

**USE OF MATERIALS BALANCES
TO ESTIMATE AGGREGATE WASTE
GENERATION IN THE US**

by

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USE OF MATERIALS BALANCES TO ESTIMATE AGGREGATE WASTE GENERATION IN THE U.S.

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ABSTRACT

Material flows and transformations for the U.S. economy for a single year (1988) are constructed from published commodity transaction data. Particular emphasis is placed on accounting for the mass difference between known commodity inputs to each industrial sector and known commodity outputs from the sector. Inputs of "free goods" (air, water, topsoil) from the environment can also be estimated from process data. The difference between total inputs and commodity outputs can be characterized as "missing mass". We attempt to account for missing mass in terms of known level of waste treatment and disposal, by environmental medium. In some cases, at least, official (EPA) contractor estimates based on other methodologies appear to be too small by significant margins. This paper summarizes the results of the first stage of a much larger study now being prepared for publication in book form.

1. Methodology

One can view each industrial sector as a transformation process, converting raw material inputs or purchased commodities from "upstream" sectors, plus "free goods" from the environment, into products for other "downstream" sectors, plus wastes. This conversion process is subject to the materials balance constraint, not only in the aggregate, but element by element. In other words, the sum of the weights of all inputs must exactly equal the sum of the weights of all outputs. When both inputs and outputs are known, it is possible to estimate wastes, making due allowance for processes utilizing the "free goods" (air, water, topsoil). Of course, in reality, there are often significant uncertainties with regard to either inputs, or outputs, or both. These arise from statistical inconsistencies, stock adjustments, imports and exports. We have attempted to take all of these into account in the full study. However the details are too complicated to present in this short paper; in general, we only give results at the macro-level, mainly in diagrammatic form.

It is important to explain what we mean by 'macro-' level in this context. In general, large-scale mass flows exceed by many orders of magnitude the flows of the most highly toxic pollutants, including trace elements. In our balancing efforts, we have attempted to construct input-output (I-O) tables for major process stages. Thus, in the case of agriculture and forest products, we try to balance the flows of carbon, oxygen, hydrogen and major nutrients (N, O). At this level of detail, it is not possible to account precisely for minor flows, e.g. of pesticide residues. Studies taking into account minor flows would have to be based on a different methodology based much more on detailed chemical and metallurgical process data than on economic data.

To avoid unnecessary and distracting biological complications, we treat biomass as a produced good of the agriculture/forestry sectors, even though much of it is arguably free. Unfortunately, this leaves us with the problem of accounting for water, both as an input and output, which cannot be done with great precision. Fortunately, great precision is probably not necessary in this case. Labor and capital inputs, such as machinery and fuel or electric power for operating the machinery, are not considered explicitly in this study. However, it should be borne in mind that a considerable fraction of aggregate industrial output is actually destined for the capital (and operating) inputs to other sectors.

Our immediate intention is to classify outputs into economic commodities and missing mass. In subsequent work the "missing mass" will be further classified, based on level of waste treatment and final disposal medium (air, water, soil). This means it is necessary to be quite careful in accounting for the consumption of oxygen (from air) in oxidation processes, and for the consumption or production of water in hydration, dehydration, dilution, dissolution and so on.

We have selected 1988 for the main study (which is international in scope) because it is the last year for which we have reasonably good international data. Unfortunately, 1988 was a very atypical year for U.S. agriculture. Where feasible, we have also included some agricultural data for 1990, a much more typical year.

2. Agriculture (SIC 01-02)

Inputs to the agriculture sector consist of sunlight, water, carbon dioxide (from the air), nitrogen fixation (also from the air), topsoil and some chemicals (fertilizers and pesticides). Commodity outputs are harvested crops. (Dairy products and meat are considered separately in the next section). Missing mass, in the aggregate, consists mainly of crop wastes, runoff, evapotranspiration, oxygen (a by-product of photosynthesis). Other losses include soil erosion, nitrogen (and phosphorus) carried away by water sources and gaseous emissions.

The production process in agriculture (also forestry, considered later) can be estimated crudely from the following basic equation of photosynthesis, viz.



(The equation describes respiration in the reverse direction). Plants fix carbon in daylight and release part of it (about half) at night. Thus, net photosynthesis is about 0.5 times gross photosynthesis. Otherwise, water is only utilized by plants as a carrier of nutrients and metabolic products, and for evaporative cooling. There is a rough average proportionality between carbon fixation rate (gross photosynthesis) and evapotranspiration, but there is no fixed relationship between water content and metabolic process; some plant parts are very high in water content, others much less so. In general it seems reasonable to assume that raw biomass contains 50% water, by weight, on average, while refined or processed food or feed commodities are considerably drier. In cases where actual data are lacking, we assume a 25% water content for processed "dry" commodities. Unfortunately, official statistics are not informative on this point.

Raw products of U.S. agriculture include truck crops (fruits, vegetables) & tree crops, field crops (grain, oilseed, hay and alfalfa, sugar beets, sugar cane, potatoes, cotton, tobacco). Harvested output of all field crops in 1988 was 421.75 MMT.¹ Truck crops totalled 51.3 MMT. Total weight of harvested crops 473 MMT. See *Table 2*.² It should also be noted that corn plants harvested whole for silage (or "hogged" on the farm) are not included in the grain production figures. This material, which is fed to animals, is classed as "harvested roughage"; it amounted to 68 MMT in 1988.

According to one estimate, the average ratio of above-ground crop residues remaining on the land to harvest weight is about 1.5 for cereals (straw), 1.0 for legumes (straw) 0.2 for tubers (tops) and sugar cane (bagasse), and 3.0 for cotton (stalks) [Smil 1993]. On this basis, total residues left above ground in 1988 would have been around 400 MMT in 1988 and 560 MMT in 1990. Thus total (above ground) biomass production was about 1140 MMT in 1988 and 1380 MMT in 1990. In the U.S. most of the crop residues are left on the land; a small

1 For the sake of clarity, it should be noted that "harvested output" of corn — by far the dominant grain — refers to shelled corn, not ears. The husks and ears are left behind on the farm, along with stalks. Similarly, wheat straw and chaff are separated from the wheat grains by the harvester, and left behind.

2 To calculate the totals it is necessary to sum up individual figures given by USDA in a variety of different units, some volumetric and some in mass terms. Unfortunately, while USDA does provide conversion coefficients, it does not calculate aggregated totals, except for grains.

fraction c. 20% is burned for fuel or used for other purposes [Smil 1993]. In China or India, by contrast, as much as 2/3 is burned as household fuel (for cooking).

Table 1. Agricultural production in the U.S. 1988 (MMT)

Commodity	Production		Exports	Imports	Consumption		Reference
	Raw	Finished			Raw	Finished	
Beef & veal	17.82	10.88	0.31	1.09	11.62	11.20	1170,1168,A131
Lamb & mutton	0.32	0.15	0.00	0.02	0.18	0.18	1169,1168,A131
Pork	9.91	7.11	0.09	0.52	7.51	4.87	1171,1168,A131
Poultry	12.95					6.37	1175
Eggs	4.44					3.86	1177
Dairy products	65.86	64.41				33.42	1173,A131
Subtotal	111.30		2.77	1.26		59.90	1149
Food grains	56.55		44.26		35.40	17.37	A129,A133,1147,1149
Feeds & fodders			11.37				1149
Feed grains & products	147.06		55.21				A129,A133,1147,1149
Oilseeds & products	49.16		26.90				A129,A133,1147,1149
Hay	114.31						A129,A133,1147,1149
Sugar cane	27.13	2.88		1.21		3.40	A129,A133,1147,1149
Sugar beets	22.51	2.97				3.40	A129,A133,1147,1149
Other field products	5.03		1.57			3.46	" + calculated
Corn syrup						7.64	207
Subtotal	421.75		139.31			35.27	
Vegetables	25.14					22.27	1166,1167
Fruits	25.60					11.51	1166,1167
Nuts	0.55						1166,1167
Fruits, nuts & vegetables			4.06	6.74			1149
Coffee, cocoa				1.48		3.40	1149
Subtotal	51.30		4.06	8.21		37.17	1147,1149
Fish	3.26		0.48	3.37	4.77	1.40	1197,A131,1210
Vegetable oils		6.40	1.30	1.35		6.66	1147,1149
SUMMARY							
Animal products	111.30		2.77	1.26		59.90	
Field products	421.75		139.31			35.27	
Vegetable products	51.30		4.06	8.21		37.17	
Fishery products	3.26		0.48	3.37		1.40	
Vegetable oils		6.40	1.30	1.35	4.77	6.66	
TOTAL	587.61		147.92	14.19		140.40	

NOTES: Poultry conversion at \$.33/lb

Egg conversion at .77 kg/dozen

Fruit & vegetable box weights averaged where not specified.

Food grains = wheat, rice, rye

Feed grains & products = corn & sorghum for grain, barley, oats

Oilseeds & products = soybeans, peanuts, cottonseed, flaxseed

Other field products = dry beans & peas, cotton lint, tobacco

Table does not display stock changes, particularly large in 1988

The difference between raw/finished food grains is used for beer & distilled spirits.

Sources: Statistical Abstract of the United States 1991 - numbered references are to Table numbers.

World Almanac 1991 - references A(nnn) are to page numbers

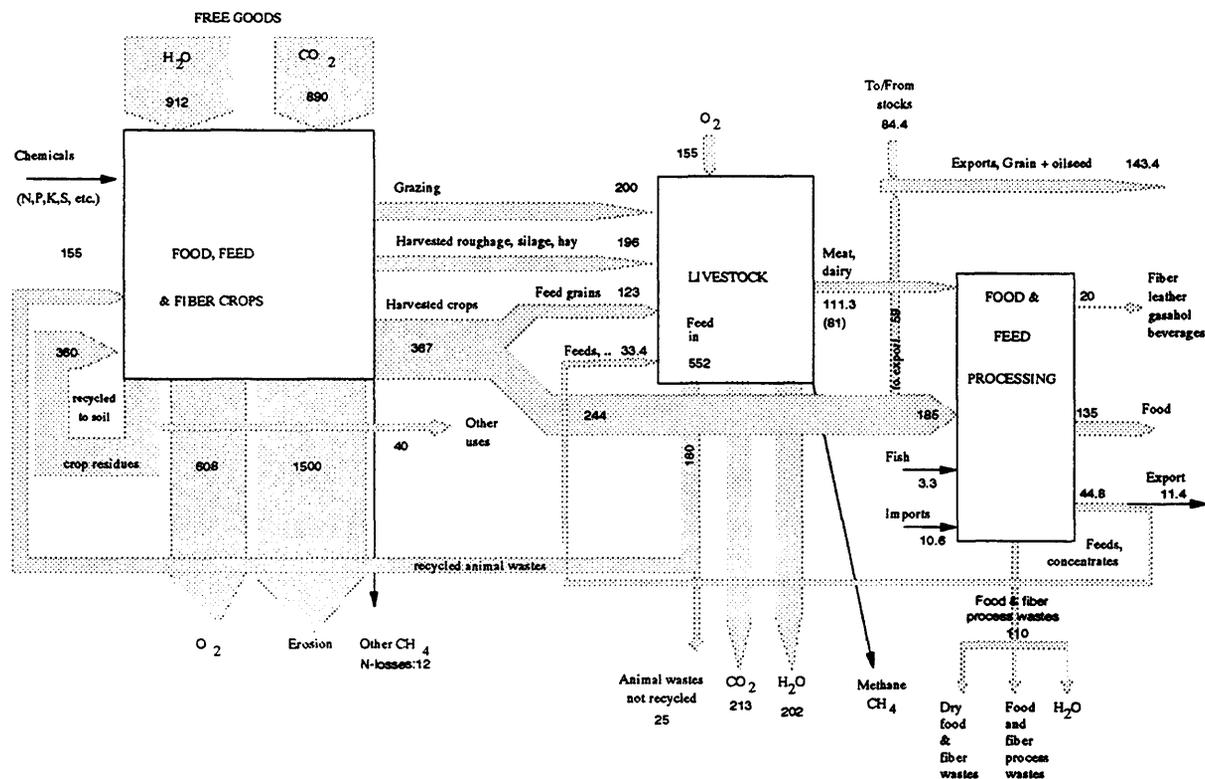


Figure 1: Mass flow & C, H & O balances in U.S. agriculture, 1988 (MMT)

The composition of this biomass is a mixture of cellulosic fiber, carbohydrates, fats and proteins, plus (50%) water, as explained above. Hence, we estimate that the dry weight of the biomass produced in 1988 was about 570 MMT and, for 1990, about 690 MMT. For each 100 units of dry output (CH₂O basis), the photosynthetic process equation implies that 146.7 MMT of CO₂ (containing 40 units of carbon) were initially extracted from the air, while 60 units of water were also converted, and 106.7 units of oxygen were returned to the atmosphere. Overall, for 1988, water inputs — not including water required for evapotranspiration — were about 912 MMT, and carbon dioxide inputs were about 890 MMT. Oxygen produced by the photosynthesis process in agriculture would have been about 608 MMT. The corresponding figures for 1990 would have been about 20% higher (by the ratio 690/570). The overall flows for U.S. agriculture (1988) are summarized graphically in Figure 1.

The above estimates do not take into account the relatively small quantities of other chemical elements embodied in the crops, notably nitrogen, phosphorus and other minerals taken up from the soil or (in the case of nitrogen) fixed by bacteria. It is of interest, however, that the three major chemical elements in (dry) plant tissue are carbon, hydrogen and oxygen. These account for

Table 2. Chemical composition of plants

Element	% of Plant
Oxygen	45
Carbon	44
Hydrogen	6
Nitrogen	2
Potassium	1
Calcium	0.6
Phosphorus	0.5
Sulfur	0.4
Magnesium	0.3
Manganese	0.05
Iron	0.02
Chlorine	0.015
Zinc	0.01
Boron	0.005
Copper	0.001
Molybdenum	0.0001
Total	99.9011
<i>Source: Dictionary of Plant Foods</i>	

95% of the total mass. Nitrogen accounts for another 2%, phosphorus for 0.5% potassium for 1% and sulfur 0.4%. these are the major nutrients that are depleted by harvesting and must be replaced by the addition of fertilizers. The remaining 1% of plant mass consists of other mineral elements (see *Table 2*) that are readily available from the soil. The flows of nutrients (N, P) in U.S. agriculture are summarized in *Figure 2*.

In 1988 127.9 MMT of grain and oilseeds (mostly soya beans) were exported, not including 11.4 MMT of "feeds and fodders" which may be from the processing sector. The remainder was consumed directly or indirectly within the U.S. Final consumption of all food products (not including beverages) for 1988 was 135 MMT, plus about 20 MMT for grain-based beverages, alcohol, cotton, wool and other products. Indirect consumption (as animal feed) accounted for most of the difference between gross production and final consumption.

