать

не менее 60 кг *N*/год

7 млрд. **человек содержат ≈ 8** ***Tg N***
Для поддержания этого резервуара *N* ежегодно фиксируется в *20-25* раз больше *N*
160-200 Tg N

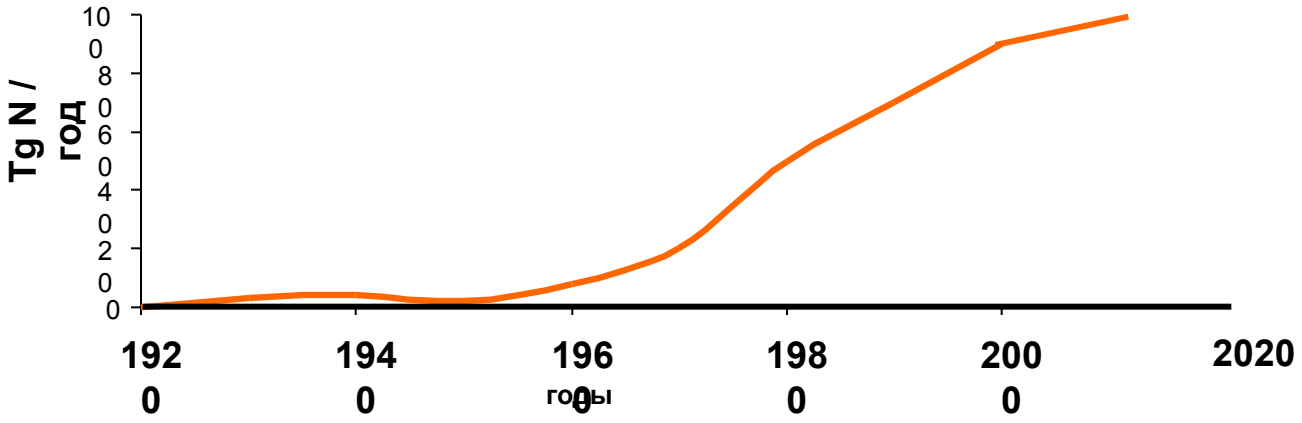
США

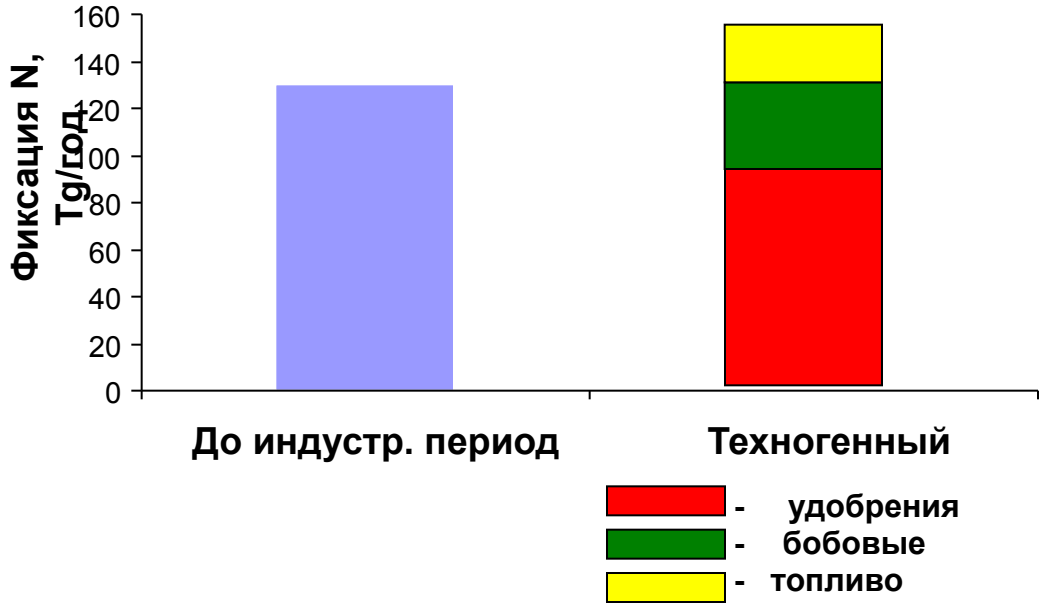
Производство:

1 кг **говядины требует *14 кг* зерна кукурузы (эквивалент), содержащей ≈ 250 г N**

1 кг **курятины (бройлер) требует *2,5 кг* зерна кукурузы (эквивалент) или ≈ 50 г N**

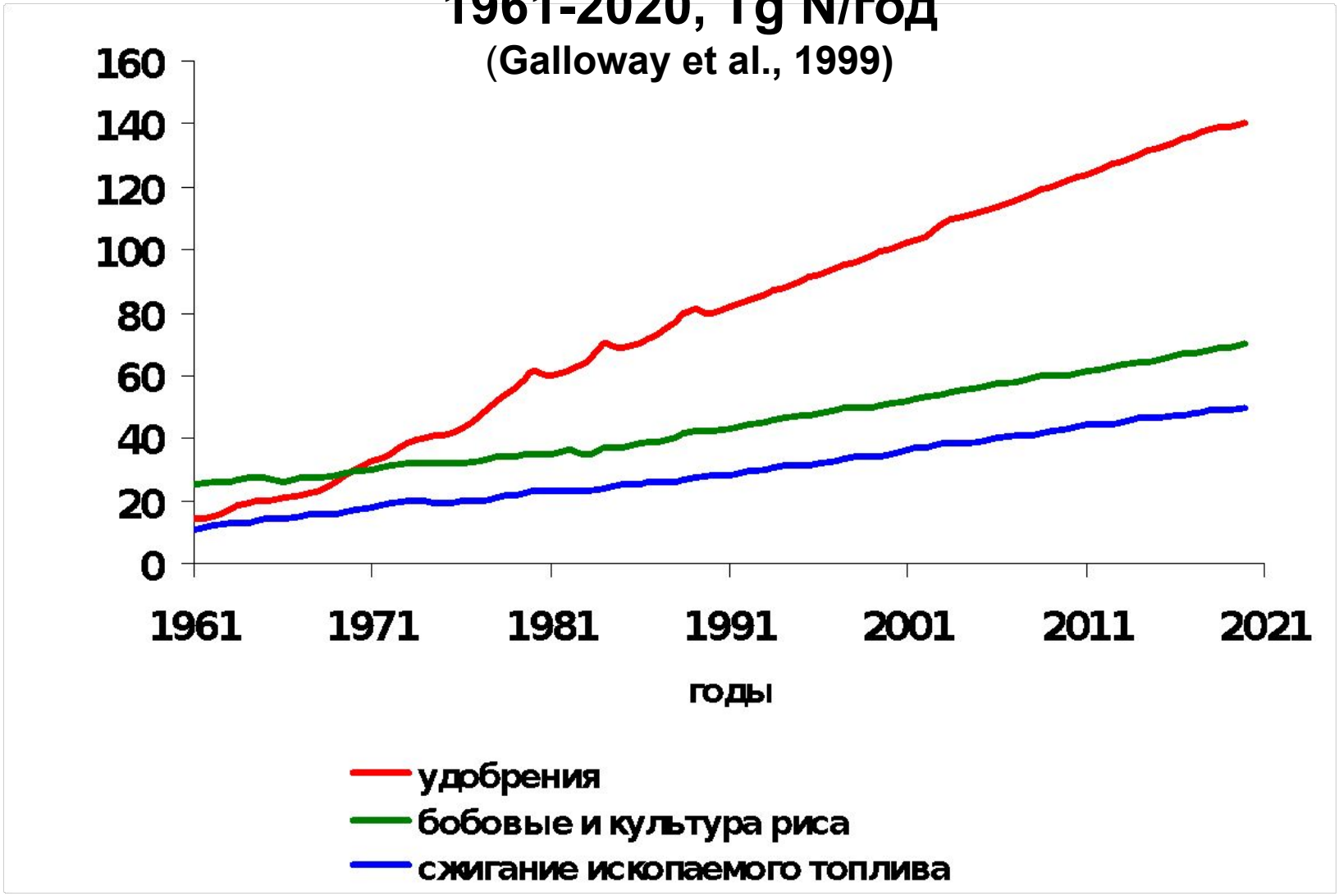
Глобальное производство азотных удобрений





Фиксация N при производстве удобрений, сжигании ископаемого топлива, выращивании бобовых и культуры риса, 1961-2020, Tg N/год

(Galloway et al., 1999)



Глобальный баланс азота

Приход (Tg N)		Расход (Tg N)	
Фиксация в атмосфере (электрические разряды)	1-30	Денитрификация	80-720
Биологическая фиксация	45-330	Речной сток	10-40
Техногенная фиксация	110-130		
Сжигание ископаемого топлива	15-45		
ВСЕГО:	171-535	ВСЕГО:	90-760

Оборачиваемость азота (Tg/год) (Tamm, 1991)

В наземных экосистемах	2000
В океаническом планктоне	4000

Экологические последствия интенсивного вовлечения техногенного азота в круговорот

Потоки азота
при сжигании ископаемого топлива
Выбросы: NO_x, NH_3

<u>Последствия:</u>

1. **Фотохимический смог**
2. **Кислотные атмосферные осадки**
3. **Разрушение озонового слоя**
4. **Парниковый эффект**

Выбросы NO_x

Мобильные источники:

легковые автомобили ≈ *6-7 млн.т/год*
тяжелые автомобили и авиация ≈ *2-3 млн.т/год*

Химическая промышленность

(без удобрений) и производство цемента ≈ *2-3 млн.т./год*

Сжигание древесины и растительных остатков ≈ 5 млн.т/год

Нитраты (NO_3^-)

- Нитраты (NO_3^-) - не токсичны!
- Нитриты (NO_2^-) консерванты против ботулизма
- NO_3^- - используется для лечения мочекаменной болезни, болезней сердца
- Растворяет почечные камни фосфатной природы.
- Дозировка до 9г $NaNO_3$ или NH_4NO_3 в сутки - без каких-либо осложнений.

Физика и химия утечки нитратов

NO_3^- - практически не сорбируется в почве

Почвы бореального пояса с pH=4,0-7,5 не сорбируют NO_3^- и другие анионы (Cl^-, SO_4^{2-}), их коллоидные частицы заряжены отрицательно

Некоторые тропические сильно выщелоченные почвы с очень кислой реакцией (pH≈3,5) могут поглощать анионы. В этих условиях коллоидные частицы несут положительный заряд

NH_4^+ в противовес NO_3^- хорошо поглощается в почвах и слабо вымывается из них

Корень нитратной проблемы:

доступность
подвижность } = уязвимость

Нитратная проблема – *«несвоевременные»* нитраты
«Несвоевременные»* нитраты так или иначе становятся нитратами *«загрязняющими»
Подвижность нитратов зависит от физического поведения воды в почве

Метгемоглобинемия или синдром «синего ребенка»

У детей младше 1 года в желудке

$$NO_3^- \rightarrow NO_2^-$$

<u>Оксигемоглобин,</u> содержит (Fe^{+++}) в окисной форме переходит в <u>метгемоглобин (</u>Fe^{++}) в закисной форме В результате снижается способность переносить O_2

Случаи метгемоглобинемии в связи с концентрацией NO_3^- в воде (Addiscott et al., 1994)

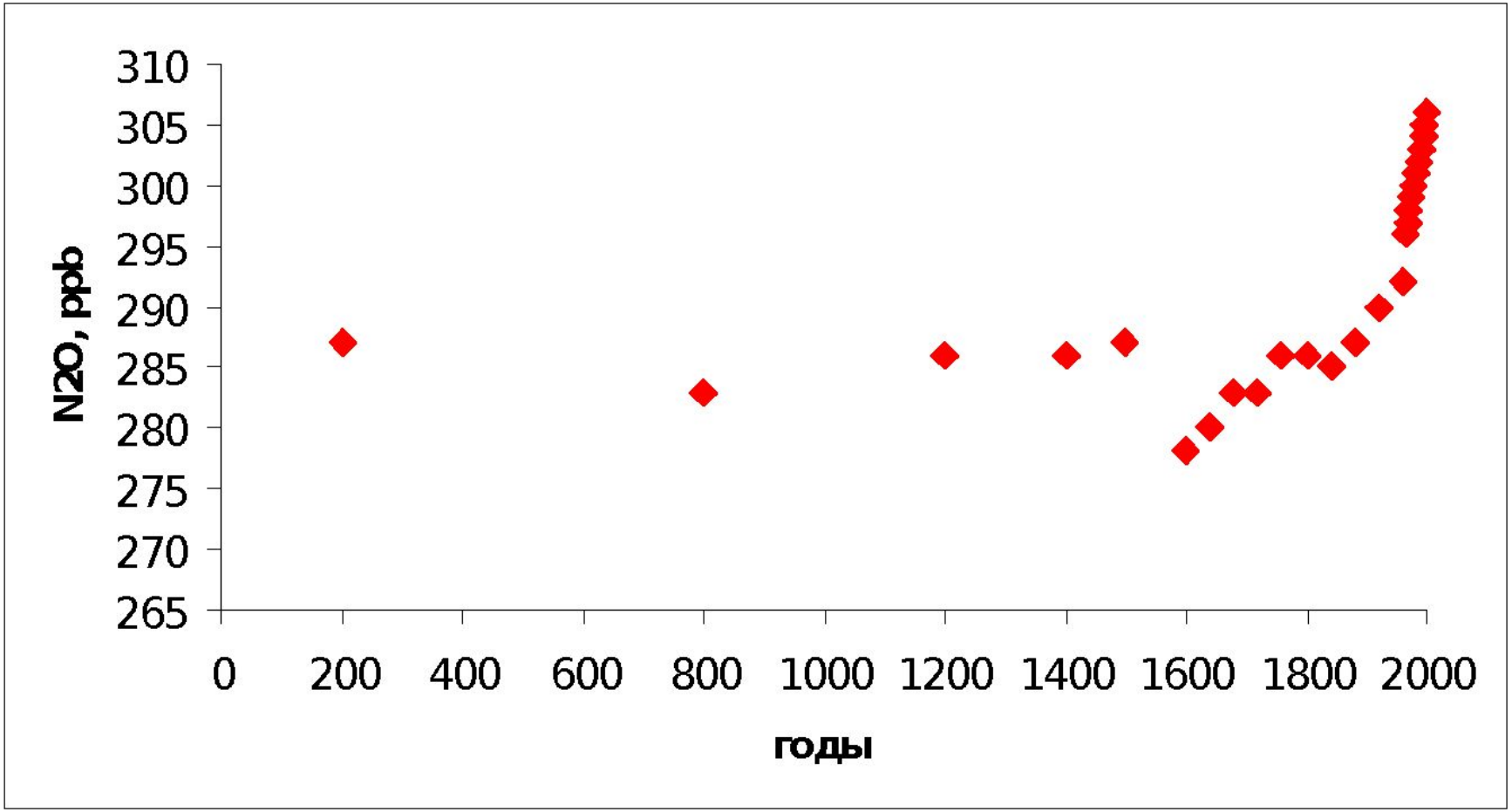
Источник	Страна	Количество случаев	Концентрация NO_3^-, мг/л
Comly (1945)	USA	2 1	388, 619 283-620
Choquette (1982)	USA	1	1200
Busch and Meyer (1982)	USA	1	545
Johnson et al. (1987)	USA	1	665
Ewing and Mayon-White (1951)	UK	2	200*), 45(P)
Acheson (1985)	UK	14	>100
Deak (1985)	Венгрия	45 1258	40-100 >100
Hye-Knudsen (1985)	Дания	1	200(P)

*) Фатальный исход

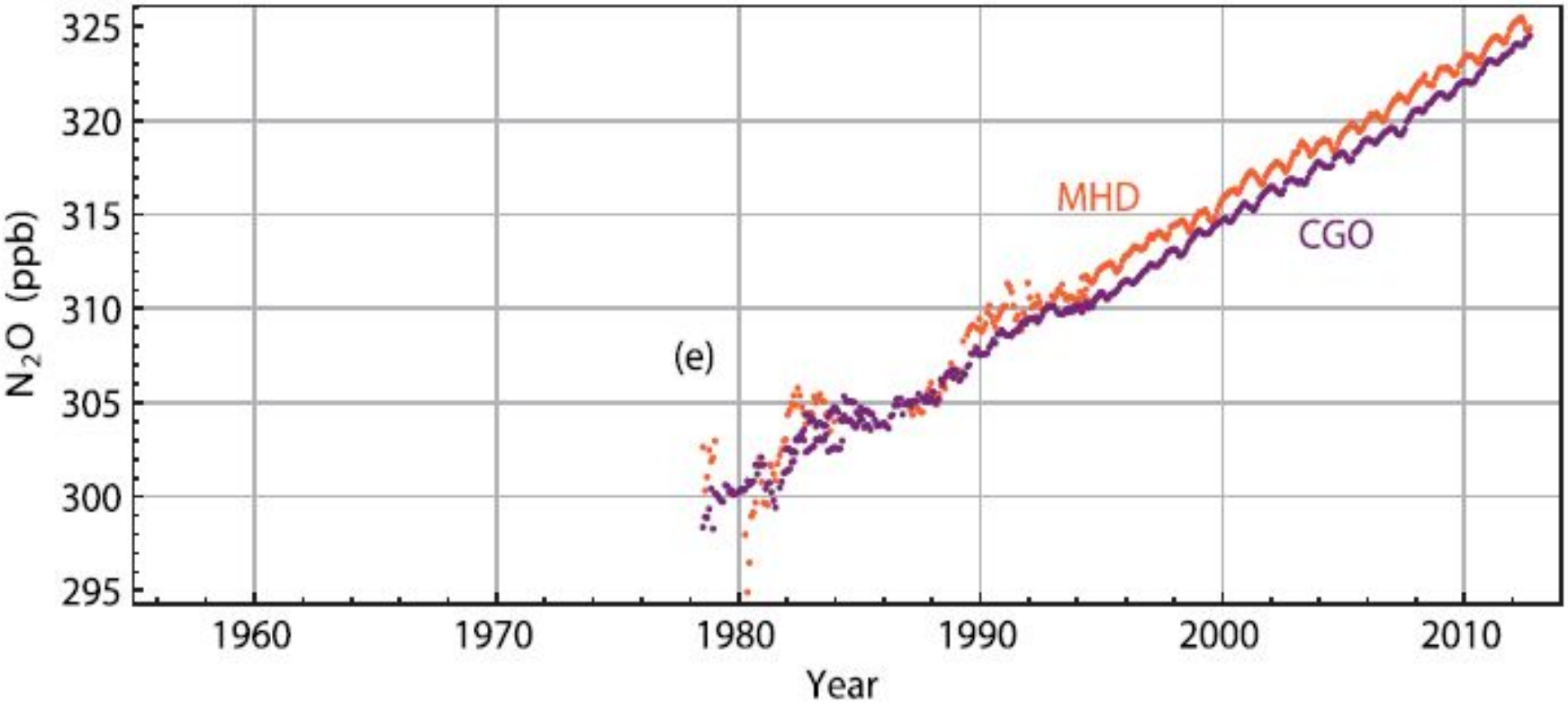
(P) Вода имела бактериальное загрязнение