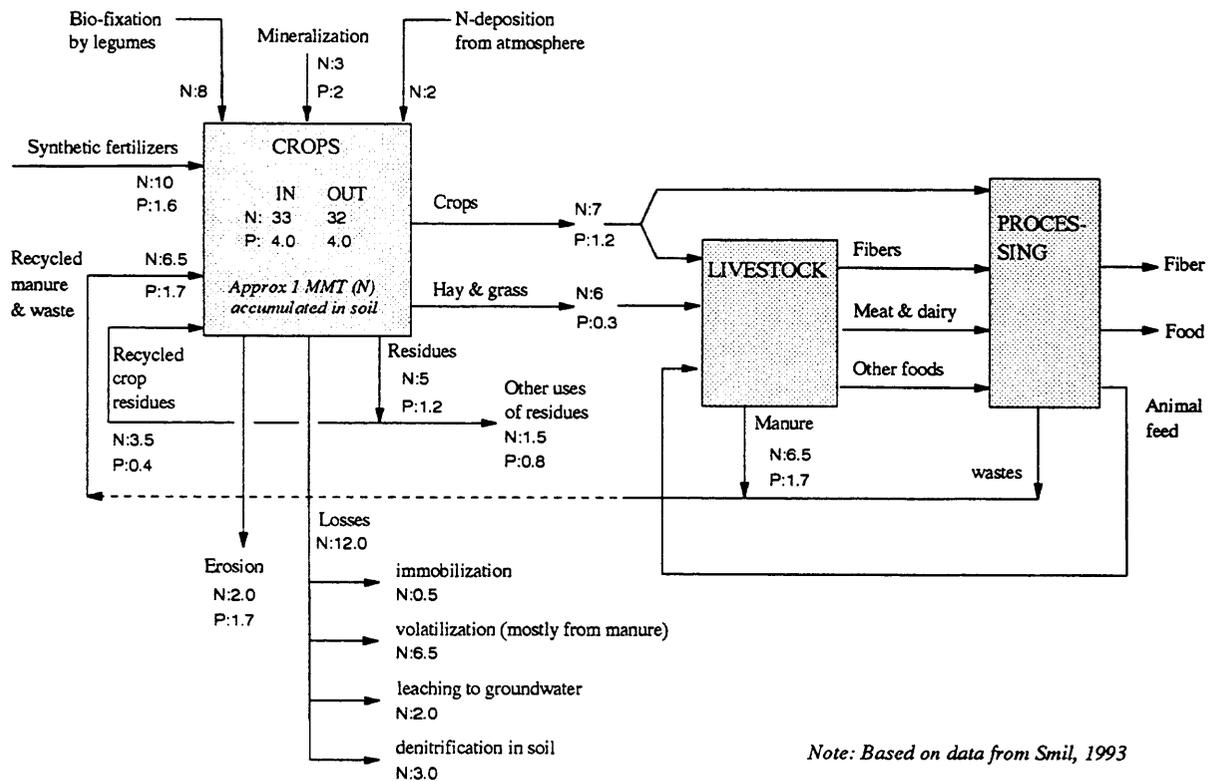


Figure 2: N & P balances in U.S. agriculture, 1988 (MMT)

According to the US Department of Agriculture, livestock in the U.S. in 1988 were fed 119.4 MMT of feed grains, plus 3.7 MMT of food grains (mostly wheat). Other harvested animal feeds included 123 MMT of hay and alfalfa, 4.76 MMT of sorghum as silage, and approximately 68 MMT of harvested roughage (such as cornstalks) mixed with other feeds, for a total of 319 MMT harvested inputs. By-products of the food processing industry such as grain mill by-products (e.g. gluten), oilseed meal, brewers and distillers dried grains, meat and fish meal, dried milk, dried beet pulp, and molasses accounted for an additional 33.4 MMT.³ Assuming the animal intake of pasturage (mainly by cattle) to be about 200 MMT,

3 Based on [USDA 1992, Table 3]. It will be noted that the totals of commercial high protein feeds remain comparatively stable from year to year (though 1988 was slightly below average), but the composition varies significantly. We are unable to account in detail for the exported "feeds and fodders" (11.4 MMT in 1988),

we can thus account for total animal feed consumption in 1988 amounting to 552.4 MMT, not including water, salt, urea or other minor inputs.

Animal feed concentrates in the U.S. average 79% digestibility. From this we can conclude that 21% of the mass of animal feed concentrates (156.3 MMT) fed to dairy cattle, beef cattle in feedlots, hogs and poultry is passed through immediately as feces. Harvested roughage, silage and hay (196 MMT) has lower digestibility, probably around 60%. This implies 40% waste as feces. The two together imply manure output from on-farm and "industrial" animal feeding operations, amounting to about 100 MMT. In addition USDA estimates that animal intake from pastures is about 200 MMT. Assuming 60% digestibility, roughly 80 MMT of manure is probably left on pastures. This figure could be too low; the digestibility of pasturage may be as low as 40%.

Of the total (c. 180 MMT), it appears that 100 MMT is generated in confinement, and of this, 75% (75 MMT) is probably recycled to croplands [Smil 1993]. The remainder of the manure from feedlots (25 MMT, about 50 solid) is lost to runoff or otherwise. Manure left on pastures (80 MMT) is returned directly to the soil — but not to croplands *per se* — and does not constitute a waste.

As regards outputs of the livestock "sector", a total of 111.3 MMT can be accounted for as the gross weight of animal carcasses and dairy products produced for the market (see below). Adjusting for the "excess" water content of raw milk (87% water), we assume that the sector produces about 81 MMT of *equivalent* animal products having the same average moisture content as feeds (50%). As noted already, feed inputs of 552 MMT and manure outputs (50% moisture basis) of 180 MMT can be accounted for, leaving $552 - 180 - 81 = 291$ MMT as metabolic (respiration) losses.

By assumption, 50% of this "lost mass" (c. 145 MMT) is carbohydrate (CH_2O) metabolized for energy, by the reverse of the photosynthesis reaction. This implies oxygen consumption by the animals of $1.067 \times 145 = 155$ MMT and $1.47 \times 145 = 213$ MMT of CO_2 output. The oxidation process also generates $0.6 \times 145 = 87$ MMT of water (vapor), in addition to the 115 MMT of water contained in the feed and not otherwise accounted for. Most of this ends up in manure or urine. The water balance is more complicated, of course, since we have not allowed for water consumed, as such, and re-excreted by the animals.

The greatest mass movement from agriculture is the loss of topsoil due to wind or water erosion. A detailed study of topsoil loss due to agriculture was carried out by the U.S. Soil Conservation Service in 1982 [Brown & Wolf 1984 p. 17]. It was found that 44% of U.S. cropland was losing topsoil at an unsustainable rate (i.e. faster than the natural rate of soil formation). The topsoil loss in 1982 was estimated at 1.53 billion metric tons. This rate of loss can be assumed to be roughly constant from year to year, although optimists believe that

which apparently originate in the processing sector [STATAB 1991, Table 1149].

- 4 N.B. The above estimates do not represent either the "fresh" weight of manure — which is relatively wet — nor the "dry" weight of its solid content. Being based on inputs, the wastes are assumed to have the same water content as the feeds, i.e. about 50%. Actual "fresh" weight of animal manure is about 4 times higher in the case of cattle and pigs, and at least double in the case of other animals.

the erosion loss rate is declining as a consequence of increasing use of "no-till" methods of cultivation. Also, it must be pointed out that eroded material is not necessarily carried out to sea (at first); it may be redeposited on the same field, or in the bed of a nearby stream.

To summarize, we estimate overall annual losses from U.S. agriculture as follows (details in the background study): topsoil erosion 1500 MMT; undigested and unrecycled feedstuffs (feces) from animals at feeding stations — not including grazing animals on pastures — amounted to around 25 MMT (50% moisture) or 12.5 MMT (dry weight). The latter is mostly undigested cellulose, but includes about 4% (0.5 MMT) N and 1% (0.125 MMT) P. Urine apparently accounts for roughly 42% of the total nitrogen-content of synthetic fertilizer, or about 4.8 MMT (N); but this is only the fertilizer contribution. The total must be about three times higher. About a quarter of this (1.2 MMT from fertilizer, 4 MMT total) is volatilized immediately as ammonia; around 2.8 MMT from fertilizer (9 MMT total) ends up in watercourses; the rest goes into groundwater or is recycled back to the land. Ammonia emissions to the atmosphere, direct from fertilizer use, seem to be about 1 MMT (N), or 10% of inputs, but volatilization losses from manure and urine add another 4 MMT. Other sources (organic decay) add a further contribution. The total for U.S. agriculture is probably around 6.5 MMT/y. Methane emissions to the atmosphere from grazing animals in the U.S. were apparently about 0.68 MMT.

3. Food and Feed Processing (SIC 20)⁵

The food/feed processing sector consists of a number of activities, including grain and oilseed milling, meat and dairy processing, cotton processing, oil products, sugar production, fermentation industries, baking, confectioneries and canning and freezing. Unfortunately, the USDA does not clearly separate these activities or identify their inputs and outputs. We attempt to do so in the following.

We estimate inputs to the food processing sector as the difference between gross agricultural production of harvested crops (473 MMT), less harvested crops fed to animals (123 MMT grains plus 114 MMT hay) less net exports of grain and oilseeds (excluding exports from stockpiles), 59 MMT, plus animal products (111), plus fish (3.26 MMT) and net imports of foodstuffs. We now estimate mass losses by category.

Domestic food products consumed (flour, prepared cereals, packaged rice, etc) from all grain mills in 1988 amounted to 17.37 MMT. This estimate is taken from data on food consumption. However, it apparently does not include grain consumed by the fermentation industries, which produce both alcoholic beverages and fuel alcohol. We estimate that about 19 MMT of grains — mostly corn — were used for fermentation products in 1988. In addition to grain products, 6.4 MMT of vegetable oils and 7.74 MMT of corn syrup were produced by grain and oilseed mills. The fermentation industries, in turn, produced 2.2 MMT of beverage alcohol and 5 MMT of (fuel) ethanol, plus 1 MMT of animal feed concentrates, and 1 MMT

⁵ Production, export and import data in this section is from the *Statistical Abstract of the United States, 1991 edition*, Tables 1148, 1149, 1156, 1163, 1166, 1167, 1168, 1173, 1175, 1177. Data on per capita consumption of foods is given in Tables 207, 208. Beverages were not taken into account.

(est.) of beverage carbohydrates. To make up the balance, we estimate outputs of 7 MMT CO₂ and 3 MMT water vapor.

Cotton is a major agricultural product that contributes little to feed and nothing to food. In 1988 the U.S. produced 9.2 MMT (net weight) of raw cotton. This was ginned to yield 3.36 MMT of cotton fiber (lint), 5.50 MMT of cottonseed, plus 0.27 MMT of linters. Linters is a fibrous material used (for felting and cellulosic chemical manufacturing), so it is not a waste. The cottonseed was allocated to mills and "other uses" including exports. The sale to mills was 4.38 MMT; 3.38 MMT was actually crushed [USDA 1992, Table 141 p.107]. The mill product was 0.56 MMT of oil and 1.53 MMT of high protein cottonseed oilcake, used for animal feed, plus 1.29 MMT of milling waste. (The latter is included with overall milling waste in *Figure 1*.)

Sugar cane weighing 27.13 MMT was reduced to 2.88 MMT of refined cane sugar; similarly sugar beets weighing 22.51 MMT yielded 2.97 MMT of beet sugar. (About 0.69 MMT of lime was also used in the latter process). Sugar refining also yielded about 0.59 MMT of molasses (equivalent dry weight), mostly fed to animals. The remainder of the sugar cane waste was mostly cellulosic "bagasse". The sugar beet process produces large quantities of pulpy material; about 1 MMT (dry) was used for animal feed in 1988 [USDA 1992 Table 73]. The mass disappearance from these two processes, alone, amounted to about 42.1 MMT. At least half of this mass loss — perhaps 60% or 25 MMT — is water vapor from the various evaporation stages in sugar production. The remaining dry mass is probably burned for energy recovery, though some residues may be discharged into rivers, via sewage plants.

In addition, truck crops (vegetables and berries) and tree crops (fruits and nuts) accounted for a harvest weight of 51.3 MMT. Exports took 4.06 MMT and imports added 8.21 MMT, for a total domestic supply of 55.45 MMT. Final consumption (on an "as purchased" basis) accounted for 37.17 MMT. The difference, 18.28 MMT was presumably waste, divided between food processing plants and retail stores. We estimate that 60% of this mass loss (11 MMT) was evaporative water loss from freeze-drying (e.g. of orange juice) and other processing. The bulk of the food process waste goes into waterways or municipal wastes from thousands of point sources, including retail shops. Some is recovered for other uses. A small amount may be burned for energy recovery.

Animal products in the U.S. can be subdivided into red meats, poultry, eggs and dairy products. The live weight of animals slaughtered for red meat in 1988 was 28.05 MMT. Salable weight of red meat, after processing, was 18.14 MMT, a reduction of roughly 10 MMT, or nearly 36%. By-products of meat processing include lard and tallow (about 3.8 MMT⁶), hides (1.02 MMT undressed⁷), dog and cat food, glue, bone meal, blood meal, meat meal and "tankage". The last two items are utilized in animal feed concentrates (2.3 MMT in 1988 [USDA 1992 Table 73]). Evidently, about 2.7 MMT remains unaccounted for. Some

6 See UN Industrial Statistics Yearbook, 1988, Tables "Lard", ISIC 3111-31, p. 112 and "Oils and fats of animals, unprocessed", ISIC 3115-07, p. 156.

7 See UN Industrial Statistics Yearbook, 1988, "Hides, cattle and horses, undressed - total production" ISIC 3111-311, p. 115. This refers to fresh weight, prior to tanning.

of this may be pet food, for which we have no explicit data. We conjecture that most of the "missing mass" is evaporative water loss in the production of meals and concentrates.

Exports of red meat products in 1988 amounted to 0.4 MMT and imports (mostly of beef) amounted to 1.63 MMT. Thus domestic supply of red meat was 19.41 MMT. However, final consumption of meat ("as purchased") was only 16.25 MMT. The difference of 3.16 MMT is waste fat and bone, largely generated by meatcutters in retail shops. This waste ends up in municipal refuse and, finally, in landfills.