Все случаи связаны с использованием воды из частных колодцев

Атмосферная концентрация N_2O за последние 2000 лет

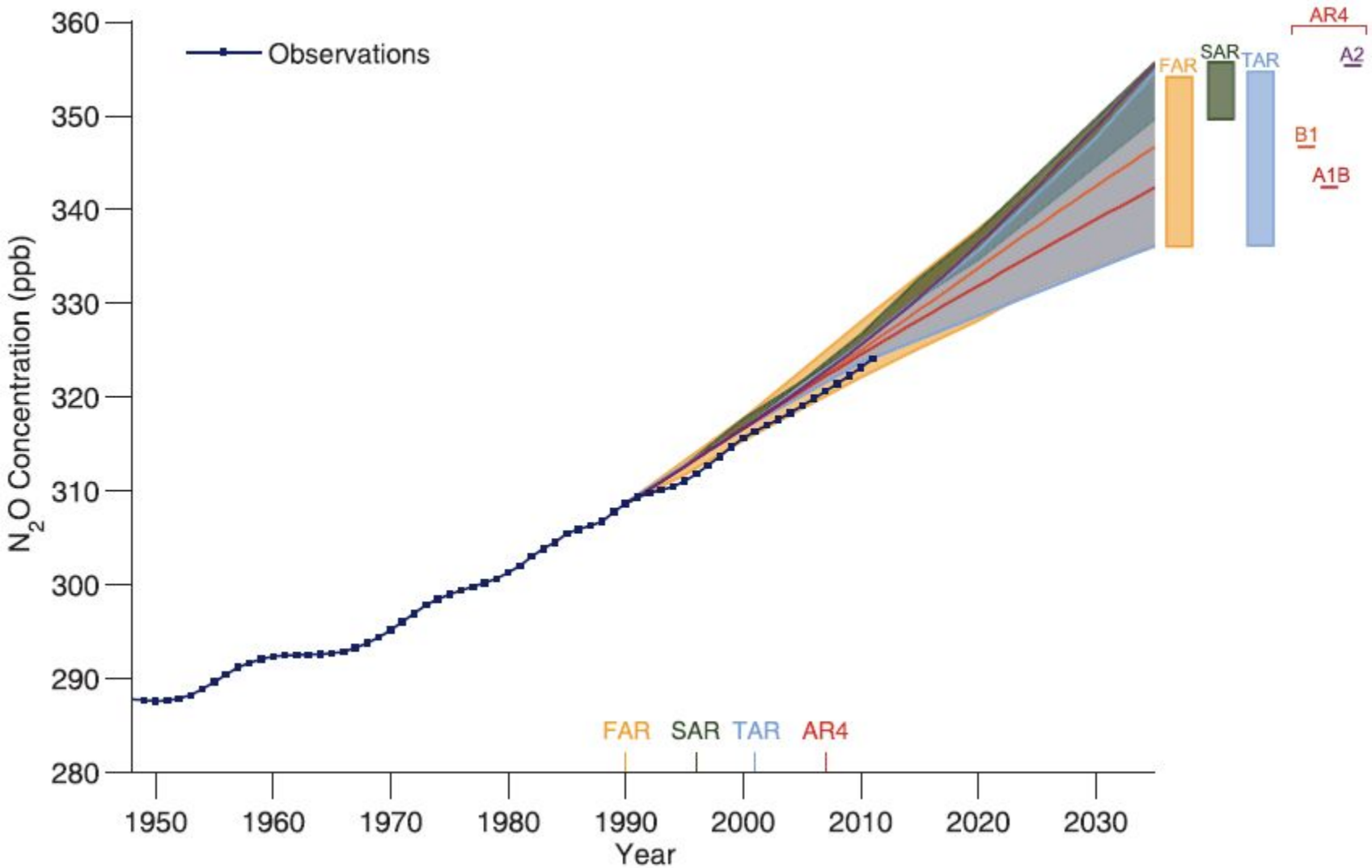


Динамика закиси азота в атмосфере



MHD – Mace-Head Northern Hemisphere
CGO – Cape Grim Station

Динамика содержание в атмосфере N_2O и прогноз ее содержания



Эмиссия закиси азота на територии России

среднее за год (1990-2010 гг.)

Источники закиси азота	Эмиссия N_2O, N, млн. т/год
Сжигание ископаемого топлива	0.30
Лесные пожары	0.07-0.22
Применение азотных удобрений	0.04
Денитрификация в почвах	0.8
Всего	1.21-1.36

Площади почвенного покрова и эмиссия закиси азота

Показатели / Регион	Площадь		$N\text{-}N_2O$	
	Млн. $км^2$	%	Млн. т	%
Мир	143.6	100	18.0	100
Россия	16.9	11.7	1.2	6.6

Нитрификация

Nitrosomonas *Nitrobacter*

$NH_4^+ \longrightarrow NH_2OH \longrightarrow NO_2^- \longrightarrow NO_3^-$

$NH_2OH \xrightarrow{\text{Химическое разложение}} N_2O,\ NO$

Денитрификация

$NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$

В стратосфере

$N_2O \longrightarrow N_2 + O$ (90% фотодиссоциация)

$N_2O + O \longrightarrow 2\ NO$ и/или $N_2 + O_2$ ($\sum$=10%)

Разрушение озона

NO каталитически разрушает озон:

$$NO+O_3 \rightarrow NO_2+O_2$$

$$N_2O+O \rightarrow NO+O_2$$

Нетто:

$$O+O_3 \rightarrow 2O_2$$

Имеются ли в будущем альтернативы применению удобрений?

Увеличение использования бобовых или других N- фиксирующих растений (например Azolla в рисовниках)	*- Ограничено*
Внедрение N-фиксирующих генов в большинство культур	*- сложная задача, вероятно не скоро*
Активация N-фиксации свободноживущих азотфиксаторов	*- мало надежды для прогресса*
Усиление ассоциативной азотфиксации большинства культур	*- может быть определенный эффект, но значительный эффект маловероятен*

ЗАПАСЫ ОБЩЕГО АЗОТА В ПОЧВАХ РОССИИ

Зоны	Площадь, млн. га	Запасы N в слое 0-100 см	
		т/га	млн. т
Полярно-Тундровая	181	6.2	1122
Лесотундровая-Северотаежная	233	7.1	1654
Среднетаежная	238	4.3	1023
Южнотаежная	237	5.7	1351
Лесостепная	126	14.2	1789
Степная	80	25.9	2064
Сухостепная	28	19.2	537
Полупустынная	15	5.2	78
Горные области	576		3000
всего	1714		12618

НАКОПЛЕНИЕ АЗОТА В РАСТИТЕЛЬНОЙ БИОМАССЕ НА ТЕРРИТОРИИ РОССИИ

Зона	Пло-щадь, млн. га	Ежегодный прирост		
		биома с-са, т/га	N, кг/га	N, аккуму-ляция, млн.т
Тундра	181	<1.0	5	0.9
Лесотундровая-	233	2.5-6.0	50	11.6
северотаежная	238	6.1-8.0	60	14.3
Среднетаежная	237	8.1-10.	80	19.0
Южнотаежная	126	0	125	15.8
Лесостепная	80	10.1-15	80	6.4
Степная	28	6.0	60	1.7
Сухостепная	15	4.0	40	0.6
Полупустынная	576	1.0-2.5	15-30	13
Горные области				
ВСЕГО	1714			83.3

Применение минеральных удобрений в мире

Удобрения	Год							
	1965	1970	1975	1980	1985	1990	1995	2000
Всего	47,0 36.6	69,3 53.2	91,4 69.6	116,7 87.6	129,6 94.4	137,8 99.8	129,7 94.4	136,4 100.0
Азотные, N	19,1 14.9	31,8 24.4	44,4 33.8	60,8 45.6	70,4 51.3	77,2 55.8	78,4 57.0	81,6 59.8
Фосфорные, P_2O_5	15,8 12.3	21,1 16.2	25,6 19.5	31,7 23.8	33,5 24.4	36,1 26.1	30,7 22.3	32,6 23.9
Калийные, K_2O	12,1 9.4	16,4 12.6	21,4 16.3	24,2 18.2	25,7 18.7	24,7 17.9	20,7 15.1	22,2 16.3

Примечание: Над чертой - млн. тонн; Под чертой - кг/га пашни.

Основные потоки глобального биогеохимического цикла азота

ПОТОКИ	Интервал величин (Tg N)
Фиксация в атмосфере (молнии)	1-30
Биологическая фиксация (всего)	45-330
в т.ч.: наземная	44-200
в океане	1-130
Техногенная фиксация	120
Сжигание ископаемого топлива	15-45
Сжигание биомассы	10-200
Биогенное высвобождение NO_x	20-230
Денитрификация (вся)	80-720
в т.ч.: наземная	40-390
в океане	40-330
Улетучивание NH_3	30-250
Атмосферные выпадения (всего)	110-360
в т.ч.: NH_3/NH_4^+	80-240
NO_x	30-120
Органический N (выпадения)	10-100
Речной сток	10-40

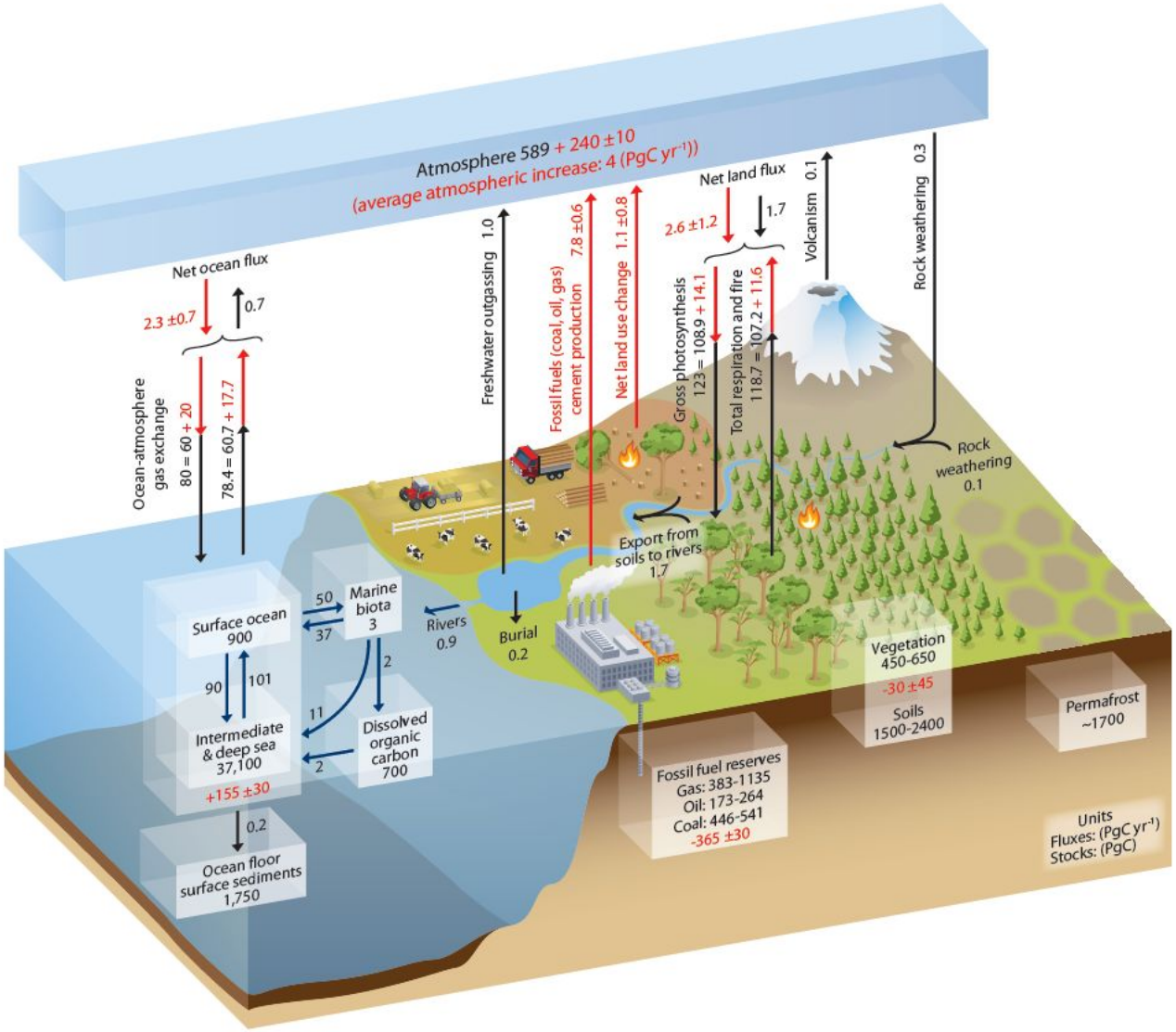

Atmosphere 589 + 240 ±10
(average atmospheric increase: 4 (PgC yr⁻¹))
Net ocean flux
2.3 ±0.7
0.7
Ocean-atmosphere gas exchange
80 = 60 + 20
78.4 = 60.7 + 17.7
Freshwater outgassing 1.0
Fossil fuels (coal, oil, gas) cement production 7.8 ±0.6
Net land use change 1.1 ±0.8
Net land flux
2.6 ±1.2
1.7
Gross photosynthesis 123 = 108.9 + 14.1
Total respiration and fire 118.7 = 107.2 + 11.6
Volcanism 0.1
Rock weathering 0.3
Rock weathering 0.1
Export from soils to rivers 1.7
Surface ocean 900
50
37
Marine biota 3
Rivers 0.9
Burial 0.2
90
101
2
11
2
Intermediate & deep sea 37,100
+155 ±30
Dissolved organic carbon 700
0.2
Ocean floor surface sediments 1,750
Vegetation 450-650
-30 ±45
Soils 1500-2400
Permafrost ~1700
Fossil fuel reserves
Gas: 383-1135
Oil: 173-264
Coal: 446-541
-365 ±30
Units
Fluxes: (PgC yr⁻¹)
Stocks: (PgC)

Figure 6.1 | Simplified schematic of the global carbon cycle. Numbers represent reservoir mass, also called 'carbon stocks' in PgC (1 PgC = 10^{15} gC) and annual carbon exchange fluxes (in PgC yr^{-1}). Black numbers and arrows indicate reservoir mass and exchange fluxes estimated for the time prior to the Industrial Era, about 1750 (see Section 6.1.1.1 for references). Fossil fuel reserves are from GEA (2006) and are consistent with numbers used by IPCC WGIII for future scenarios. The sediment storage is a sum of 150 PgC of the organic carbon in the mixed layer (Emerson and Hedges, 1988) and 1600 PgC of the deep-sea $CaCO_3$ sediments available to neutralize fossil fuel CO_2 (Archer et al., 1998). Red arrows and numbers indicate annual 'anthropogenic' fluxes averaged over the 2000–2009 time period. These fluxes are a perturbation of the carbon cycle during Industrial Era post 1750. These fluxes (red arrows) are: *Fossil fuel and cement emissions of CO_2* (Section 6.3.1), *Net land use change* (Section 6.3.2), and the *Average atmospheric increase* of CO_2 in the atmosphere, also called 'CO_2 growth rate' (Section 6.3). The uptake of anthropogenic CO_2 by the ocean and by terrestrial ecosystems, often called 'carbon sinks' are the red arrows part of *Net land flux* and *Net ocean flux*. Red numbers in the reservoirs denote cumulative changes of anthropogenic carbon over the Industrial Period 1750–2011 (column 2 in Table 6.1). By convention, a positive cumulative change means that a reservoir has gained carbon since 1750. The cumulative change of anthropogenic carbon in the terrestrial reservoir is the sum of carbon cumulatively lost through land use change and carbon accumulated since 1750 in other ecosystems (Table 6.1). Note that the mass balance of the two ocean carbon stocks *Surface ocean* and *Intermediate and deep ocean* includes a yearly accumulation of anthropogenic carbon (not shown). Uncertainties are reported as 90% confidence intervals. Emission estimates and land and ocean sinks (in red) are from Table 6.1 in Section 6.3. The change of gross terrestrial fluxes (red arrows of *Gross photosynthesis* and *Total respiration and fires*) has been estimated from CMIP5 model results (Section 6.4). The change in air–sea exchange fluxes (red arrows of ocean atmosphere gas exchange) have been estimated from the difference in atmospheric partial pressure of CO_2 since 1750 (Sarmiento and Gruber, 2006). Individual gross fluxes and their changes since the beginning of the Industrial Era have typical uncertainties of more than 20%, while their differences (*Net land flux* and *Net ocean flux* in the figure) are determined from independent measurements with a much higher accuracy (see Section 6.3). Therefore, to achieve an overall balance, the values of the more uncertain gross fluxes have been adjusted so that their difference matches the *Net land flux* and *Net ocean flux* estimates. Fluxes from volcanic eruptions, rock weathering (silicates and carbonates weathering reactions resulting into a small uptake of atmospheric CO_2), export of carbon from soils to rivers, burial of carbon in freshwater lakes and reservoirs and transport of carbon by rivers to the ocean are all assumed to be pre-industrial fluxes, that is, unchanged during 1750–2011. Some recent studies (Section 6.3) indicate that this assumption is likely not verified, but global estimates of the Industrial Era perturbation of all these fluxes was not available from peer-reviewed literature. The atmospheric inventories have been calculated using a conversion factor of 2.12 PgC per ppm (Prather et al., 2012).

6.1.2.1 Carbon Dioxide and the Global Carbon Cycle

Since the beginning of the Industrial Era, humans have been producing energy by burning of fossil fuels (coal, oil and gas), a process that

The second major source of anthropogenic CO_2 emissions to the atmosphere is caused by changes in land use (mainly deforestation), which causes globally a net reduction in land carbon storage, although recovery from past land use change can cause a net gain in in land