In the case of poultry, live weight was 12.95 MMT in 1988. Dressed carcass weight of poultry for the US was either 9.5 MMT or 10.07 MMT⁸. This implies a by-product and waste flow at the processing plant of 3.0-3.5 MMT, part of which (2.0-2.5 MMT) is probably recycled as animal feed. The rest (mostly feathers) is dumped or burned. Final consumption of poultry ("as purchased") was 6.37 MMT in 1988. Thus, a further loss of 3.1-3.5 MMT presumably occurred at the retail level. The latter ends up in garbage as municipal refuse or in waterways (as BOD).

The grain and oilseed milling sector is rather complex. Marketed grain/oilseed milling products consist of vegetable oils (6.4 MMT), flour (17.4 MMT), and corn syrup (7.7 MMT), adding up to 31.5 MMT. The imputed output of feed concentrates, by this calculation, is thus $62.2 - 31.5 = 30.7$ MMT. (We calculated, above, that 31.6 MMT must have been produced. The match is quite close). On the other hand, if we assume the calculated production figure (31.6 MMT) to be correct, the imputed mass difference is 9.7 MMT, or about 13.3%. This also seems entirely reasonable.

In summary, we have identified "mass losses" from the domestic food processing sector as follows: grain and oilseed milling 9.7 MMT, fermentation wastes 3.0 MMT, sugar milling 42.7 MMT, vegetable and fruit canning and freezing 18.3 MMT, meat and poultry packing 1.0 MMT (plus about 6.3 MMT in retail shops), dairy processing 26.1 MMT, egg marketing 0.6 MMT, and fish packing and retailing 4.6 MMT. For the sector as a whole (including losses in retail shops) this adds up to 112.3 MMT, plus an additional 6.8 MMT of carbon dioxide from fermentation.

Of the 112.3 MMT of mass disappearance identified in 1988 (*Figure 1*), it appears that at least 66.2 MMT consisted of water vapor from evaporative processes in the manufacture of cheese and dried milk products, sugar and corn syrup production, drying and freeze-drying of fruits (such as oranges for juice, prunes and raisins), and from the production of meat meal and fish meal. An additional 34.5 MMT of mass losses was solid waste of vegetable origin, from sugar beets/cane, fruit and vegetable and grain milling. Some of this consisted of fruit/vegetable skins and stems, nut shells, pits and seeds, inedible leaves, spoilage, and so forth. Usually these would be generated in quantities too small to be dried and burned efficiently. However the sugar and grain milling wastes (c. 27 MMT) could probably be

8 See UN Industrial Statistics Yearbook, 1988 "Poultry, dressed, fresh (Total production)", ISIC 3511-10, p. 96 and "Poultry, dressed, fresh (Industrial Production)" ISIC 3511-101 [UNIS 1988, p. 99]. For mysterious reasons, the latter figure is slightly larger.

burned for energy recovery. The remainder (11.6 MMT) was organic wastes of animal, or fish, origin and not suitable for combustion.

Even the bulky and "dry" food processing wastes still contain quite a bit of water, probably 25% or so. If the bulky combustible waste biomass of vegetable origin (i.e. 27 MMT) is assumed to have been burned for energy recovery, and if the dry mass (say 20 MMT) is assumed to be chemically similar to cellulose, the CO₂ generated would be around 29.4 MMT, consuming about 21.3 MMT of oxygen and producing about 12 MMT of water vapor in addition to the 7 MMT embodied in the organic material. Of course, the same amount of CO₂ would be generated by natural decay processes, as long as they occur in aerobic conditions.

The material losses that we have identified as likely waste streams are "dry" in the sense that they do not include the weight of washing, cooking, or process water. They also do not assume *a priori* mass reduction by combustion of biomass for energy recovery. In this connection, a survey by Science Applications Inc. (SAI) commissioned by EPA, attempted to identify dry wastes from the industrial sectors [SAI 1985]. The SAI estimate of dry weight of wastes from SIC 20 was 6.3 MMT (based on 1976 data). This strongly suggests that combustible wastes were, in fact, mostly burned for mass reduction. A significant fraction of the incombustible organic wastes of animal origin (11.6 MMT) and vegetable origin (7.1 MMT) were actually downstream in the retail sector. Thus, our analysis is consistent with SAI's results.

4. Forestry and Wood Products: Timber Tracts (SIC 081), Lumber (SIC 24) & Pulp & Paper (SIC 26)

Wood products are derived from timber tracts, which belong to the "forestry" sector (SIC 08). As in the case of agriculture, the primary inputs are land, water and carbon dioxide from the air. Major outputs are timber and oxygen; minor outputs include gums, barks, maple sap and such. Several important natural resins and solvents (e.g. turpentine, "naval stores") are derived from gums. Downstream chemical products based on wood distillates include acetone, methyl alcohol, pine oil (pinenes), terpenes, tall oil, and tanning extracts.

Neglecting the minor products, we can construct a rough mass balance for the timber tracts. The data given below implies that the total mass of raw product that was harvested in 1988 was 355 MMT on an air-dried (15% moisture) basis, which implies a dry content of 302 MMT, of which 2% consists of mineral "ash" (see below) and the remainder (296 MMT) is roughly equivalent to cellulose. This implies a carbon content of 118.5 MMT. This, in turn, requires an input of 433 MMT of carbon dioxide from the air, plus 177.5 MMT of water, for photosynthesis. Oxygen generated thereby was 314.5 MMT. Assuming the harvested wood has an original moisture content of 48%, an additional water input of 170 MMT is implied. Thus, total water input must have been $177.5 + 170 = 347.5$ MMT. Subtracting the water content of the air-dried wood output (53 MMT) from the original water content of the wood (170 MMT) implies a loss from wood dehydration of 117 MMT.

Terrestrial vegetation (trees) has an estimated carbon-nitrogen-phosphorus ratio of 800:10:1 [Deevey 1970]. Since most of the nutrients are embodied in the bark and foliage, this is an over-estimate for harvested wood. However, if it were correct, the nitrogen content of the wood removed from the forests would be of the order of 1.5 MMT, while the phosphorus

content would be of the order of 0.15 MMT. As noted later, the phosphorus content of wood ash is about 1% of the ash; the ash itself amounts to 2% of the total mass of debarked wood. This implies a total mineral (ash) content of 6 MMT for the wood harvested, and a probable phosphorus content of the order of 0.06 MMT, which is only 40% of the loss rate implied by the Deevey C:N:P ratio. Not all of this is removed from the forest, since some debarking operations are carried out at the logging site.

The total mass of roundwood consumed by U.S. lumber and plywood mills (10,120 mcfre @ 20 kg/cf) was roughly 202 MMT. The mass of lumber produced in 1988 was about 43.9 MMT [Ulrich 1990, Table 7]. The mass of plywood and veneer produced was 11.1 MMT; hardboard, insulating board and particleboard amounted to 8.8 MMT. Total processed wood products added up to 63.8 MMT. Allowing for 54 MMT of wood chips from lumber mills used for pulping, plus exports of 3 MMT, we can account for about 121 MMT. The residue was therefore approximately 81 MMT. Assuming 4% (8 MMT) waste [USOTA 1984], it appears that 73 MMT must have been recycled as fuel for energy. Of this, 15% (12 MMT) was moisture, and the rest (61 MMT) was dry weight.

Based on 1988 data on wood consumption for pulping cited above (96.7 million cords @ 80 cf/cord) the total weight of inputs comes to 147 MMT. The weight of inputs from domestic pulpwood (4885 mcfre, @ 19 kg/cf) was just over 93 MMT, leaving 54 MMT for the weight of chips from lumber mills, less net exports.

U.S. domestic woodpulp production was 63.8 million tons or 57.9 MMT [STATAB 1991, Table 1195]⁹. Consumption of domestic primary pulp was 56.8 MMT [ibid]. According to UN data, total U.S. woodpulp production in 1988 was 55.5 MMT, plus 0.3 MMT from other sources of fiber. Domestic production of pulp was essentially entirely from domestic resources.¹⁰ This leaves a statistical discrepancy of 1.3 MMT, which is probably insignificant. U.S. (net) exports of woodpulp in 1988 were 0.535 MMT while chemical uses (of dissolving grade pulp) amounted to 1.24 MMT. Thus, virgin pulp available for domestic paper production was $56.8 - 1.7 = 55.1$ MMT.

In addition, wastepaper recovered within the industry was reported to be 23.8 MMT¹¹. Not all of this was post-consumption waste; some was internal scrap recycling within the paper production sector. To obtain a match between inputs and outputs of the paper sector, we calculate that 16.1 MMT of recycled pulp must have been consumed, of which 5.3 MMT was from internal waste and the rest was post-consumption wastepaper. Allowing for internal recycling, exports and other uses, 12.5 MMT of wastepaper would have been re-pulped.

9 These data are essentially consistent with Ulrich [Ulrich 1990, Table 51]; however Ulrich's Table 51 appears inconsistent with Ulrich's Table 7 as regards imports and exports of pulp. However the latter figures include pulp imputed to downstream paper and paperboard products. We account for imports and exports of downstream products separately.

10 Imports of "pulp products" shown in Ulrich (1990), Table 4, apparently refer to pulp itself, and to the pulp equivalent of paper and paper products, not pulpwood. The U.S. was a net exporter of pulp and a net importer of paper products.

11 This was out of 23.8 MMT collected for recycling, of which 5.4 MMT was exported and 0.6 MMT was used for other purposes [STATAB 1991, Table 1194].

About 10% (1.3 MMT) of this mass would have been lost in the re-pulping process, consisting mostly of inorganic fillers and coatings [USOTA 1984 Figure 24], leaving 11.2 MMT as secondary pulp for paper and paper-board production. Thus total domestic pulp supply (excluding internal recycle) was around 65.9 MMT in 1988. Adding 5 MMT of fillers and other chemicals¹², the domestic output of paper and paper products was 70.9 MMT.

The UN data for pulp is subdivided by pulping process. Mechanical pulp (5.39 MMT) was virtually entirely used for newsprint (for which domestic production was 5.36 MMT). The other pulp types were, in order of quantity: sulfate or Kraft pulp (43.53 MMT); semi-chemical pulp (3.95 MMT); sulfite pulp (1.415 MMT). Finally, "dissolving grade" pulp for chemical use (e.g. in rayon manufacturing) amounted to 1.24 MMT.

In the case of pulping feeds, (147 MMT) around 22 MMT (15%) was moisture in the wood. The pulp output (55.8 MMT) included only 10% (i.e. 5.6 MMT) moisture. Overall, then, the apparent mass disappearance between pulpwood and pulp in 1988 was $147 - 56 = 91$ MMT, of which $(22 - 5.6) = 16.4$ MMT was presumably water. This would have left 74.6 MMT (dry weight) of waste organic material. The organic wastes consist of lignin, hemi-celluloses, and resins. Small amounts of lignin are recovered for use as ligno-sulfonates; virtually none of the hemi-celluloses are currently recovered for chemical use¹³.

Most of the waste organic material was burnt on-site for energy and chemical recovery. We don't have data for 1988, but in 1991 the American Forest and Paper Association (AFPA) estimated that 83,170 million (short) tons, or 75.3 MMT of dry waste organic material content of "black liquor" was used as fuel.¹⁴ The energy recycling figure in 1988 was presumably about 2.5 MMT smaller, or 72.8 MMT, based on relative pulp production levels. The two numbers are as close as can reasonably be expected, given the approximations made in the calculation.

All of the pulping processes except the mechanical ones use chemical reagents — notably sodium hydroxide or sulfurous acid — to "digest" (i.e. dissolve) the lignin and separate it from the cellulose fibers in the wood. In principle, these chemical reagents are mostly recovered and recycled internally. In practice, of course, recovery is incomplete and some

- 12 Actually this is a lower limit, since it includes only inorganic materials (kaolin, alum, etc) that we have been able to account for explicitly from published sources.
- 13 An attractive future possibility is to ferment or otherwise convert the hemicellulosics (sugars) to ethanol. Until now, all known fermenting agents produce an enzyme, lactate dehydrogenase, that breaks down the hemicellulosics into a mixture of ethanol and lactic acid. Fortunately, a new discovery at Imperial College, London, may change this situation. It is a mutant strain of the fermenting bacterium, *Bacillus stearothermophilus*, which lacks the enzyme and thus converts hemi-cellulosics directly to ethanol, without the usual mixture of lactic acid. Unfortunately, the mutation appears unstable and the organism reverts back to the original form which produce the enzyme. Thus, the current challenge is to bio-engineer a strain that lacks the gene.
- 14 This does not take into account the bark, which constitutes about 11.5% of the raw weight of roundwood [USOTA 1984 Table 5]. We have completely omitted bark from our calculations by assuming that a cord of roughwood is equivalent to 80 cf of debarked (peeled) roundwood equivalent. This suggests that about 10 MMT of bark would be produced by debarking operations, which preceded pulping proper. Based on 48% moisture content; 10 MMT raw weight might be consistent with 5 MMT dry weight. (Bark is burned as "hog fuel").

makeup chemicals are required. In fact, makeup requirements and imputed overall losses and wastes are quite considerable.

Chemical consumption by the U.S. pulp and paper sector for 1988 can be estimated as follows. The sodium sulfate consumed by the entire U.S. pulp and paper sector in 1988 was 0.48 MMT [USBuMines 1989 "Sodium Sulfate" Table 4, converted to metric units]. Similarly soda ash consumed by the sector was 110 KMT [ibid "Soda Ash", Table 3, converted to metric units]. The total elemental sulfur actually consumed was 8 KMT [ibid "Sulfur", Table 12]. Consumption of lime by the sector was 1.14 MMT [ibid "Lime" Table 5, converted to metric units]. The industry consumed 0.856 MMT of sulfuric acid [ibid "Sulfur" Table 12]. Most of the foregoing appear to have been used in pulping.

Other chemical inputs to the pulp and paper industry were used primarily in bleaching. Most virgin chemical pulps for paper are bleached. In 1988 the primary bleaching agents were elemental chlorine (Cl_2), caustic soda and chlorine dioxide. The latter is manufactured in-house from sodium chlorate, because chlorine dioxide is explosive and too dangerous to ship. In 1988 the paper and pulp industry was still the second largest user of chlorine, taking 1.5 MMT or 14% of total U.S. chlorine output [USBuMines 1989 "Salt" p. 849; MIT 1993 Figure 2.5]. In 1988 the U.S. pulp and paper industry consumed 2.3 MMT of caustic soda (24% of production) [USBuMines 1989 "Salt" p. 849]. It also consumed 0.341 MMT of sodium chloride (salt) [USBuMines 1989 "Salt" Table 18, converted to metric units]. The other chemical used in large quantities is sodium chlorate. Production in 1974 was reported as 0.19 MMT of which 70% was used for pulp bleaching [Lowenheim & Moran 1975 "Sodium Chlorate"]. U.S. production in 1988 was 0.242 MMT, and consumption was probably somewhat higher, thanks to imports. The 70% share attributable to pulp bleaching in 1974 is probably a minimum for 1988.¹⁵ On this basis, we estimate that 1988 consumption of sodium chlorate by the pulp sector was at least 0.2 MMT.

The chemicals listed above are used for process makeup purposes (which sum up to 6.94 MMT) are not embodied in the product, and must therefore be included in the production waste stream. It follows from materials balance considerations that the annual discharges of chemical wastes from the pulp and paper industry must be roughly equal to the annual inputs, element by element. As it happens, net "dry" wastes (e.g. sludges) of 8.5 million short tons (7.7 MMT) were reported by an EPA contractor for the early 1980's [SAI 1985]. This is roughly consistent with our estimate of $6.9 + 1.8 = 8.7$ MMT losses from primary pulping and bleaching. However, it may not include the additional wastes from re-pulping of waste paper.

Bleaching wastes are mostly (90%) sodium chloride (salt) but it is estimated that 10% of the chlorine used is chemically bound to lignins and other organic materials in the pulp. This material constitutes a significant part of the process waste. Roughly 6% of the mass of the raw pulp is lost during bleaching. The bleaching effluent contains significant quantities of

15 U.S. production in just the third quarter of 1992 was 130,615 metric tons, which implies an annual rate of over 0.5 MMT, twice the level of 1988. In the same quarter, apparent consumption was 203,078 metric tons, of which 37% was imported [USDOC 1992]. The explanation is that chlorine dioxide has been very rapidly substituting for elemental chlorine as a bleach for pulp. It seems obvious that most of the increase in U.S. demand since 1988 is for conversion to chlorine dioxide.

chlorinated organic compounds with very high molecular weights. In fact, from 70% to 95% of spent chlorination and alkali extraction liquors have molecular weights greater than 1000. Such compounds cannot be separated, quantified or identified by present means. However measurable traces of dioxins (TCDDs) and furans (TCDF's) are found among these wastes [Holmbom 1991]

The Kraft process emissions of greatest environmental concern are non-condensable sulfur-containing gases (hydrogen sulfide, methyl and ethyl mercaptans, dimethyl sulfide, etc). These are generated at the rate of about 2.5 kg/tonne of pulp [IBRD 1980]. For sulfate pulp in *toto*, uncontrolled emissions of sulfur-containing gases would have been about 0.1 MMT.

EPA has estimated airborne effluents (excluding CO₂) from the sector to be about 1.15 MMT [USEPA 1991].

A partial list of chemicals used in the paper industry (as opposed to pulping) and embodied in the product includes clay (kaolin) for filling and coating, titanium dioxide for whiteness, and aluminum sulfate (alum) to improve the ink-absorbing quality of printing paper. Allowing for 5 MMT of fillers and other chemicals embodied in paper products, it can be seen that total inputs to U.S. paper mills in 1988 added up to 73.7 MMT. Paper and pulp products produced domestically from woodpulp amounted to 69.53 MMT according to UN data and 70.85 MMT according to U.S. data.¹⁶ The difference is probably not significant.

Within the forest products sector taken as a whole, we can account for roughly 193 MMT (15% moisture basis) of wood and wood wastes burned for fuel in 1988, which is somewhat more than half of the harvested amount. This consisted of 60 MMT harvested for fuelwood, as such, 61 MMT wood chips and scrap from lumbering and wood products operations, and 72 MMT of pulping wastes. Of course, the heat energy from the latter two categories of wastes was recovered for use within the industry. Allowing for 2% ash for fuelwood and 1% for lumber and pulpwood, combustion would have required about 170 MMT of oxygen from the air and generated 233.5 MMT of carbon dioxide and 124.1 MMT of water vapor.

Wood combustion produces another waste product, wood ash. The combustion of debarked wood chips and scrap yields 1%-2.5% ash; debarked wood chips and sawdust yield 0.5%-1.4% ash [Oberberger 1994, Table 2]. We can assume fuelwood averages 2% ash (or a total of 1.2 MMT), while industrial wood and pulp average 1% ash content. This implies 0.6 MMT ash from the combustion of scrap industrial wood, and a similar amount that is incorporated in water treatment sludge from pulping (and thus already counted). Altogether, in addition to wastes already mentioned, we must add 1.8 MMT wood ash. The composite mass flows for the U.S. timber products sector, together with lumber and pulp/paper in 1988 are summarized in *Figure 3*. Imports and exports are not shown explicitly, although both are significant. The flows are normalized for U.S. *consumption* of the intermediates, lumber and wood products, and pulp. Thus the upstream and downstream activities are indicated without reference to actual location. However there are substantial additional imports of final paper products, not shown.

16 U.S. production of paper products in 1988 consisted of 5.364 MMT of bleached newsprint (made from mechanical pulp), 19.59 MMT of printing and writing paper — coated and bleached — plus 44.57 MMT of "other machine made paper and paperboard", of which 36.056 MMT consisted of Kraft paper and paperboard [STATAB 1991, Table 1192].

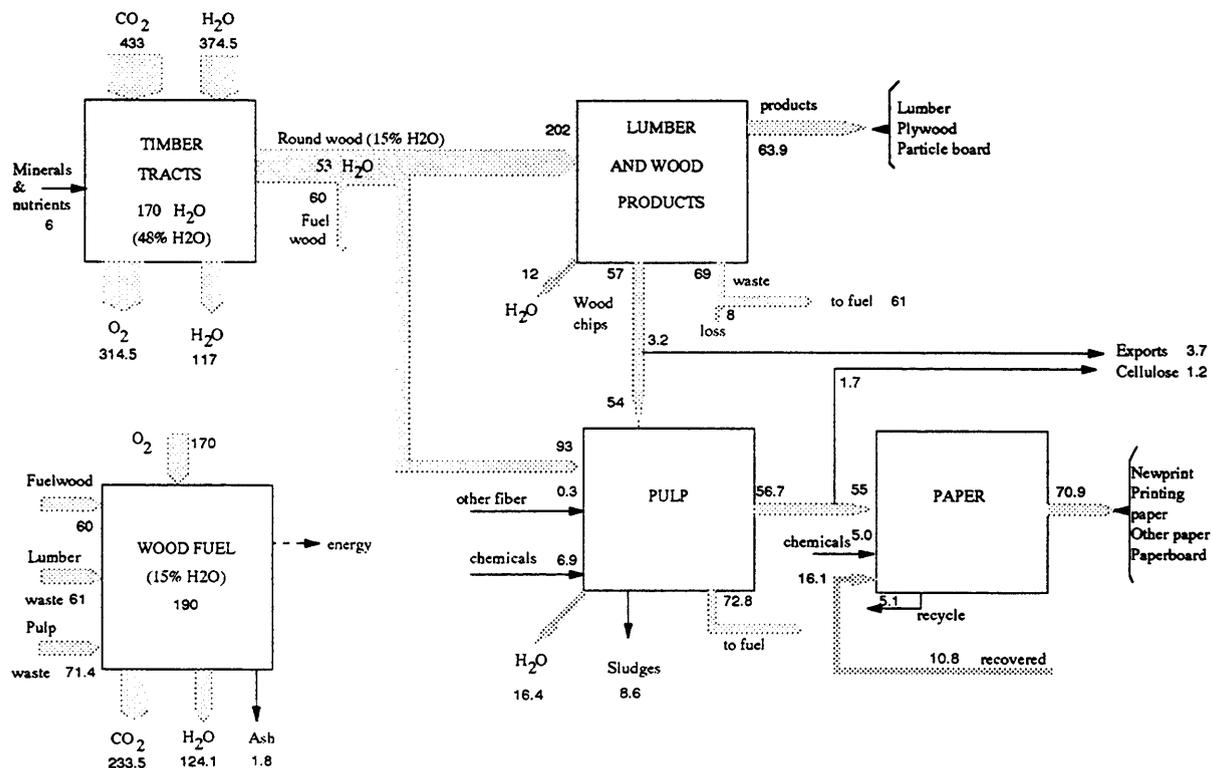


Figure 3: U.S. timber, pulp & paper industries, 1988 (MMT)

Roughly 30% of the paper and paperboard consumed in the U.S. was collected for recycling in 1988. The "unrecycled" fraction of final consumption, amounting to 59.1 MMT, was either burned or disposed of in landfills. Ultimately, all of it is converted to either CO₂ or methane (from anaerobic decay in landfills). Assuming only CO₂ is produced, production would have been 86.6 MMT.

5. Mining (Metal Ores) & Quarrying (SIC 10, 14)¹⁷

There are two types of waste associated with mining *per se*. These are (i) earth displaced in the process of searching for and removing ore (overburden) and (ii) unwanted contaminants (gangue) removed on-site by physical methods, such as screening, washing, settling, flotation, centrifuging and so on. The material shipped to the next stage of processing is, typically, a "concentrate" that is fed into a downstream process, either smelting (for metals) or combustion for fuels¹⁸. Smelting wastes are discussed in connection with the metallurgical

¹⁷ Data on materials handled is from *Minerals Yearbook, 1989*, Volume 1, Tables 10, 11 on pp. 69, 70. The rest of the data on metals and minerals came from individual chapters.

¹⁸ In the case of iron, concentrates for blast furnaces (pellets and sinter) are treated differently. Pellets are produced at the mine, while sinter is included in the smelting sector rather than in the mining sector. For consistency, we adopt this convention. In the case of aluminum, the "concentration" stage is taken to be the chemical conversion of bauxite ore into pure aluminum oxide (alumina). This process is conventionally included in the inorganic chemical industry (SIC 2819). Phosphate rock concentration (yielding fertilizer grade "superphosphate" is included in the fertilizer industry (SIC 2873). Phosphorus metal and phosphoric acid from phosphorus are both

industry (SIC 33); combustion wastes are discussed separately in connection with fossil fuel combustion.

The Bureau of Mines estimates that mineral exploration and mine development activities in 1988 (not including energy fuels) generated 190 MMT of waste material, mostly from overburden stripping. Active mines also produced more than a billion MT of mineral waste, prior to the concentration stage of processing; again most of this is overburden and some tunnelling. Total overburden moved by U.S. mines was 1192 MMT; overburden moved to supply U.S. metals consumption, adjusted for both imports and exports, was 1140 MMT.

Mining and quarrying activities altogether consumed 1.87 MMT of industrial explosives, of which 85% was ammonium nitrate based. We have calculated that about 5% of the mass of explosive was probably converted to N_2O , 14% to NO and 5% to N_2O . This implies N_2O emissions of 0.09 MMT and NO_x emissions of about 0.27 MMT from explosives alone.

Total concentration wastes for metals mined and concentrated domestically were about 780 MMT, including uranium (discussed later). Adjusting for imports and exports reduces the total slightly to 730 MMT. The most common physical concentration process is froth flotation. It is used, especially, to separate sulfide minerals of copper, lead, zinc, molybdenum and silver from lighter minerals such as silicates, aluminates and carbonates. It is also used to concentrate phosphate rock and, to a minor extent, for coal cleaning. The most recent data available is for 1985 [USBuMines 1987]. In that year 380 MT of mineral ores were concentrated by flotation, yielding 71.5 MMT of concentrates and 309 MMT of (dry equivalent) mineral wastes. Water used in the process was 947 billion gallons, or 3580 MMT. Wastes from flotation are generally disposed of in ponds, mostly in dry areas. Chemical reagents used amounted to 0.63 MMT. Grinding mills required 8 billion kwh of electricity and 134,000 MT of rods and balls.

Aluminum and iron ores are not concentrated by flotation. In the case of aluminum, the ore is bauxite, which is a relatively pure mineral that is already quite concentrated (about 30% Al). It is further concentrated to relatively pure Al_2O_3 by the so-called Bayer process, included in the inorganic chemical industry (SIC 2819), then reduced by electrolysis rather than carbothermic smelting. In 1988 8.2 MMT of bauxite ore was concentrated to 4.6 MMT of alumina (and some calcined bauxite) in the U.S. Almost all of the bauxite was imported. Primary aluminum production in the U.S. also consumed 3.2 MMT of imported alumina.

Iron ore mined in the U.S. is concentrated for blast furnaces by two processes, pelletizing (at the mine) and sintering. The latter process is carried out near the blast furnace, because it utilizes significant quantities of iron-rich "reverts", such as mill scale and dust, from later stages in the iron/steel production process. Blast furnace feed (concentrates) average 63% iron, whereas domestic iron ore is only about 20% iron. In 1988 197 MMT of crude iron ore was concentrated into 57 MMT of furnace feed, leaving 140 MMT of wastes.

Non-metallic minerals are mined or quarried in very large tonnages domestically. Stone (including limestone) is the largest item (1.15 billion MT), followed by sand & gravel (863 MMT). Imports and exports are comparatively small. Unlike the case of metals, overburden

also included with inorganic chemicals in SIC 2819.

wastes are small in relation to production (except for clay, where the waste amounts to 35.7 MMT). The same is true of (domestic) concentration wastes, except for phosphates (179 MMT), potash (8.9 MMT) and soda ash from Trona (7.0 MMT).

Phosphate rock mining and processing is an extremely important activity, since phosphate fertilizers are absolutely essential for modern agriculture. Unfortunately the ore is not of very high grade, and is rather contaminated, especially with cadmium, fluorine and uranium. (In fact, some uranium was recovered from phosphate rock in the past). In the U.S. 451.8 MMT of raw materials were handled to produce 224.1 MMT of crude phosphate rock in 1988. The difference was presumably overburden, which was mostly left in previously mined areas. The crude ore was concentrated, mainly by flotation, to 45.4 MMT of concentrated fluoroapatite mineral — roughly $(\text{CaF})\cdot\text{Ca}_4(\text{PO}_4)_3$ — which was, in turn, treated by sulfuric acid (the "wet process") to yield fertilizer grade phosphoric acid (13.2 MMT phosphorus pentoxide, P_2O_5). This refining operation is considered to be part of the chemical industry (SIC 28741) and will not be discussed further here.

Uranium mining in the U.S. produced about 15 MMT of ore in 1980. This was reduced (mostly by flotation) to 19,500 MT of U_3O_8 concentrate ("yellow cake"), which yielded 4740 MT of refined uranium oxide (nuclear fuel). Thus 3600 metric tons of ore were needed to produce a metric ton of concentrated UO_2 pellets [LeBel 1982, Table 6.1]. Uranium production has been declining sharply; production in 1991 was 580,000 MT of ore and 1150 MT of "yellow cake", down 96% from 1980. Uranium mining added 15 MMT to the 1980 figure for concentration waste, but due to declining demand, it was nearer 1 MMT in 1988 (we don't have an exact figure for that year).