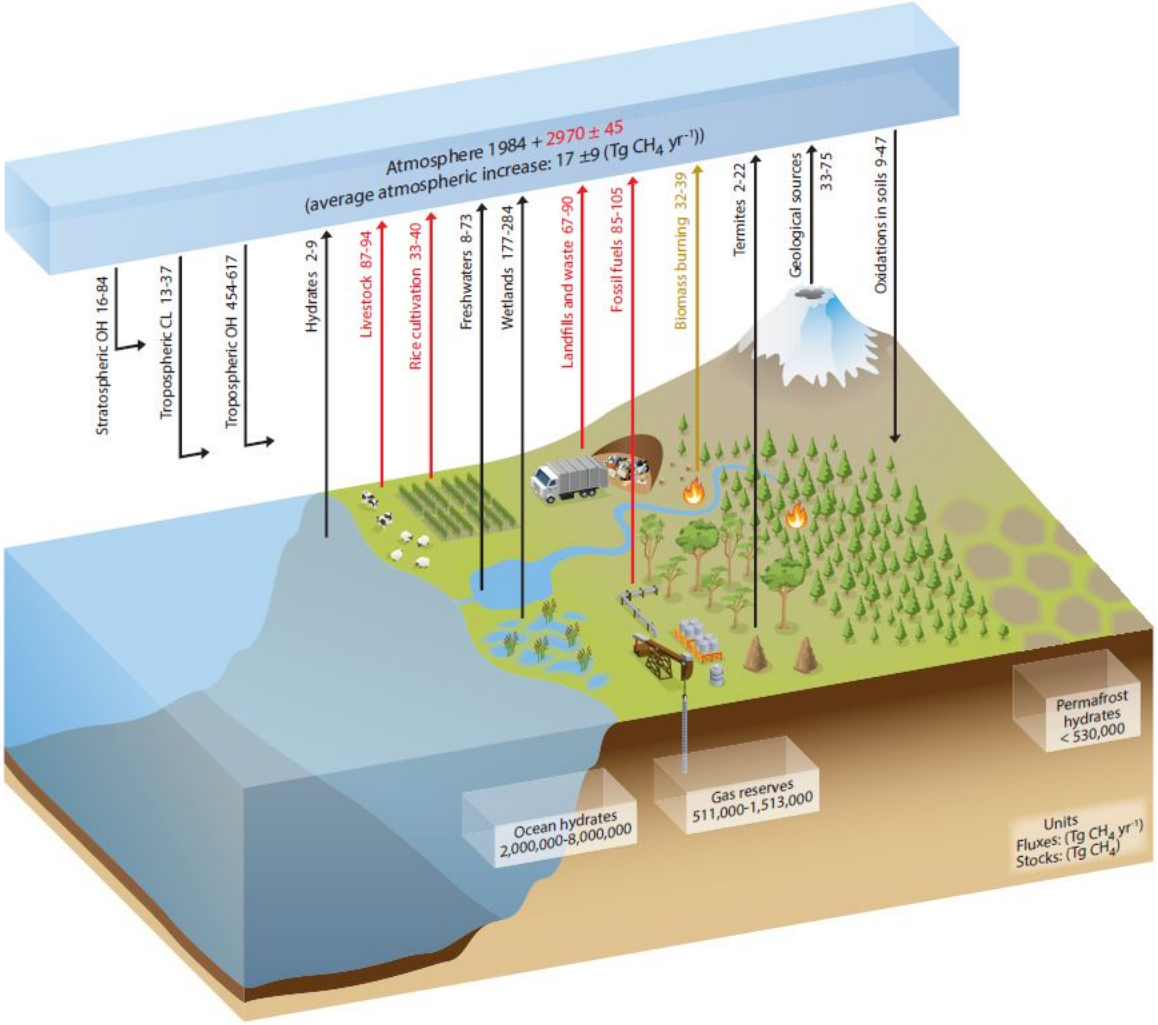


Figure 6.2 | Schematic of the global cycle of CH_4. Numbers represent annual fluxes in Tg(CH_4) yr^{-1} estimated for the time period 2000–2009 and CH_4 reservoirs in Tg (CH_4): the atmosphere and three geological reservoirs (hydrates on land and in the ocean floor and gas reserves) (see Section 6.3.3). Black arrows denote 'natural' fluxes, that is, fluxes that are not directly caused by human activities since 1750, red arrows anthropogenic fluxes, and the light brown arrow denotes a combined natural + anthropogenic flux. Note that human activities (e.g., land use) may have modified indirectly the global magnitude of the natural fluxes (Section 6.3.3). Ranges represent minimum and maximum values from cited references as given in Table 6.8 in Section 6.3.3. Gas reserves are from GEA (2006) and are consistent with numbers used by IPCC WG III for future scenarios. Hydrate reservoir sizes are from Archer et al. (2007). The atmospheric inventories have been calculated using a conversion factor of 2.7476 TgCH_4 per ppb (Prather et al., 2012). The assumed preindustrial annual mean globally averaged CH_4 concentration was 722 ± 25 ppb taking the average of the Antarctic Law Dome ice core observations (MacFarling-Meure et al., 2006) and the measurements from the GRIP ice core in Greenland (Blunier et al., 1995; see also Table 2.1). The atmospheric inventory in the year 2011 is based on an annual globally averaged CH_4 concentration of 1803 ± 4 ppb in the year 2011 (see Table 2.1). It is the sum of the atmospheric increase between 1750 and 2011 (in red) and of the pre-industrial inventory (in black). The *average atmospheric increase* each year, also called growth rate, is based on a measured concentration increase of 2.2 ppb yr^{-1} during the time period 2000–2009 (Dlugokencky et al., 2011).

6.1.3 Connections Between Carbon and the Nitrogen and Oxygen Cycles

6.1.3.1 Global Nitrogen Cycle Including Nitrous Oxide

The biogeochemical cycles of nitrogen and carbon are tightly coupled with each other owing to the metabolic needs of organisms for these two elements. Changes in the availability of one element will influence not only biological productivity but also availability and requirements for the other element (Gruber and Galloway, 2008) and in the longer term, the structure and functioning of ecosystems as well.

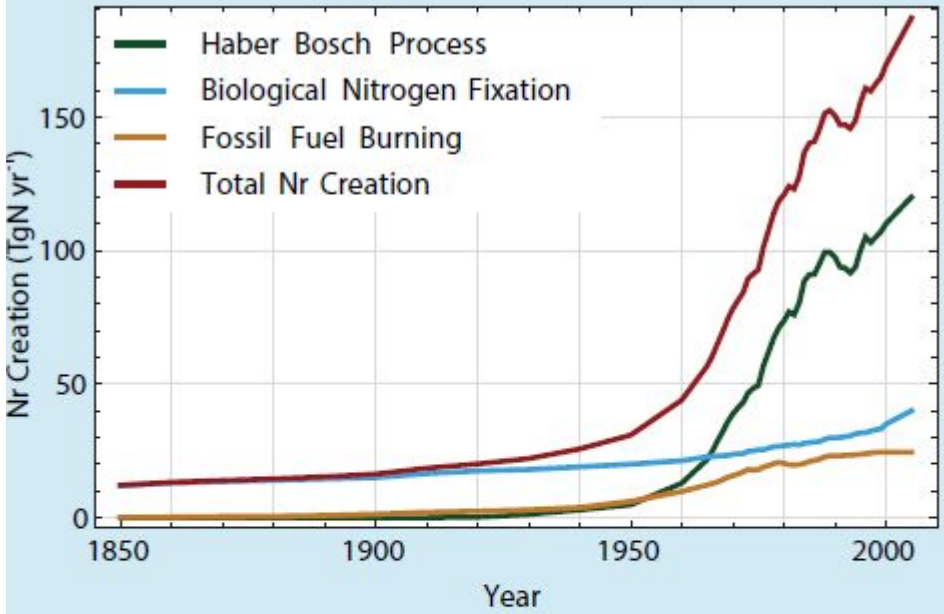
Before the Industrial Era, the creation of reactive nitrogen Nr (all nitrogen species other than N_2) from non-reactive atmospheric N_2 occurred primarily through two natural processes: lightning and biological nitrogen fixation (BNF). BNF is a set of reactions that convert N_2 to ammonia in a microbially mediated process. This input of Nr to the land and ocean biosphere was in balance with the loss of Nr though denitrification, a process that returns N_2 back to the atmosphere (Ayres et al., 1994). This equilibrium has been broken since the beginning of the Industrial Era. Nr is produced by human activities and delivered to ecosystems. During the last decades, the production of Nr by humans has been much greater than the natural production (Figure 6.4a; Section 6.3.4.3). There are three main anthropogenic sources of Nr: (1) the Haber-Bosch industrial process, used to make NH_3 from N_2, for nitrogen fertilisers and as a feedstock for some industries; (2) the cultivation of legumes and other crops, which increases BNF; and (3) the combustion of fossil fuels, which converts atmospheric N_2 and fossil fuel nitrogen into nitrogen oxides (NO_x) emitted to the atmosphere and re-deposited at the surface (Figure 6.4a). In addition, there is a small flux from the mobilization of sequestered Nr from nitrogen-rich sedimentary rocks (Morford et al., 2011) (not shown in Figure 6.4a).

The amount of anthropogenic Nr converted back to non-reactive N_2 by denitrification is much smaller than the amount of Nr produced each year, that is, about 30 to 60% of the total Nr production, with a large uncertainty (Galloway et al., 2004; Canfield et al., 2010; Bouwman et al., 2013). What is more certain is the amount of N_2O emitted to the atmosphere. Anthropogenic sources of N_2O are about the same size as natural terrestrial sources (see Section 6.3.4 and Table 6.9 for the global N_2O budget). In addition, emissions of Nr to the atmosphere, as NH_3 and NO_x, are caused by agriculture and fossil fuel combustion. A portion of the emitted NH_3 and NO_x is deposited over the continents, while the rest gets transported by winds and deposited over the oceans. This atmospheric deposition flux of Nr over the oceans is comparable to the flux going from soils to rivers and delivered to the coastal ocean (Galloway et al., 2004; Suntharalingam et al., 2012). The increase of Nr creation during the Industrial Era, the connections among its impacts, including on climate and the connections with the carbon cycle are presented in Box 6.2.

For the global ocean, the best BNF estimate is 160 TgN yr^{-1}, which is roughly the midpoint of the minimum estimate of 140 TgN yr^{-1} of Deutsch et al. (2007) and the maximum estimate of 177 TgN yr^{-1} (Groszkopf et al., 2012). The probability that this estimate will need an upward revision in the near future is high because several additional processes are not yet considered (Voss et al., 2013).

The three most relevant questions regarding the anthropogenic perturbation of the nitrogen cycle with respect to global change are: (1) What are the interactions with the carbon cycle, and the effects on carbon sinks (see Sections 6.3.2.6.5 and 6.4.2.1), (2) What are the effects of increased Nr on the radiative forcing of nitrate aerosols (Chapter 7, 7.3.2) and tropospheric ozone (Chapters 8), (3) What are the impacts of the excess of Nr on humans and ecosystems (health, biodiversity, eutrophication, not treated in this report, but see, for example, EPA, 2011b; Sutton et al., 2011).

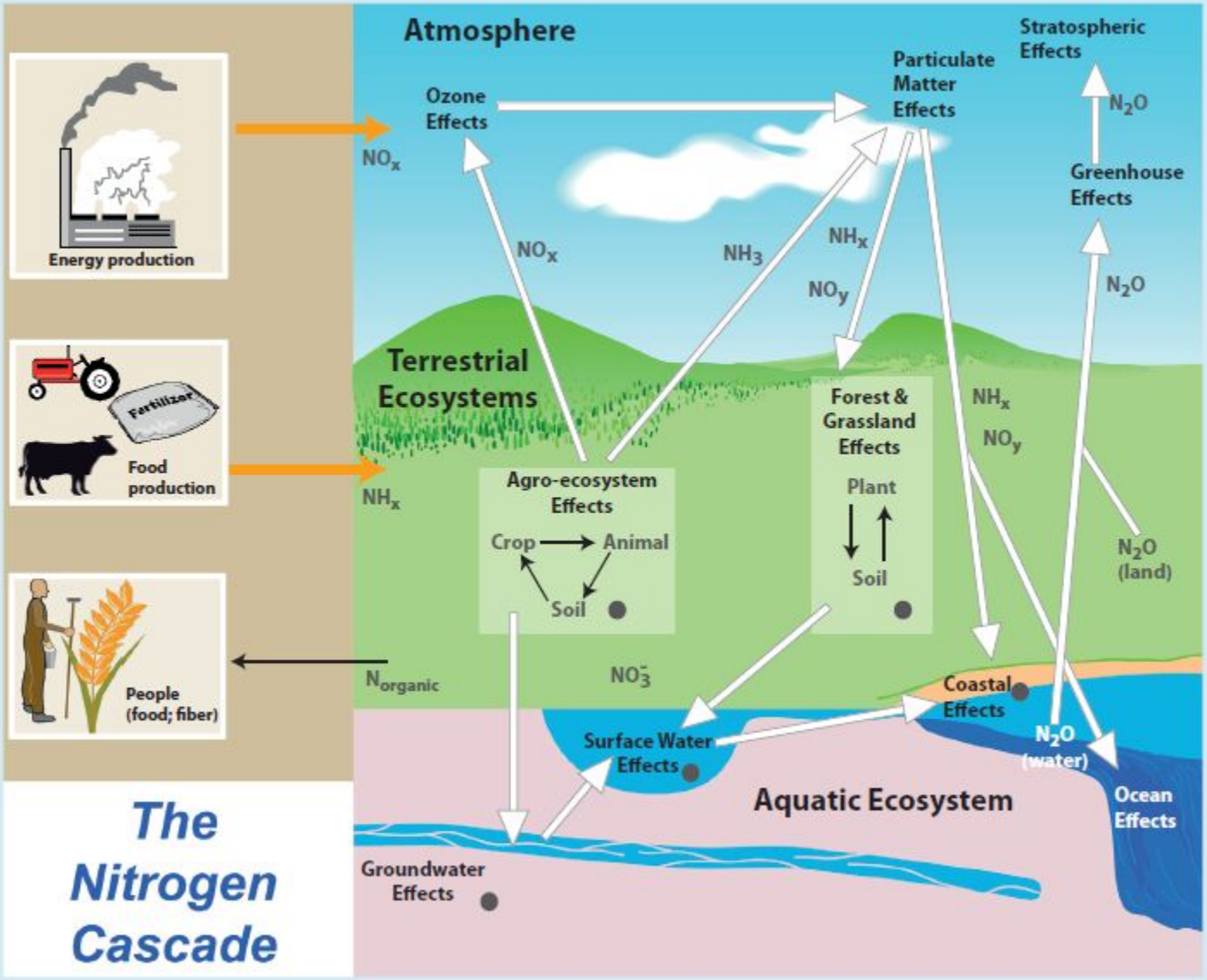
Essentially all of the Nr formed by human activity is spread into the environment, either at the point of creation (i.e., fossil fuel combustion) or after it is used in food production and in industry. Once in the environment, Nr has a number of negative impacts if not converted back into N_2. In addition to its contributions to climate change and stratospheric ozone depletion, Nr contributes to the formation of smog; increases the haziness of the troposphere; contributes to the acidification of soils and freshwaters; and increases the productivity in forests, grasslands, open and coastal waters and open ocean, which can lead to eutrophication and reduction

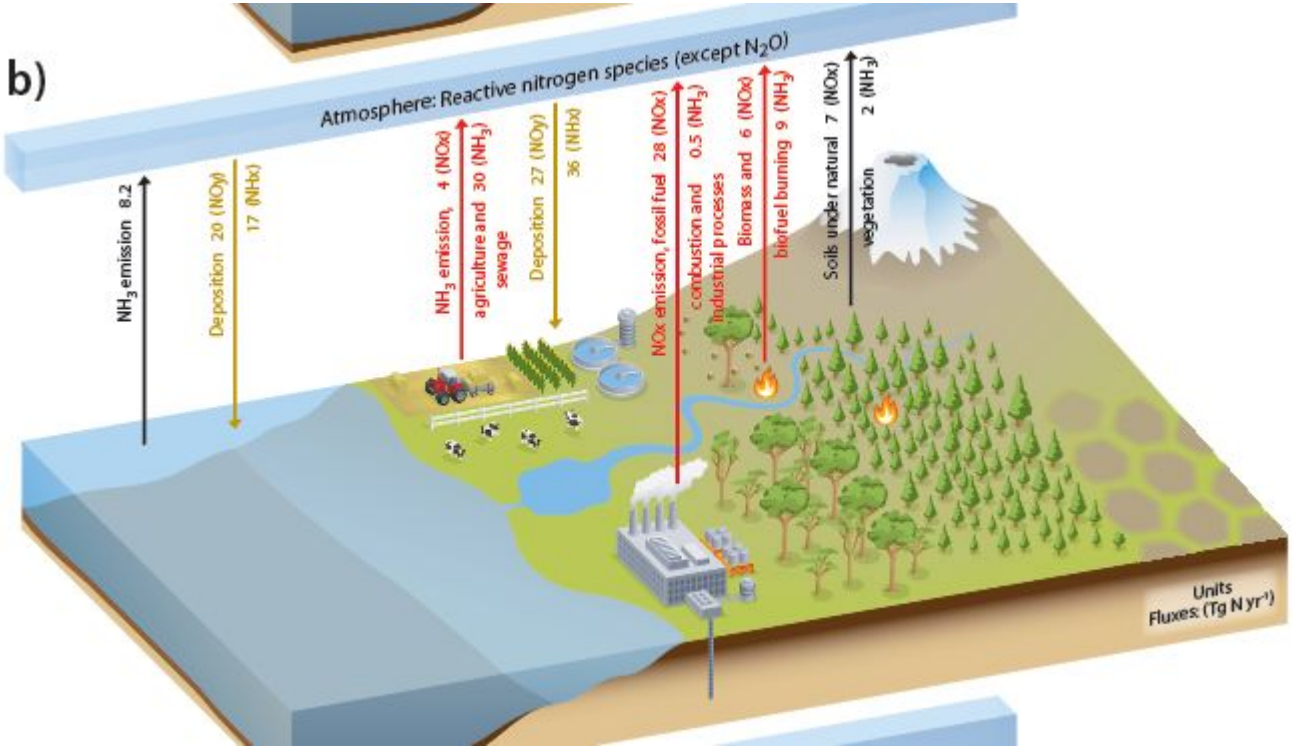


Box 6.2, Figure 1 | Anthropogenic reactive nitrogen (Nr) creation rates (in TgN yr^{-1}) from fossil fuel burning (orange line), cultivation-induced biological nitrogen fixation (blue line), Haber–Bosch process (green line) and total creation (red line). Source: Galloway et al. (2003), Galloway et al. (2008). Note that updates are given in Table 6.9. The only one with significant changes in the more recent literature is cultivation-induced BNF) which Herridge et al. (2008) estimated to be 60 TgN yr^{-1}. The data are only reported since 1850, as no published estimate is available since 1750.

in biodiversity in terrestrial and aquatic ecosystems. In addition, Nr-induced increases in nitrogen oxides, aerosols, tropospheric ozone, and nitrates in drinking water have negative impacts on human health (Galloway et al., 2008; Davidson et al., 2012). Once the nitrogen atoms become reactive (e.g., NH_3, NO_x), any given Nr atom can contribute to all of the impacts noted above in sequence. This is called the nitrogen cascade (Galloway et al., 2003; Box 6.2, Figure 2). The nitrogen cascade is the sequential transfer of the same Nr atom through the atmosphere, terrestrial ecosystems, freshwater ecosystems and marine ecosystems that results in multiple effects in each reservoir. Because of the nitrogen cascade, the creation of any molecule of Nr from N_2, at any location, has the potential to affect climate, either directly or indirectly, as explained in this box This potential exists until the Nr gets converted back to N_2.

The most important processes causing direct links between anthropogenic Nr and climate change include (Erisman et al., 2011): (1) N_2O formation during industrial processes (e.g., fertiliser production), combustion, or microbial conversion of substrate containing nitrogen—notably after fertiliser and manure application to soils. N_2O is a strong greenhouse gas (GHG), (2) emission of anthropogenic NO_x leading to (a) formation of tropospheric O_3, (which is the third most important GHG), (b) a decrease of CH_4 and (c) the formation of nitrate aerosols. Aerosol formation affects radiative forcing, as nitrogen-containing aerosols have a direct cooling effect in addition to an indirect cooling effect through cloud formation and (3) NH_3 emission to the atmosphere which contributes to aerosol formation. The first process has a warming effect. The second has both a warming (as a GHG) and a cooling (through the formation of the OH radical in the troposphere which reacts with CH_4, and through aerosol formation) effect. The net effect of all three NO_x-related contributions is cooling. The third process has a cooling effect.


Atmosphere
Stratospheric Effects
Particulate Matter Effects
Ozone Effects
N_2O
NO_x
Greenhouse Effects
NO_x
NH_3
NH_x
NO_y
N_2O
Energy production
Terrestrial Ecosystems
Forest & Grassland Effects
NH_x
NO_y
Fertilizer
Food production
NH_x
Agro-ecosystem Effects
Crop
Animal
Soil
Plant
Soil
N_2O (land)
People (food; fiber)
$N_{organic}$
NO_3^-
Coastal Effects
Surface Water Effects
N_2O (water)
Aquatic Ecosystem
Ocean Effects
Groundwater Effects
The Nitrogen Cascade


b)
Atmosphere: Reactive nitrogen species (except N_2O)
NH_3 emission 8.2
Deposition 20 (NOy)
17 (NHx)
NH_3 emission, 4 (NOx)
agriculture and 30 (NH_3)
sewage
Deposition 27 (NOy)
36 (NHx)
NOx emission, fossil fuel 28 (NOx)
combustion and 0.5 (NH_3)
industrial processes
Biomass and 6 (NOx)
biofuel burning 9 (NH_3)
Soils under natural 7 (NOx)
vegetation 2 (NH_3)
Units
Fluxes: (Tg N yr^{-1})