Mine wastes from metal and non-metallic mineral production within the U.S. in 1988 can be summarized as follows. For metal ores, overburden wastes were 1192 MMT and concentration wastes were 784 MMT, including alumina and crude phosphate rock processing, or about 965 MMT and 600 MMT, respectively, without them (both belong to the chemical industry, SIC 28). The metals "system" is discussed further, and summarized diagrammatically, in connection with metals smelting and refining (SIC 33)

For non-metallic minerals (excluding coal) overburden wastes were 47 MMT and concentration wastes were 15.9 MMT (excluding phosphates). The non-metallic minerals that are ultimately transformed into inorganic chemicals (phosphates, potash and soda ash) are discussed further in connection with chemicals (SIC 28).

The overall total for metals and minerals amounts to 1239 MMT in overburden wastes, and 800 MMT concentration wastes, essentially dry weight, including alumina and phosphates. Details are given in *Tables 3 & 4*. It can be seen that the totals for mineral mining wastes in the U.S. are actually about 2.05 billion metric tons (dry), excluding water used for flotation. It is interesting to contrast this with other published estimates. The only one we could find was a figure for 1985, reported by an EPA contractor, namely 1.4 billion metric tons [SAI 1985]. But the latter figure is far too low, since it supposedly included the coal mining sectors also (SIC 11-12), which we discuss below.

Table 3. Production & waste allocation for primary U.S. metal production 1988 (1000 metric tons)

	US domestic mine production			US domestic concentrate production			US primary metal production (domestic & foreign ores)		
	Total material handled	Ore treated or sold	Overburden	Production (metal content)	production (gross weight) (d)	Concentration wastes	Concentrate consumption (gross weight)(d)	Primary production total	Smelting/refining losses
	A	B	A-B		C	B-C	D	E	D-E
Bauxite/Aluminum	8246 (e)	1107 (e)	7140		4575	4395	7730	3944	3786
Copper	523446	218631	304814	1341	5364	213267	5794	1406	4388
Gold	536146	117934	418212	0.201	0.201	117934	392	0.138	392
Lead	9707	6450	3257	385	481	5969	83694	392	98
Molybdenum	127006 (b)	72212	54794	43	172	72040	103	26	77
Platinum Group	34189	11396 (c)	22793	0.005	0.005	11396	.0003	0.0003	
Silver	48444 (c)	15876	32568	1.661	1.661	15874	2	1.718	
Zinc	21149	9106 (c)	12043	244	432	8674	429	241	188
Uranium Oxide(a)	22000	15200	6800		20	15180	20	5	15
NF Total	1330333	467912	862420		11046	460334	14960	6016	8944
Iron	300278	197766	102512		57515	140251	83694	49242	34452
TOTAL	1630611	665678	964932		68561	600581	98654	55258	43396

- NOTES: (a) 1980 data
(b) Assumes 3:1 ratio material handled to ore - as with gold/silver
(c) Zinc data from page 1159 has been subtracted from "other" on page 59 of Minerals Yearbook 1989 to construct approximate platinum data.
(d) Where direct figures for gross weight of concentrate were unavailable, they were calculated by applying reasonable concentration ratios to the metal content.
(e) Bauxite at US Mines. Included in total of "ore treated".
(f) Crude bauxite ore, dry equivalent. Includes net imports. Not included in "ore treated" total.

Source: Calculated from data in U.S. Bureau of Mines, Minerals Yearbooks, 1988 & 1989.

Table 4. Production & waste allocation for U.S. industrial mineral production from domestic & foreign ores, 1988 (1000 metric tons)

	Total material handled P.70 A.	Ore treated or sold P.69 B.	Domestic production from detail tables C.	Exports D.	Imports E.	Apparent Consumption C-D+E	Overburden loss A-B	Concentration losses B-C
Abrasives, natural	232	156	156			156	76	0
Barite	404	404	404	0.205	1207	1611	0	0
Clays	83370	44633	44515	3535	33	41013	38737	118
Diatomite	3420	695	629	147	0	482	2725	66
Feldspar	649	649	649	12	287	924	0	0
Gypsum	18325	14869	14869	246	8782	23405	3456	0
Mica	130	130	130	6	12	136	0	0
Perlite	586	586	585	0	0	585	0	1
Phosphorus	451778	224075	45389	0	0	45389	227703	178686
Potassium Salts	12247	11884	2999	579	6964	9384	363	8885
Pumice	423	374	353	1	28	380	49	21
Salt	34470	34470	34470	802	4966	38634	0	0
Sand & gravel	863640	863640	863531	1837	357	862051	0	109
Soda ash	15728	15728	8738	2238	257	6757	0	6990
Stone (88 is est.)	1151000	1150000	1148533	3304	3300	1148529	1000	1467
Talc, soapstone, pyrophyllite	1179	1234	1234	382	80	932	-54	0
Vermiculite	3393	1769	275	18	32	289	1624	1495
CALCULATED TOTAL	2640974	2365295	2167459	13108	26305	2180656	275679	197836

Source: [U.S. Bureau of Mines, Minerals Yearbooks, 1988 & 1989].

6. Mineral Fuels: Coal Mining & Oil & Gas Drilling (SIC 11-13)¹⁹

Coal mining is the largest single source of waste materials. Based on data supplied by the U.S. Department of Energy [anon], 9 cubic yards or 81 cubic feet of waste (mostly overburden) are moved for each short ton of coal mined, at an average weight of 160 lb per cf [Rogich 1994]. For 81 cf, this implies a waste overburden of 12,960 lb. (6.5 tons) per ton of coal. Since national soft coal production in 1988 was 862.1 MMT (at the mine), total materials handled in coal mining, exclusive of the coal itself, was apparently of the order of 5600 MMT or 5.6 billion metric tons. (This is more than 3 times the rate of loss of topsoil by erosion).

Coal mining is also a source of methane, since methane is trapped in the coal seams and is released when the coal is pulverized. We later consider the methane from all fossil fuel related activities together, however.

In addition, most utility coal is washed to remove pyrites and ash, resulting in a significant further production of waste refuse. In 1975 about 41% of soft coal produced was cleaned, resulting in 16 tons of coal refuse for every 100 tons of coal washed, for an 84% yield²⁰. By 1991 the percentage beneficiated figure had doubled. In 1988, therefore we assume that $(0.8) \times (16) = 12.8$ tons of sulfurous refuse were produced (at the mine) per ton of coal mined. Given that 862 MMT were shipped, approximately 975-1000 MMT must have been mined, generating beneficiation wastes of about 125 MMT, give or take 10 MMT. (This sulfurous refuse is a significant cause of acid mine drainage). The 1983 Census of Manufactures reported that coal mines discharged 470 MMT (340 mgd) of water, including washing water. Combustion emissions are discussed later.

Of the produced coal, exports took 86.2 MMT, imports were 1.94 MMT and roughly 43 MMT went to coke ovens, producing about 30 MMT of finished coke, 7.6 MMT of coke oven gas, 3.9 MMT of tar and breeze and small quantities of other by-products (including ammonium sulfate). There are minor fugitive emissions, mainly from the coke quenching process. The mass flows and wastes in the coal system are shown in *Figure 4*.

Petroleum and natural gas production involve relatively little waste, except water. During 1988 the U.S. oil and gas industry drilled 25,000 wells and drilled 124 million feet of holes. Assuming 6" pipe for the holes, the material actually removed from the holes would have been 5.5 liters per linear foot, or 682 million liters. Recalling that a liter of water weighs 1 kg, by definition, and assuming an average specific gravity of 3 for drilling wastes displaced by pipe, or about 2 MMT, plus (roughly) another 4-5 MMT or so of material that was removed and displaced by the drilling mud (allowing for water content). We therefore estimate a total of 6-7 MMT for drilling wastes (earth and rock).

19 Data on materials handled is from *Minerals Yearbook, 1989*, Volume 1, Tables 10, 11 on pp. 69, 70. The rest of the data on metals and minerals came from individual chapters.

20 The quantity of refuse produced obviously depends on the intensity of the beneficiation (washing) process. For comparison, the only coal cleaning process described in an official report of the U.S. Department of Energy, entitled "Technology Characterizations" [USDOE 1980, p. 33] had only a 70% yield in mass terms and a 90% yield in energy terms. Specifically, 1,428 tons of "run of mine" coal produced 1000 tons of "clean" coal.

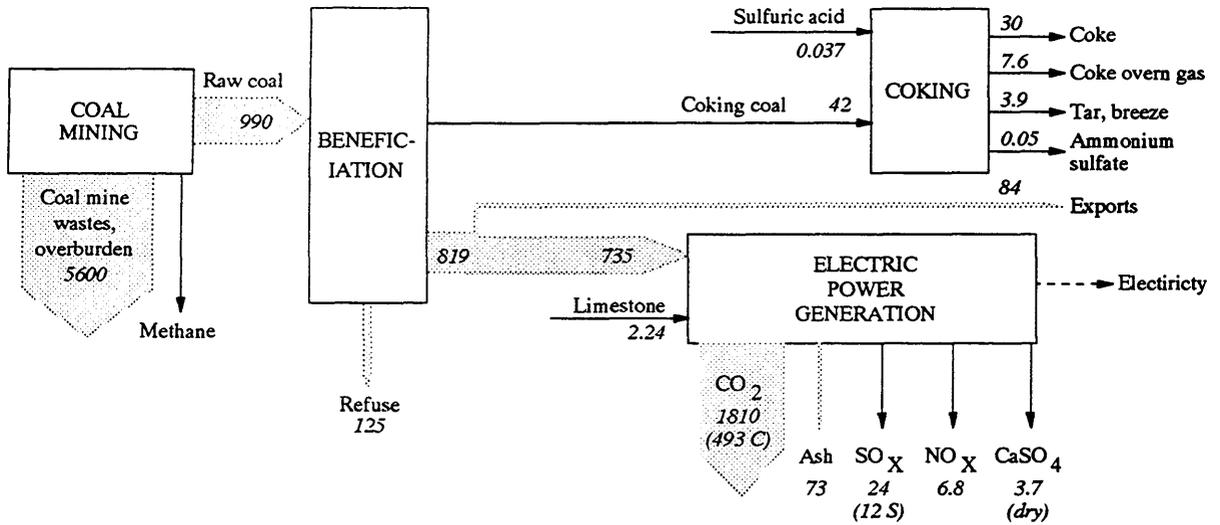


Figure 4: U.S. coal system 1988 (MMT)

Drilling muds constitute a much larger waste category. Drilling muds are, on average, 86% water (much of which is taken from the wells themselves), plus 3% oil, 2% polymers and 9% other materials [USOTA 1992]. The latter include clay, barite, chrome lignin sulfonates, etc. As an indicator, it might be mentioned that petroleum drilling accounts for virtually the whole national consumption of the mineral barite, or 1.4 MT. Clays, notably bentonite and fullers earth, accounted for 1 MMT. On this basis, drilling muds must have weighed at least 25 MMT. EPA has estimated that drilling fluids used in 1985 weighed 63 million tons, or 55 MMT [USOTA 1992]. Additional "associated wastes" amounted to 2 MMT. Most of these wastes are stored in ponds, where the water gradually evaporates.

EPA estimated that 3.7 billion tons of "produced waters" were generated by drilling activities in 1985 [USOTA 1992]. About 62% was reinjected in oil and gas recovery operations, leaving 1.4 billion tons (1270 MMT). These produced waters are usually saline and thus constitute a disposal problem of some magnitude. (Most of this is injected into wells). The excess of "produced waters" would help to reconcile the water data for the mining sector as a whole, as noted in the previous section. The 1983 Census of Manufactures reported about 700 MMT (523 mgd) of water used for cooling in the gas fractionation process.

Natural gas distribution (by pipeline) is a source of methane leakage to the atmosphere. In the U.S. it is estimated that 17.15 MMT (3.5% of total production, 4.6% of the total quantity transported) disappeared from the system and was presumably lost to the atmosphere in this way [OECD/IEA 1991]. Further losses occur in local distribution.

7. Petroleum Refining (SIC 29)²¹

Total output of crude oil in the U.S. in 1988 was 402.6 MMT. Exports were 0.6 MMT and imports were 269.05 MMT, for a total domestic crude oil supply of 671.0 MMT. Reported

21 All data in this section was extracted from a single source, [OECD/IEA 1991] *Energy Statistics of OECD Countries, 1980-1989* :664-665.

inputs of crude oil to domestic oil refineries were 678.684 MMT (leaving a statistical discrepancy of 9.1 MMT). In addition, refineries consumed 17.15 MMT of natural gas as fuel, 16.230 MMT of natural gas liquids, and 22.585 MMT of intermediate feedstocks (of which 16.864 MMT was imported and 6.319 MMT was internal transfers of "gasoil" to be upgraded). Subtracting the latter from both inputs and outputs we are left with a total of 728.33 MMT of net inputs. See *Table 5*.

Table 5. U.S. energy statistics 1988 (MMT)

Commodity	Production		Exports		Imports		Consumption	
	Raw	Finished	Raw	Finished	Raw	Finished	Raw	Finished
REFINERY INPUTS								
crude oil	402.585		0.634		269.053		680.687	
Feedstocks						16.864	22.585	
NGL		51.325		1.617		7.108		
REFINERY PRODUCTS								
LPG		15.906						56.272
Motor Gas		297.439		1.069		19.351		315.690
Av gas		1.020				0.020		1.074
Jet fuel		63.935		1.362		3.802		66.893
Kerosene		4.347		0.054		0.173		4.689
Diesel		143.258		3.419		12.943		146.315
Residual fuel oil		56.789		11.044		32.818		61.429
Naphtha		6.170		0.479		3.216		8.864
Petroleum coke		36.131		15.344		0.110		20.709
Other		54.073		2.626		5.865		57.072
TOTAL PETROLEUM	402.585	679.068	0.634	35.397	269.053	95.162	703.272	739.007
Coal & coke	862.066	29.397	86.203	0.992	1.936	2.439	801.647	30.844
Natural gas (.714 kg/m ³)		484.013				3.457		363.258
NGL to chemical industry							16.230	
TOTAL OTHER FUEL		513.410	86.203	0.992	1.936	5.896	817.877	394.102
TOTAL	1264.651	1243.803	86.837	38.006	270.989	108.166	1521.149	1133.109

Source: [OECD/IEA 1991 :pp 664-665]

Crude oil is desalted before refining. Water pollution from this process contains emulsified oil as well as salts, ammonia, sulfides and phenols. Also, this process involves considerable water use.

Refinery products identified included non-condensable refinery gases amounting to 34.072 MMT and salable products adding up to 679.068 MMT, or 672.749 MMT after subtracting the 6.319 MMT of gasoil that was internally recycled. Petrochemicals are also derived to some extent from so-called "light ends" from petroleum refining²². To be sure, the crude oil itself contains relatively little of these dissolved volatiles. A typical U.S. refinery using Texas

²² Light ends are compounds with boiling points in the range of butane (about 0 degrees C) and below. Methane and the light alkanes (C₂ - C₄) fall into this category.

or Louisiana crude oil might yield 1.3 % light ends (refinery off-gas) by volume, from the initial distillation. However, subsequent refining processes (such as catalytic cracking, catalytic reforming and delayed coking) also yield large quantities of light ends. Most of these by-product volatiles are used internally within the refinery complex. The C₄ gases (butylene, isobutane and n-butane) are mostly alkylated or blended directly into gasoline. The C₃ gases (propane, propylene) are collected and liquefied under pressure for use as domestic fuel (LPG). The mixed C₁ and C₂ gases (methane, ethane and ethylene) are mainly used as fuel for steam generation to provide heat energy for the refinery itself. Large amounts of hydrogen-rich off-gases are produced in refineries, but these are mostly used for hydro-treatment of naphtha or for hydro-forming within the refinery. Similarly, catalytic reformat (derived from naphtha), is the major source of aromatic feedstocks, known as BTX (benzene-toluene-xylene), although most of this material is blended into gasoline to increase the octane number.

Nevertheless, light ends also constitute a source of aliphatic petrochemical feedstocks. In brief, light alkane feedstocks like ethane (C₂H₆), propane (C₃H₈), and butanes (C₄H₁₀) — along with some naphtha and heavy gas oil (HGO) — are dehydrogenated in a pyrolysis furnace (within the refinery complex) to yield ethylene (C₂H₄), propylene (C₃H₆), butadiene (C₄H₆), butene, butylene (C₄H₈) and other C₄ olefins. Crude petroleum-based feedstocks consisted of LPG (22.459 MMT), naphtha (8.864 MMT), and refinery gases, or "light ends" (1.12 MMT). See section 7.2 "Organic chemicals".

In summary, apparent mass losses during refining (input mass unaccounted for) amounted to 728.33–672.75=55.58MMT, or 7.6% of input mass. In other words, the efficiency of mass conversion was 92.4%. Presumably virtually all of the missing mass consists of carbon dioxide, carbon monoxide or hydrocarbons, including fugitive volatile organic compounds (VOC's). EPA estimated airborne effluents from the sector as 2 MMT [USEPA 1991], presumably not including carbon dioxide. This is consistent with materials balance arguments. VOC's from petroleum refining include significant quantities of benzene, toluene, xylene and other aromatics, many of which are carcinogenic²³.

Crude oil contains small quantities of sulfur and mineral ash (of the order of 0.1%), depending on its origin. (For example, Venezuelan oil is particularly high in sulfur). The petroleum refining industry recovers sulfur from crude oil and produces some sulfuric acid as a by-product (2.4 MMT H₂SO₄, or 0.786 MMT S). Most of this sulfuric acid is used, initially, within the refinery, for bleaching. However, over half of the spent acid recovered and sold as a by-product (1.3 MMT). Most of the ash in crude oil probably remains with the refinery solid wastes and sludges. Assuming 0.1% ash in the crude oil would imply 0.7 MMT of solid waste. (The actual figure may be higher or lower). The spent sulfuric acid (2.1 MMT) is presumably neutralized, either by reaction with some of the alkaline minerals (NaO, KO, MgO, CaO) in the ash content of crude oil, or by added lime.

Refineries also utilize purchased materials from other sectors in the refining process, including salt (0.72 MMT) and clays (used as zeolite catalysts, 0.122 MMT) which subsequently reappear in (mostly solid or liquid) wastes. Since these materials do not appear in products,

23 Benzene, ethylbenzene, toluene & xylenes constitute, respectively, 0.1%, 0.51%, 0.19% and 0.88% of average crude oil by volume [Gaines & Wolsky 1981]. They are, of course, a much higher percentage of the volatiles.

they must be part of the waste stream. Consumption of salt is reported, but its use is unclear; it may be a precursor to in-house caustic soda production [Gaines & Wolsky 1981].

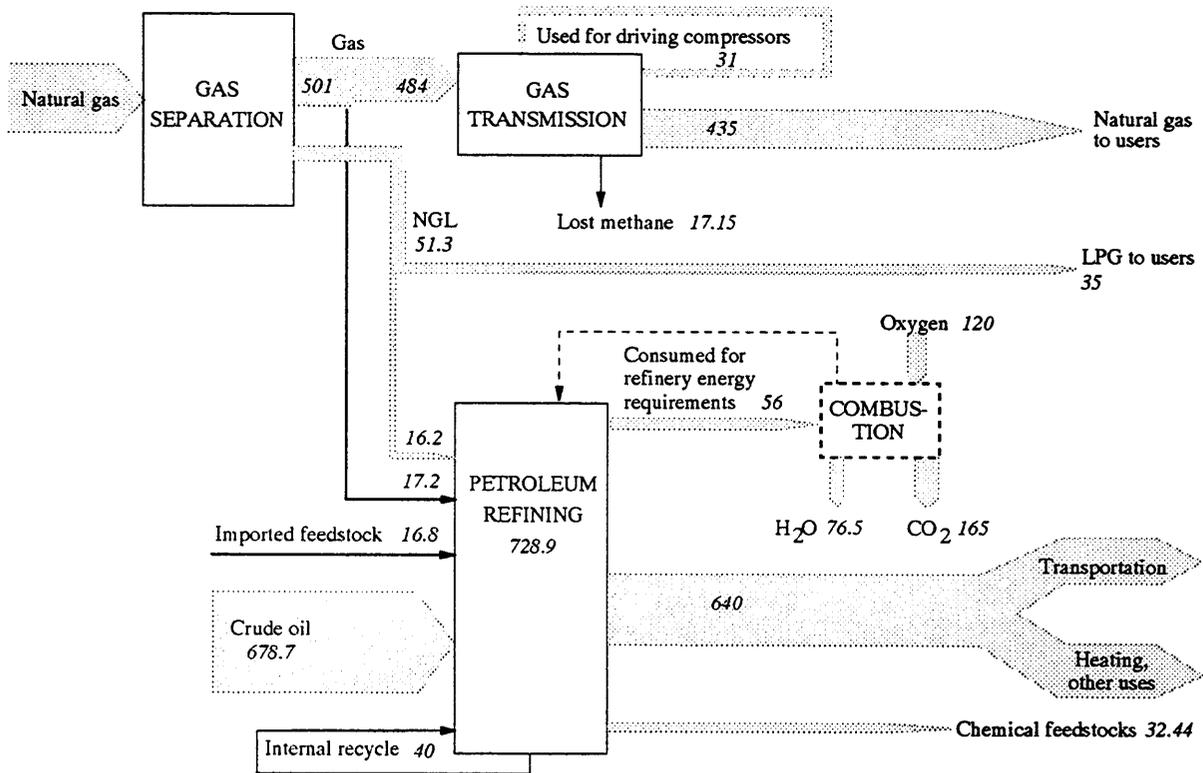


Figure 5: U.S. oil & gas system 1988 (MMT)

Mass flows in the petroleum, gas and refinery sectors, taken together, are shown in Figure 5. As noted above, the mass "loss" in refineries amounted to 55.6 MMT, or 7.6% of the mass of hydrocarbon inputs. This mass loss is partly fugitive emissions (VOC's), — estimated to be 2 MMT — but most of it is flared or recovered for refinery heat and power. Assuming the missing mass to consist mostly of molecules of the form C_NH_{2N+2} we can safely assume the carbon content to be between 80% and 85%, or about 45 MMT. This corresponds to an atmospheric oxygen intake of 120 MMT, eventual CO_2 output of roughly 165 MMT, plus a water vapor output of 76.5 MMT.

An EPA contractor estimated dry wastes by the petroleum refining sector to have been 1.25 MMT (1981 data). Given the fact that neutralized sulfuric acid wastes alone would account for considerably more than this, we estimate the solid wastes from refineries to be 3-4 MMT, i.e. 3 times larger than the EPA contractor estimate. (To estimate it more accurately we would need more complete data on materials inputs to the sector). EPA's estimate of total non-hazardous waste produced by the sector in 1985 was 150 MMT. Since the "missing mass" in the sector was only 55.6 MMT (including purchased inputs), and most of this must have been combustion products and VOC's, it is clear that most of the waste mass counted by EPA must have been water.

8. Chemicals (SIC 28)

The chemical industry is far too complex to describe in adequate detail in the brief space available. Of course the major distinction to be made is between inorganic and organic chemicals. The latter are derived mostly from natural gas, natural gas liquids, or petrochemical feedstocks (SIC 29). We discuss the organic chemicals later.

8.1. Inorganic chemicals

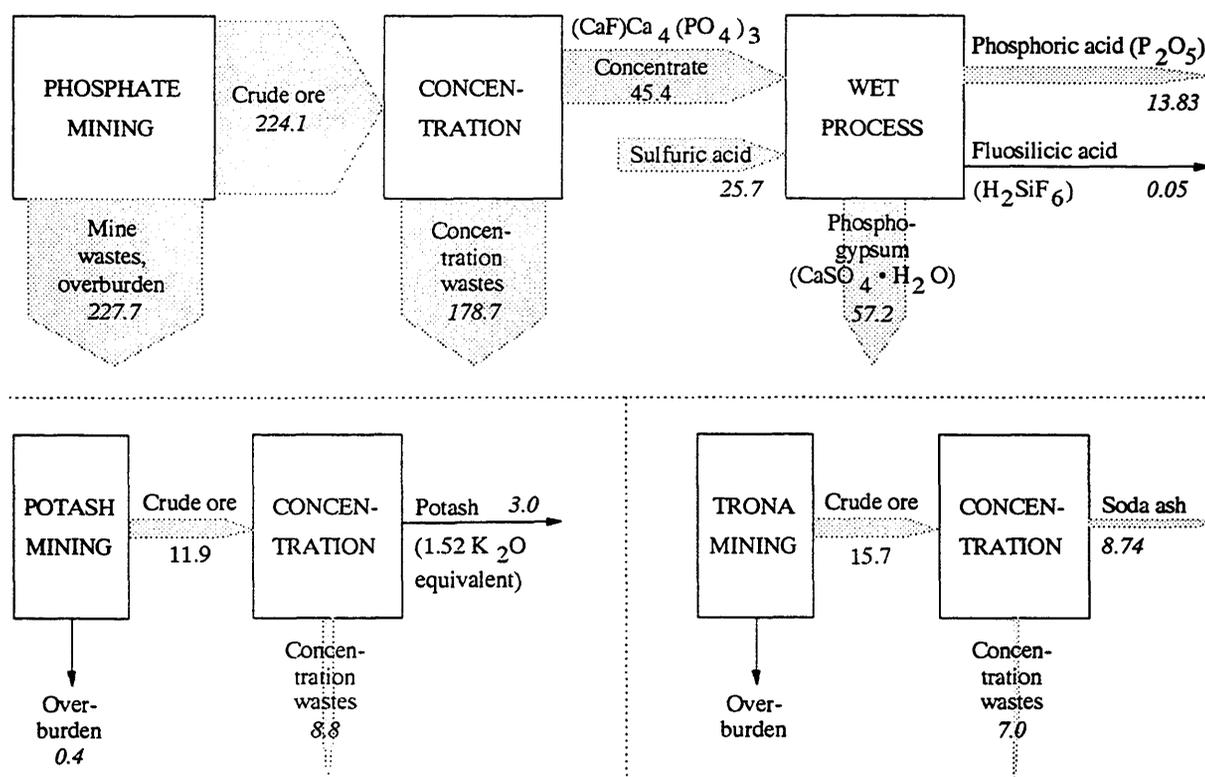


Figure 6: Phosphates, potash & soda ash, U.S. 1988 (MMT)

The inorganic chemicals are derived either from non-metallic minerals (such as sulfur, phosphates, potash, soda ash and salt), or from the atmosphere. A few inorganics are derived from metal ores or metals. A summary diagram for phosphates, potash and soda ash, beginning with extraction and beneficiation, is given in Figure 6. The most important inorganic chemicals other than the three noted above, are ammonia, sulfur (sulfuric acid), and salt (chlorine and sodium hydroxide). See Figure 7. The major groupings are discussed in the following sections. Others are mostly derived from these. For instance, nitric acid and urea are both made from ammonia.

Domestic production of ammonia in 1988 was 12.544 MMT (N-content). Net imports (imports less exports) plus stock changes increased apparent domestic consumption of ammonia to 14.745 MMT (N). In addition, there were significant imports and exports of N-chemicals. The major (net) import items were urea (0.483 MMT N) and ammonium nitrate (0.091 MMT N), while major (net) export items were ammonium phosphates (1.150 MMT

N) and ammonium sulfate (0.155 MMT N). In all, fertilizers accounted for nearly 80% of the supply of fixed nitrogen. See *Figure 7*.