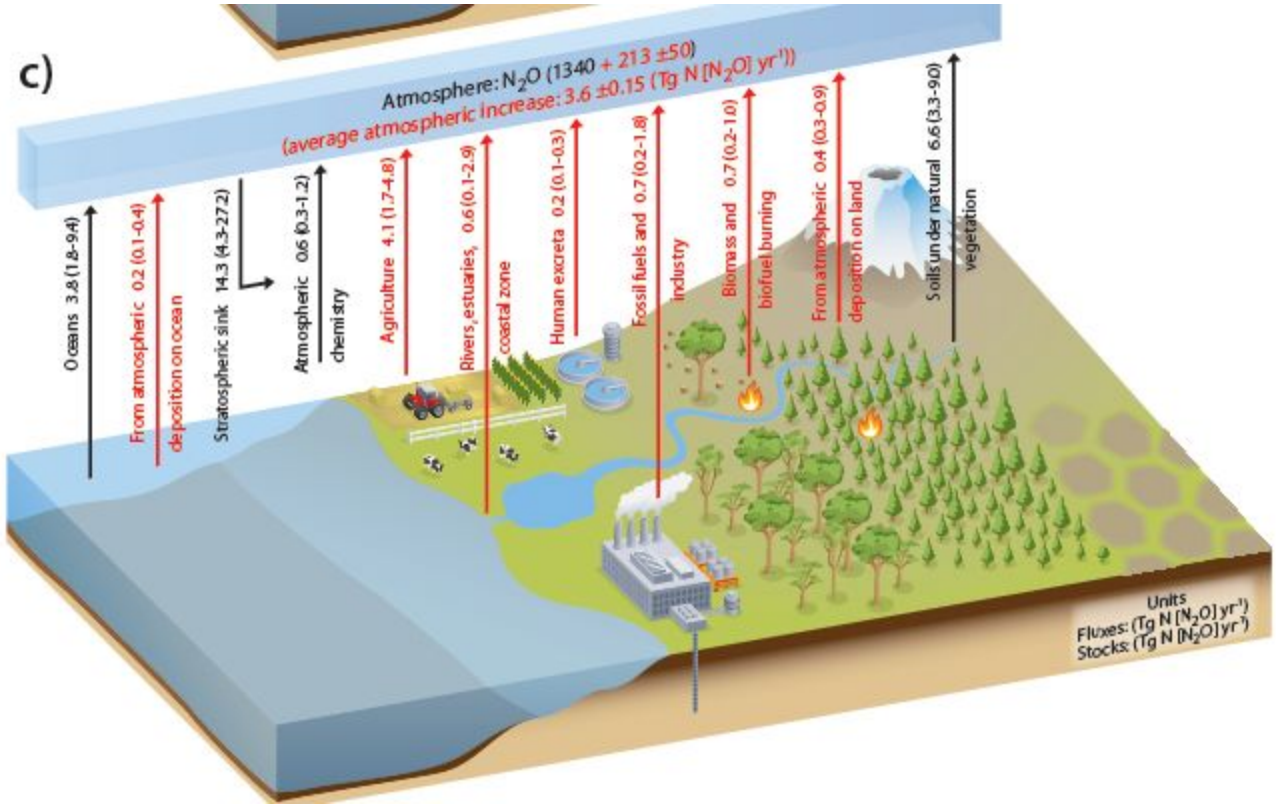
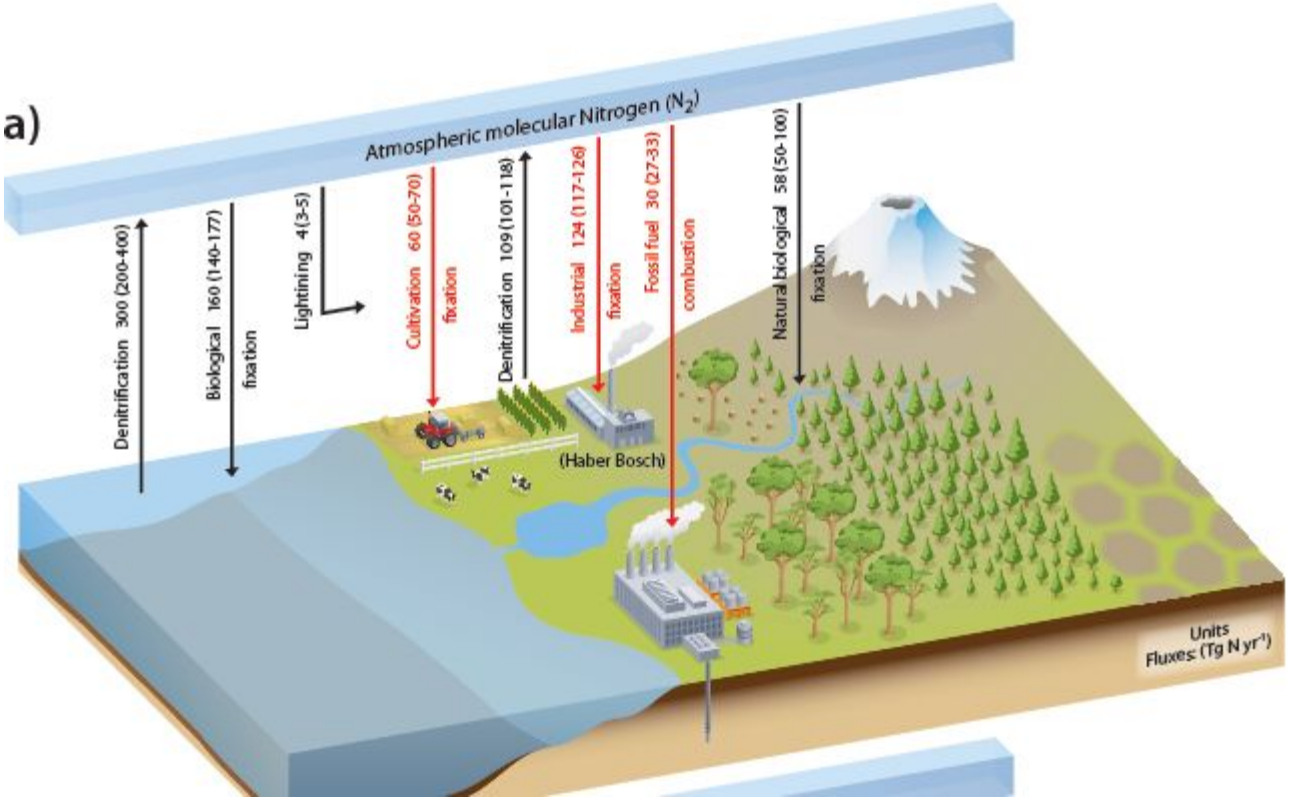
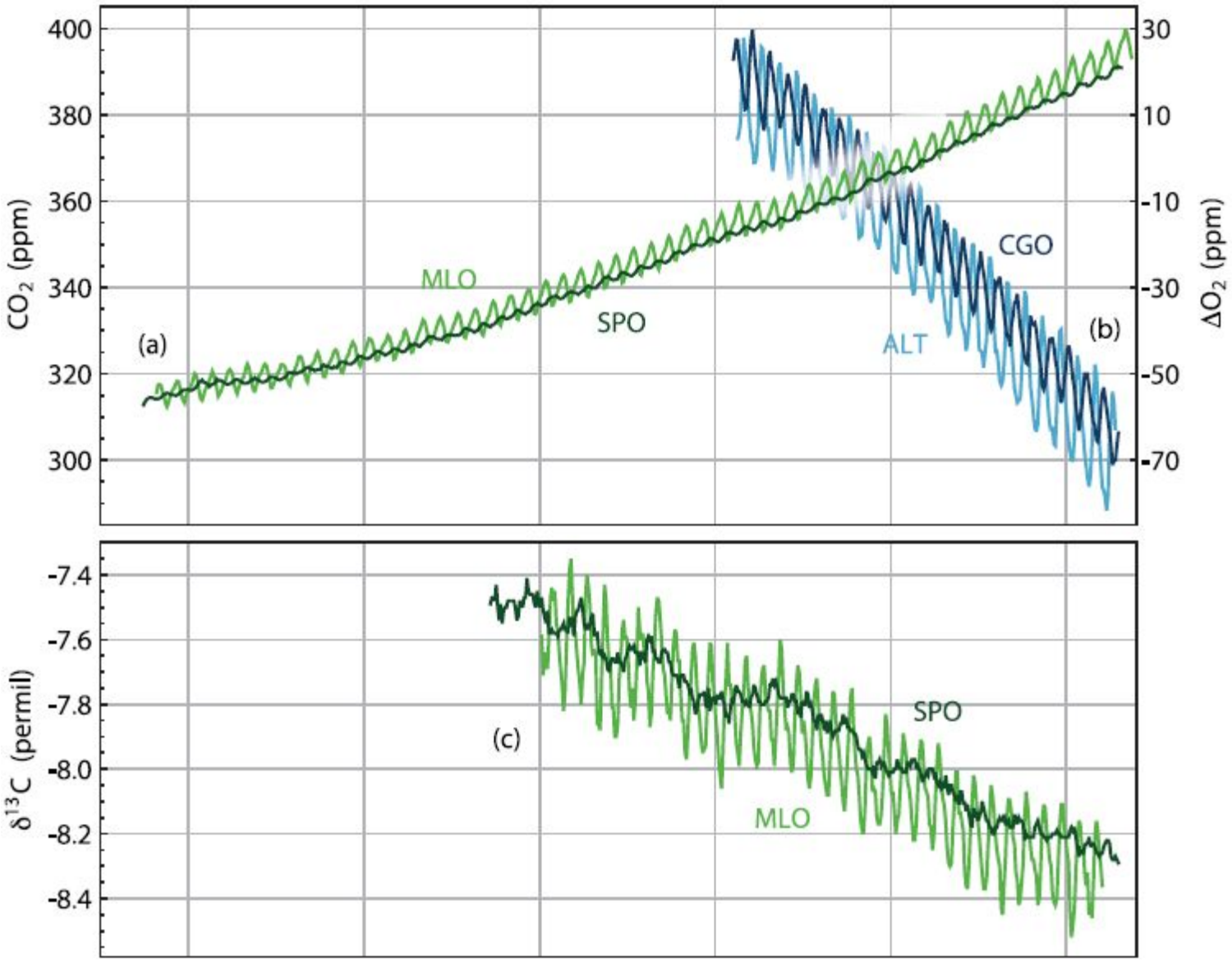


Figure 6.4 | Schematic of the global nitrogen cycle. (a) The natural and anthropogenic processes that create reactive nitrogen and the corresponding rates of denitrification that convert reactive nitrogen back to N_2. (b) The flows of the reactive nitrogen species NO_y and NH_x. (c) The stratospheric sink of N_2O is the sum of losses via photolysis and reaction with O(1D) (oxygen radical in the 1D excited state; Table 6.9). The global magnitude of this sink is adjusted here in order to be equal to the difference between the total sources and the observed growth rate. This value falls within literature estimates (Volk et al., 1997). The atmospheric inventories have been calculated using a conversion factor of 4.79 TgN (N_2O) per ppb (Prather et al., 2012).