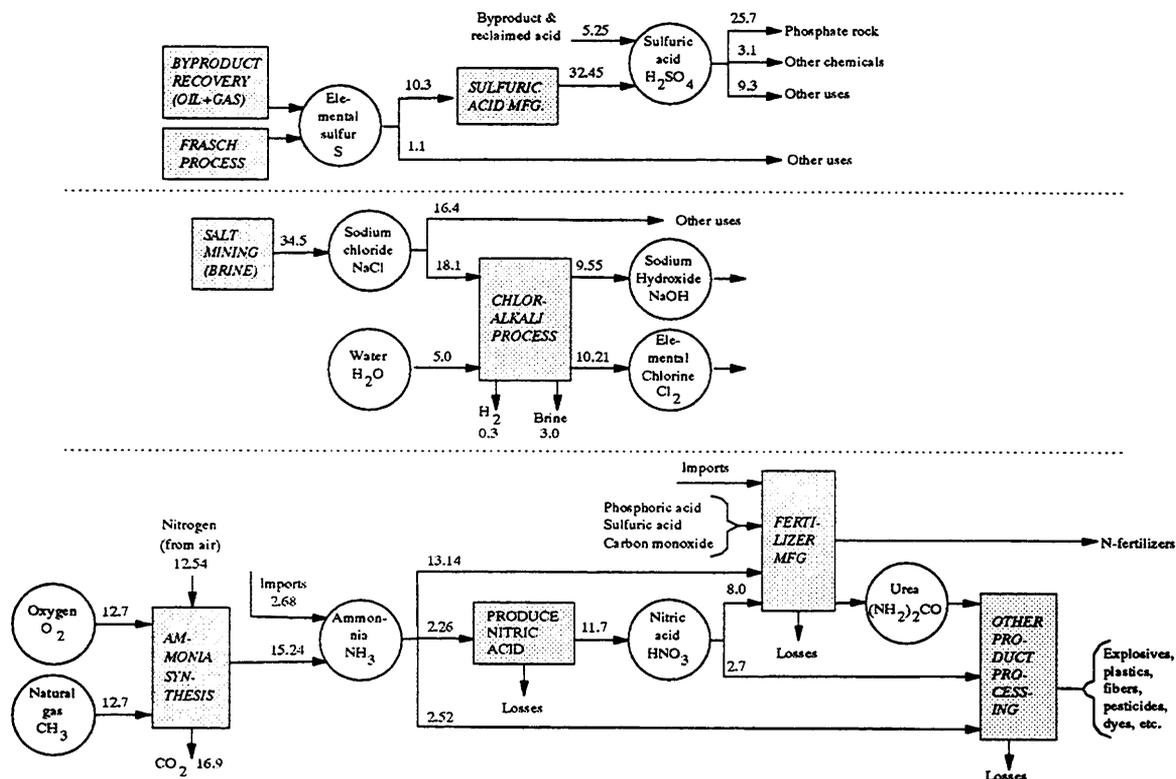


Figure 7: Ammonia, sulfur & salt, U.S. 1988 (MMT)

The N-content of monomers embodied in plastics and resins in 1988 (SIC 282) added up to 0.669 MMT. Nitrate and nitro-explosives (excluding amines) accounted for about 0.777 MMT (N). Urea fed to animals accounts for 1.55 MMT (N); unspecified uses of nitric acid — including phosphate rock processing and steel pickling — accounted for 0.135 MMT (N). Other identifiable final uses, including dyes, rubber chemicals, herbicides and pesticides, and sodium cyanide used in the gold mining industry, add up to 0.153 MMT (N). Process losses are probably at least 2%. (Nitrogen wastes are smaller than they might otherwise be, however, because ammonia-bearing waste streams are easily neutralized by sulfuric acid to produce a useful by-product fertilizer, ammonium sulfate). We estimate that process losses, altogether, will account for 0.3 to 0.35 MMT (N). There is some possibility of under-counting of the use of nitrogen in mixed fertilizers, where published data seems to be spotty. However, lacking further information, we assume the remaining "missing" nitrogen (about 0.4 MMT) is allocated mostly to household cleaning agents and other consumer products. In summary, we can account for about 0.737 MMT of fixed nitrogen embodied in products of the synthetic organic chemicals sector, and of the order of 0.16 MMT of nitrogenous losses associated with organic synthesis, for a total of 0.9 MMT.

In terms of pollution of the environment, the 2% loss rate suggested above would be insignificant in comparison with dissipative uses of nitrogenous chemicals. Apart from fertilizers and animal feeds, these include industrial explosives, pesticides and herbicides, dyes, surfactants, flotation agents, rubber accelerators, plasticizers, gas conditioning agents, and so on. In fact, except for the plastics and resins (and plasticizers), it is safe to assume that

virtually all nitrogenous chemicals are soon dissipated in normal use, but mainly by other sectors, or final consumers. In the case of plastics and fibers, the dissipation is merely slower.

Sulfuric acid (37.7 MMT in 1988) is derived from elemental sulfur (11.584 MMT in 1988). It is the starting point for most sulfur based chemicals. See *Figure 7*. Elemental sulfur is also recovered from natural gas processors and petroleum refineries. What is recovered in petroleum refineries was mostly also used there (0.958 MMT S-content), but almost half of the spent acid from refineries was later reclaimed: 0.43 MMT (S). Sulfuric acid was recovered from copper, zinc and lead smelters (1.125 MMT S-content, 1988), but again, much of that (0.543 MMT S-content) was used in mining operations, by the acid leach process. In the case of copper mines, copper sulfate is recovered from the leach piles, and this is recycled, but much of the leaching acid remains in the ore heaps where it presumably reacts with other minerals and remains as insoluble sulfates.

By far the largest use of sulfuric acid is for phosphate rock processing: 8.404 MMT (S). This use was discussed previously. Another important use of sulfuric acid is in the sulfate (Kraft) pulping process, 0.288 MMT (S), also discussed previously. The "pickling" process for cleaning rolled steel prior to galvanizing or tin-plating used 0.074 MMT (S) as acid, of which 0.022 MMT (S) was recovered. Sulfuric acid containing an additional 0.024 MMT (S) was used by other metallurgical processes (mainly metal plating). Automotive batteries accounted for a further 0.051 MMT (S), of which 0.036 MMT was reclaimed. The above items, plus exports, add up to 11.162 MMT of embodied sulfur, or >90% of the total. The remainder, 1.172 MT of embodied sulfur is either used elsewhere in the chemical industry or for unidentified non-chemical purposes.

Excluding phosphates and sulfuric acid itself, about 5.04 MMT (1.645 MMT S) of sulfuric acid, plus 0.684 MMT of elemental sulfur, was consumed by the non-phosphate part of the chemical industry in 1988. Industrial inorganic chemicals, including pigments, consumed about 0.9 MMT (S), mostly as acid. Of the sulfur used in chemicals, 0.566 MMT (S) was eventually converted into ammonium sulfate fertilizer, mostly as a by-product of other chemical processes using sulfuric acid (e.g. caprolactam — a nylon monomer — and hydrogen cyanide). Of the rest, 0.170 MMT (S) was embodied in aluminum sulfate, mainly for the paper industry; 0.185 MMT (S) was in the form of by-product sodium sulfate, consumed in pulp manufacture. Apparently 0.460 MMT of elemental sulfur was used for "other" agricultural chemicals. The organic side of the chemical industry consumed at least 0.7 MMT, (identified) mostly as acid. Of this, drugs and pesticides accounted for only 0.02 MMT, and detergents for 0.06 MMT; the major uses were for the manufacture of organic chemical intermediates and synthetic rubbers and plastics. However, except for drugs, pesticides and detergents, virtually no sulfur is embodied in organic chemicals. Hence, at least 0.6 MMT (S) was consumed and lost in organic processing. In addition, there was 0.824 MMT (S) as sulfuric acid and 0.297 MMT elemental S in the "unidentified and export" category. For reasons discussed below, we think most of this was also consumed in the organic chemical industry, probably much of it in small quantities.

These waste flows were in several chemical forms, including H_2S , SO_2 , ammonium bisulfate, calcium sulfite and calcium sulfate. (To mention one example, hydrofluoric acid manufacture in 1988 would have accounted for about 0.24 MMT (S), generating calcium sulfate waste).

Phosphate rock is the only source of phosphorus chemicals, including fertilizers. The starting point was fertilizer grade phosphoric acid (13.833 MMT, P_2O_5 -content).²⁴ Of the 1988 production, exports — mostly as ammonium phosphates — accounted for 2.608 MMT, leaving 10.549 MMT for domestic consumption. Most of this, 9.329 (88.4%) was converted into "wet process" phosphoric acid (H_3PO_4). Elemental phosphorus production in the U.S. in 1988 was 0.32 MMT (0.79 MMT P_2O_5 equivalent), of which 85% is reconverted to pure "furnace grade" phosphoric acid for chemical manufacturing. Some of this goes back into fertilizer (to make triple superphosphate), but about 40% of it was used to manufacture sodium tripolyphosphate, or STPP ($Na_5P_3O_{10}$), a detergent builder. Production of this chemical in 1988 was 0.497 MMT, with a P_2O_5 equivalent of 0.309 MMT. The detergent industry is shifting to an alternative, tetrasodium pyrophosphate, which contains less phosphorus. Some phosphoric acid is used as a flavoring agent in the food and soft drink industry.

A minor but growing use of phosphorus is in the manufacture of lubricating oil additives such as zinc dithiophosphate, which starts from phosphorus pentasulfide (made by direct reaction of phosphorus metal and elemental sulfur). This use accounted for 0.015 MMT of phosphorus metal in 1974; we estimate 0.02 MMT currently, corresponding to about 0.05 MMT (P_2O_5) equivalent.

The starting point for organic phosphate synthesis is phosphorus trichloride (PCl_3). Production figures are not published, but on the basis of absorbing 1% of chlorine output (see "chlorine" below), we can conclude that about 0.03 MMT of phosphorus metal or 0.075 MMT (P_2O_5) would have been required. The trichloride is later converted to phosphorus oxychloride ($POCl_3$) by direct reaction with chlorine and phosphorus pentoxide P_2O_5 . The oxychloride, in turn, is the basis of organic phosphate esters that now have many uses. The most important of them is the plasticizer tricresyl phosphate (TCPP). Phosphate esters are also used as flame retardants and fire resistant hydraulic fluids. Such phosphate esters totalled .043 MMT (P_2O_5) in 1990 [USITC 1991].

All of the uses mentioned above are inherently dissipative. No more than 0.2 MMT of elemental phosphorus is embodied in chemicals used to manufacture other chemical products (mainly detergents).

Elemental chlorine together with sodium hydroxide (NaOH) — caustic soda — are co-produced by electrolysis of sodium chloride (salt), mainly in the form of brine. See *Figure 7*. In 1988 U.S. salt production was 35 MMT, of which 18.1 MMT was consumed by chlor-alkali producers. U.S. chlorine output in 1988 was 10.21 MMT, plus 9.55 MMT of sodium hydroxide [Chemical & Engineering News, June, 1992].²⁵ The wastes from this process (mostly spent brines) amount to about 15% of the weight of the products, or about 3 MMT. The mass balance is made up from water on the input side (about 5 MMT) and a small amount of hydrogen gas (0.3 MMT) released from the electrolytic cells.

24 Phosphorus pentoxide dissolved in water is phosphoric acid, the active ingredient in most phosphate fertilizers (e.g. "superphosphates"). It is not used, generally, in pure form.

25 The electrolytic process for chlorine production from brine yields 1.1 units of sodium hydroxide per unit of chlorine, with inputs of 1.75 units of sodium chloride. However, some chlorine is produced from magnesium chloride and some is regenerated from hydrochloric acid, so the ratios are not exact.

Major uses of chlorine in the U.S. in 1988 included chemicals manufacturing (76%), water and sewage treatment (5%), pulp & paper bleaching (14%), titanium dioxide manufacturing from rutile (3%), and misc. 2% (including silicon processing). The elemental chlorine used for bleaching in the pulp and paper industry has become a very contentious subject in recent years, due to the discovery of dioxin traces in bleached paper products. As a consequence — whether justified or not — this bleaching process is currently being phased out in Europe and may be phased out later in North America. The likely future alternative is "oxygen bleaching", using chlorine oxide (from sodium chlorate²⁶) or hydrogen peroxide.

Chemical end-uses in 1988 broke down as follows: bleaches — e.g. calcium and sodium hypochlorite— (7.8% of Cl), other inorganics 3% (phosgene 2%, phosphorus trichloride 1%), ethylene dichloride or EDC 40.5%; chlorinated alkanes 15% (chlorinated methanes 9%; chlorinated ethanes 5%, others 1%), epichlorohydrin 1%, ethyl chloride 3.5%, chlorinated benzenes 1.5%, chloroprene, 1% and misc. 3% (including HCl used outside the industry). These add up to about 76% of 1988 U.S. chlorine output.

One of the major intermediates is hydrochloric acid (HCl). Some is made by direct chlorination of hydrogen (3% of Cl, 9% of HCl). Most HCl (about 91%) is recovered as a by-product of one of the chlorination processes, especially the chlorohydrin process for propylene oxide production. The latter consumes 8.3% of chlorine output, initially, but this chlorine is entirely recycled internally as HCl. The other major source of HCl is the process that converts EDC to vinyl chloride monomer (VCM); but HCl is also consumed by a parallel process that produces EDC by hydrochlorination of ethylene. These two processes are deliberately combined. Other end uses of HCl include ethyl chloride (used for tetraethyl lead production, now nearly phased out) and hypochlorite bleaches, for instance.

By far the biggest single intermediate is EDC, the intermediate leading to PVC. However PVC only accounts for 24% of produced chlorine; part of the chlorine contained in EDC is reclaimed again as HCl. EDC also has other end-products, such as trichloro-ethylene and perchloro-ethylene. Some is also exported. Another important intermediate is epichlorohydrin, an intermediate to epoxy's; phosgene (COCl_2) is an intermediate to isocyanate pesticides and urethanes. Chlorinated benzenes are also intermediates to a variety of products.

Virtually all uses of chlorine are dissipative, with the major exception of PVC, which is used for structural purposes (e.g. water and sewer pipes, siding, window frames, calendered products and bottles). PVC — from vinyl chloride monomer — accounts for 24% of U.S. elemental chlorine output.

Most of the uses (e.g. of solvents) are not in the chemical industry itself. However, chlorination processes are relatively inefficient. Hence, recycling of waste streams is commonplace and a fairly large proportion of the input chlorine eventually becomes a production waste in manufacturing other downstream chemicals. For instance, in the production of VCM from ethylene dichloride, the loss rate is around 3% [Manzone 1993]. About 60% of this waste stream consists of non-volatiles (heavy ends) is "recycled" into chlorinated solvents and 40% is volatiles that are destroyed by incineration, with some

26 Sodium chlorate (for bleaching paper pulp) is almost unique among chlorine chemicals, in that it is not manufactured from elemental chlorine; it is made directly from sodium chloride (salt).

recovery of hydrogen chloride. In general, a 3% loss rate for chlorination processes seems realistic.

The other halogens are bromine, fluorine and iodine. The latter is not used in significant quantities. Bromine consumption in the U.S. in 1988 was 163,300 tonnes (0.163 MMT). Exact figures are unavailable, but the Bureau of Mines estimated that about 25% was used in drilling fluids (mostly as calcium and zinc bromides), and 15% was used in water treatment as a biocide for slime control. Fire retardants — tetrabromobisphenol-A and decabromodiphenyl oxide (known as "halons") — accounted for about 30% of total usage. About 15% was used in agriculture as a soil fumigant (methyl bromide) while 18% was consumed as ethylene dibromide (EDB) added to leaded gasoline as a scavenger to prevent lead deposition on valves. (This use is being phased out). An unknown, but small, amount was used to manufacture a red pigment (pigment 168) for metallized paint for automobiles. Evidently around 60% was used in organic chemicals, half olefin-based and half aromatic (e.g. phenol) based. Uses are dissipative.

Fluorine consumption in the U.S. was 551,000 tonnes (0.551 MMT) in 1988, but this included non-chemical uses, such as fluxes for the steel industry. Synthetic cryolite for the aluminum industry may have used some HF, although for this purpose the U.S. industry is converting to the use of by-product fluosilicic acid from phosphate rock processing.