Box 6.2, Figure 2 | Illustration of the nitrogen cascade showing the sequential effects that a single atom of nitrogen in its various molecular forms can have in various reservoirs after it has been converted from nonreactive N_2 to a reactive form by energy and food production (orange arrows). Once created the reactive nitrogen has the potential to continue to contribute to impacts until it is converted back to N_2. The small black circle indicates that there is the potential for denitrification to occur within that reservoir. NH_3 = ammonia; NH_x = ammonia plus ammonium; NO_3^- = nitrate; NO_x = nitrogen oxides; NO_y = NO_x and other combinations of nitrogen and oxygen (except N_2O); N_2O = nitrous oxide. (Adapted with permission from the GEO Yearbook 2003, United Nations Environmental Programme (UNEP), 2004 which was based on Galloway et al., 2003.)


a)
Atmospheric molecular Nitrogen (N_2)
Denitrification 300 (200-400)
Biological 160 (140-177)
fixation
Lightining 4 (3-5)
Cultivation 60 (50-70)
fixation
Denitrification 109 (101-118)
Industrial 124 (117-126)
fixation
Fossil fuel 30 (27-33)
combustion
Natural biological 58 (50-100)
fixation
(Haber Bosch)
Units
Fluxes (Tg N yr⁻¹)

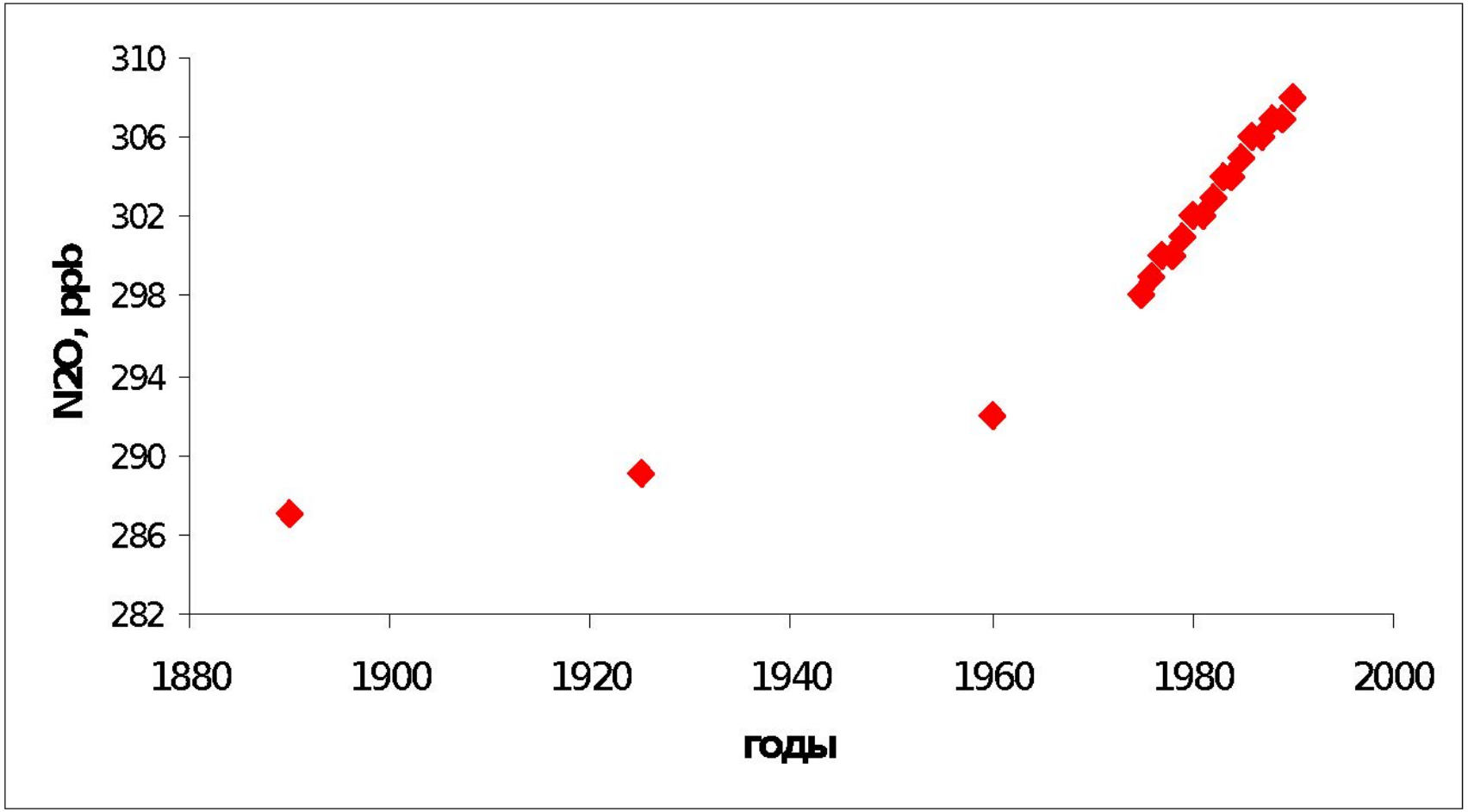

400
380
360
340
320
300
CO_2 (ppm)
30
10
-10
-30
-50
-70
ΔO_2 (ppm)
(a)
(b)
MLO
SPO
ALT
CGO
-7.4
-7.6
-7.8
-8.0
-8.2
-8.4
$\delta^{13}C$ (permil)
(c)
SPO
MLO

Box 6.2 | Nitrogen Cycle and Climate-Carbon Cycle Feedbacks

Human creation of reactive nitrogen by the Haber–Bosch process (see Sections 6.1.3 and 6.3.4), fossil fuel combustion and agricultural biological nitrogen fixation (BNF) dominate Nr creation relative to biological nitrogen fixation in natural terrestrial ecosystems. This dominance impacts on the radiation balance of the Earth (covered by the IPCC; see, e.g., Chapters 7 and 8), and affects human health and ecosystem health as well (EPA, 2011b; Sutton et al., 2011).

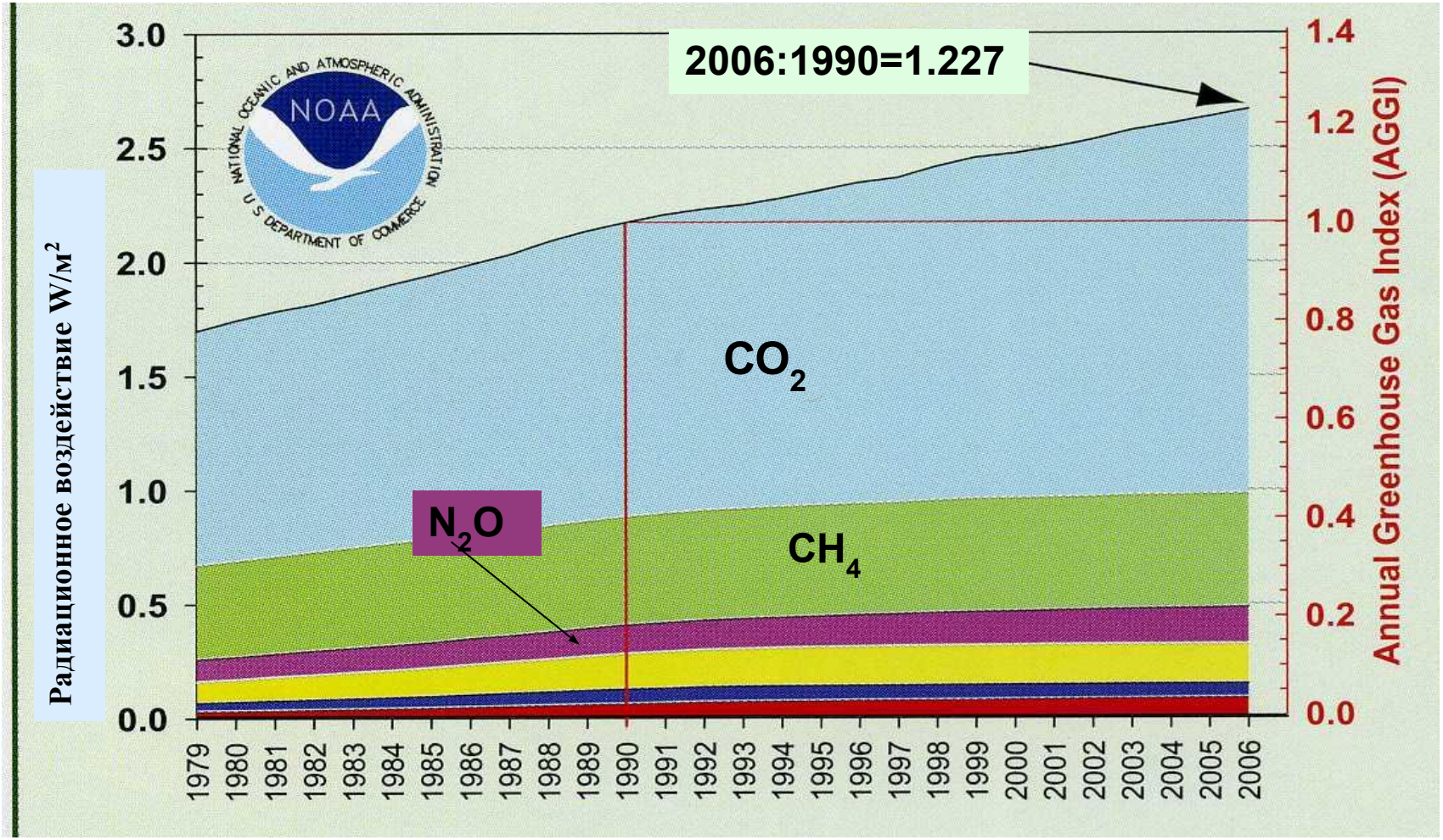
The Nr creation from 1850 to 2005 is shown in Box 6.2 (Figure 1). After mid-1970s, human production of Nr exceeded natural production. During the 2000s food production (mineral fertilisers, legumes) accounts for three-quarters of Nr created by humans, with fossil fuel combustion and industrial uses accounting equally for the remainder (Galloway et al., 2008; Canfield et al., 2010; Sutton et al., 2011).

Атмосферная концентрация N_2O за последние 120 лет



Изменение радиационного воздействия долгоживущих парниковых газов в атмосфере

(1990 год принят за единицу)



(цитировано по WMO, 2008)