Most chemical uses of fluorine begin with hydrofluoric acid (HF), produced by reacting sulfuric acid and fluorspar (CaF_2). U.S. production of the acid in 1988 was 195,777 tonnes (196 KMT), consuming roughly 0.24 MMT (S) of sulfuric acid and generating calcium sulfate as a waste. Some HF was used in petroleum refining (as an alkylation catalyst) and some was used in uranium refining (uranium hexafluoride, UF_6). However, probably most of the fluorine was consumed in the manufacture of CFC's and HCFC's, notably CCl_3F or CFC-11 (100 KT @10% F); CCl_2F_2 or CFC-12 (175 KMT @ 24% F), and CHClF_2 or HCFC-22 (148 KMT @ 34% F). Altogether these three CFC's alone accounted for about 92 KMT (F), or over 100 KMT of HF. In addition, other CFC's and the fluorocarbon polymers (e.g. "Teflon") presumably accounted for most of the rest.

In 1988, as noted above, 9.55 MMT of sodium hydroxide — caustic soda — were produced as a co-product of chlorine production. Major uses of caustic soda in 1973 were: the chemical industry (46%), in the pulp and paper industry (16%), the preparation of alumina by the Bayer process and to make synthetic cryolite for aluminum manufacturing (6%), petroleum refining (6%), dyeing of textiles (4%), rayon manufacturing (3%), soap and detergents (3%), cellulose acetate (2%) and miscellaneous purposes (14%), including exports [Lowenheim & Moran 1975, p. 742]. As of 1988, the pulp and paper industry had increased its share to 24% (2.7 MMT). The aluminum industry consumed just under 4% (0.37 MMT), a slight decline. The other uses probably declined roughly in proportion.

Taking into account alumina and soap/detergent manufacturing, around 48% (4.5 MMT) of caustic soda was probably absorbed by the chemical manufacturing sector. Most sodium-containing inorganic chemicals (such as sodium silicate or sodium dichromate) start from less expensive sodium carbonate (soda ash), rather than sodium hydroxide. Sodium is not a significant component of synthetic organic chemicals, with one exception. Sodium salts of coconut oil acids (274.8 KMT), and tallow acids (459.8 KMT) are major components of

liquid detergents. (We cannot readily estimate the average sodium content of these, but we conjecture that it is less than 10%, which implies 0.2-0.3 MMT NaCO_3 equivalent). This is consistent with the 3% share noted above. Otherwise, virtually all of the produced sodium hydroxide was dissipated within the chemical sector itself. Thus, we estimate that dissipative losses of caustic soda within the chemical industry account for about 4.2 MMT.

Soda ash is another alkali sodium chemical that was once manufactured synthetically (by the Solvay process). However sodium carbonate is now extracted from brines and evaporite deposits from the western U.S. Out of the U.S. production in 1988, 2.117 MMT was exported (net). Domestic uses of sodium carbonate accounted for 7.6 MMT (of which 1 MMT was taken from stocks). Traditionally, it is used in glass manufacturing (50%), alkaline cleaners (12%), pulp & paper (2%), flue gas scrubbing (2%) and water treatment (1%). The glass industry uses about 0.28 metric tons of soda ash per metric ton of glass.

Around 22% (1.9 MMT) of soda ash is used in other (mostly inorganic) chemical manufacturing. Important sodium chemicals based on sodium carbonate as a feedstock were as follows: sodium tripolyphosphate (STPP), of which 1988 production was 0.497 MMT (0.124 MMT Na), sodium silicate (0.736 MMT), sodium cyanide (0.154 MMT), sodium dichromate, etc. Most of these sodium containing chemicals are dissipated in final use, of course.

Aluminum chemicals — notably alumina and aluminum sulfate — have been mentioned in various places above. However, alumina — though classed as an inorganic chemical — is really a feedstock for aluminum refining, and need not be discussed further here. Aluminum sulfate, produced by reacting alumina with sulfuric acid (see "sulfur", above) is used in the paper industry.

Silicon chemicals of importance include sodium silicate, silicones and silanes (used in the production of ultrapure polycrystalline or amorphous silicon for semiconductors. The major inorganic silicon chemical is sodium silicate, already mentioned previously (0.736 MMT). Organic silicon chemistry is highly specialized and there is little data. However, it is reported that production of silicone resins for synthetic rubber amounted to 94.7 KMT in 1990.

Compounds of iron, chromium, copper, lead, titanium and zinc also have important chemical uses, especially for pigments. Titanium dioxide has already been mentioned in connection with chlorine. It is the most important metallic pigment — being used for most exterior paints, as well as in paper. U.S. production in 1988 was 0.926 MMT, mostly from ilmenite. For each ton of TiO_2 produced, 1.2 tons of waste is generated, implying 1.11 MMT of waste from this source in 1988.

Iron oxide is a red pigment, largely from natural sources. Ferrous chloride and ferrous sulfate are by-products of steel pickling with hydrochloric and sulfuric acids, respectively. Ferrous chloride is used to some extent as a soil conditioner. Ferrous sulfate (in low grade forms) is available in tonnages (2-4 MMT/y) far greater than usage. It is used to some extent make iron oxide, to manufacture ferrites, as a catalyst, in sewage treatment, etc. However, much of it must be disposed of as a waste.

Copper sulfate (34.2 KMT) is the basis of most copper chemicals (fungicides, algicides, pesticides, catalysts, flotation reagents, etc). It is made by reacting scrap copper with sulfuric acid. Its uses are dissipative (mainly in agriculture and wood preservatives).

Chrome chemicals are mostly derived from sodium dichromate (145 KMT, Cr₂O₃ equivalent). The largest use in 1988 was for wood preservatives (in combination with arsenic and copper); this use accounted for 47.23 KMT of sodium dichromate equivalent, 43 % of 1991 demand. Chromic acid is used for electro-plating and metal treatment (15% of 1991 demand) and as the base for producing other chromium chemicals. Leather tanning accounts for 9% of U.S. dichromate demand in 1991. It uses chromium (III) sulfate to protect the organic material from attack by micro-organisms. Chromium pigments (green, yellow) were a major use in the early 1980's, but had dropped to 8% of domestic demand by 1991. (Demand in 1988 was about 14 KMT). Virtually no copper or chromium were used in the manufacture of synthetic organic chemicals, except as catalysts. All chemical uses of chromium except for electroplating are essentially dissipative.

Lead sulfates and oxides are primarily pigments, but also the basis for other lead chemicals such as TEL. They are still produced in fairly large, though decreasing, quantities. Lead oxides for pigments, including litharge, red lead, and white lead accounted for 0.551 MMT, gross weight, of which 0.522 MMT was lead. Tetraethyl and tetramethyl lead (TEL, TML) were once produced in very large quantities as a gasoline additive, although production and use have declined sharply since 1970 as a result of environmental regulation. We estimate that U.S. production of these additives in 1988 was approximately 35 KMT (based on the ratio of ethyl dibromide to TEL in earlier years), almost entirely consisting of lead itself. They are classed as synthetic organic chemicals. Fuel uses of TEL are obviously dissipative.

Zinc chemicals produced in 1988 were as follows: zinc oxide (directly from ore by the so-called French process), 34.53 KMT; zinc sulfate 12.97 KMT; zinc chloride 8.48 KMT. Zinc oxide is used mainly in tire manufacturing and as a pigment. Zinc chloride is mainly used as an electrolyte in dry cells. Minor quantities of zinc were used in pesticides (e.g. zineb) and to manufacture catalysts. Except for these uses, zinc is not consumed in the production of synthetic organic chemicals. All final uses are dissipative.

8.2. Synthetic organic chemicals

Most organic industrial chemicals are based on petrochemical (hydrocarbon) feedstocks. There are three basic categories: (1) *paraffins (alkanes)*, which are saturated aliphatic (straight or branched-chain) hydrocarbons, the most important of which are methane, ethane, propane, isobutane, and n-butane; (2) *olefins (alkenes)*, unsaturated aliphatics with one or more double bonds, e.g. ethylene, propylene, butylene, butadiene); (3) *cyclics and aromatics* e.g. benzene, toluene, xylenes, cyclopentane, cyclohexane and naphthalene. There is a fourth, *miscellaneous*, group of non-hydrocarbons including oxygenated compounds of organic origin, cellulose, fatty acids and related chemicals.

Some of the primary feedstocks of alkanes and aromatics, totalling 32.44 MMT in 1988 were derived from natural gas liquids (22.46 MMT), refinery off-gas (1.12 MMT) and naphtha (8.864 MMT) [OECD 1991]. Separate data are no longer collected for ethane, propane and

butane, probably due to the prevalence of mixed streams generated and converted within the petroleum refining sector.

For our purposes it is convenient to exclude the C₂-C₄ alkanes (ethane, propane, isobutane and n-butane) from consideration, since virtually all organic chemical products — except methanol; — are derived from the corresponding olefins. The latter, in turn, are almost entirely used for chemical conversion. Primary products for chemical conversion, including methane, C₂-C₄ olefins, C₅ and "other" aliphatics (including methane), and aromatics, consumed in the U.S. amounted to approximately 63.6 MMT in 1988, according to the U.S. Bureau of Mines [USBM 1991, "Non-renewable Organic Materials", Table 4], including net imports of 7.64 MMT. The remainder was derived from petroleum refineries (32.44 MMT, see previous section) and, natural gas (23.5 MMT est.).

Not all of this material was converted into petro-chemical products. For instance, U.S. refineries produced 10.61 MMT of benzene, toluene and xylenes (known as BTX), but the annual report of Chemical Engineering News listed only 4.08 MMT as "chemicals"; the implication is that 6.6 MMT was used by the refineries as gasoline additives. In addition, refineries produced significant quantities of hydrogen (from the dehydrogenation process); we have no exact figures, but chemistry suggests that hydrogen would have accounted for about 10% of the input mass, or 6 MMT. Most of this was presumably used for other refinery operations, especially hydrogen reforming and hydrogen desulfurization. Some of the input material (mostly gas) was burned to provide energy for the dehydrogenation and cracking furnaces. Again, we have no precise data, but 5% (3 MMT) seems a reasonable estimate.

A further 1-2% (0.6-1.2 MMT) may have been lost as VOC emissions. Even so, we cannot fully account for the outputs. For instance, it is not clear from the data whether natural gas consumed for ammonia production is, or is not, included. (Urea, made from ammonia, is included as an organic chemical product). Methanol is certainly one of the primary products, but most methanol is imported, and the domestic product (1.85 MMT in 1988 could not account for very much of the "missing" feedstocks (8.8 MMT).

To simplify somewhat, we consider the "true" feedstocks to the organic chemical industry to be C₂-C₅ olefins (33.35 MMT, approximately), aromatics (BTX and naphthalenes, 5.78 MMT, excluding the BTX diverted to gasoline additives), and methanol (4.0 MMT). The grand total of hydrocarbon feedstocks, plus methanol, appears to have been 42.1 MMT in 1988. Some of this production — especially C₄-C₅ and higher order aliphatics — was not actually used to manufacture other chemicals. Some was used as octane-boosters in gasoline, or as solvents, some was converted to hydrogen (mostly used in the refining process) or to carbon black.²⁷ However most downstream synthetic organic chemicals are derived from the above starting points (or the inorganic intermediates discussed previously). Olefins, in particular, are almost entirely converted immediately to polymers or other chemical intermediates such as alcohols and/or resins. In addition we must account for miscellaneous organics such as glycerol (about 0.25 MMT, derived from animal or vegetable oils, fatty acids from vegetable oils used in

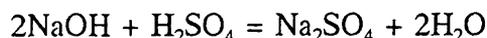
27 Carbon black is used mainly for tires, of which it constitutes roughly 29% by weight [ECOPLAN 1992]. Total tire production in the U.S. for 1988 was roughly 2.2 MMT, accounting for 0.64 MMT of carbon, or 0.7 MMT of hydrocarbon feeds. There are other significant uses of carbon black, such as printing ink. However, most carbon black is made directly from natural gas. We do not include it as a chemical product.

liquid detergent manufacture, (0.735 MMT) plus soluble cellulose used for cellulose acetate, but not rayon (0.5 MMT).²⁸

We also include specified fractions of the major inorganics discussed above. The latter include N-chemicals, chlorine chemicals, sulfuric acid, and sodium hydroxide not used for other purposes and accounted for elsewhere. The last two reagents, in particular, are used in great quantities, but very little of the reactive element in either case is embodied in final products.

As regards chemicals, the situation is confused by imports, exports and byproducts at various stages. In the case of ammonia, over 90% goes to fertilizers, explosives and other identified inorganics.) We can account for 0.737 MMT (N-content) embodied in organic chemicals, plus about 0.16 MMT of associated process losses in 1988. So 0.9 MMT (N) *in toto*, was consumed in making synthetic organic chemicals in 1988, mainly plastics and fibers. Total weight of ammonia used would therefore have been about 1.1 MMT. For sulfur, the amount embodied in organic products was very small (0.08 MMT) but the amount used dissipatively in the industry was at least 0.6 MMT (S) and — thanks to the large amount unaccounted for — could have been as much as 1.9 MMT (S), of which as much as 1.45 MMT (S) could have been in the form of sulfuric acid [USBM 1989 "Sulfur"]. This would correspond to about 4.5 MMT of the acid. In the case of chlorine (see above), we saw that about 6.6 MMT was used within the chemical industry to make organic chemicals or final products. As regards caustic soda, it appears that 4.2 MMT was used for acid neutralization within the chemical industry as a whole. In addition, small amounts of fluorine (180 KMT), bromine (100 KMT), and phosphorus pentoxide (75 KMT) were used.²⁹

Uncertainties in the sulfuric acid and caustic soda requirements can be reduced, based on the knowledge that all acids and alkalis must be neutralized. Moreover, apart from small amounts of hydrochloric, nitric and hydrofluoric acid, sulfuric acid is the dominant source of acidity (H^+), while caustic soda and ammonium hydroxide are essentially the only sources of balancing hydroxyls (OH^-). However, ammonium sulfate is virtually all recovered as fertilizers, and both N and S have already been accounted for. Thus virtually all other sodium and sulfur inputs *must* end up in waste streams (largely as sodium sulfate), since they are not embodied in products. The basic neutralization reaction is



28 Note that soluble cellulose is used to manufacture viscose rayon, cellulose acetate, and cellophane, among other products. Production in 1988 was 1.24 MMT, of which about 60% was used for rayon. Rayon is not counted as a product of the organic chemical industry.

29 Although about 200 KMT of phosphorus was used in detergents, most of it is inorganic: sodium triphosphate (STPP) and tetra-sodium pyrophosphate.

On this basis (ignoring other acids, for the moment) it would appear that we need $98/80 = 1.22$ mass units of sulfuric acid per unit of caustic soda. Thus, if 4.2 MMT of caustic soda is neutralized in the organic sector, we would need 5.15 MMT of sulfuric acid, and so on.³⁰

Based on the above analysis, we argue that in the synthetic organic chemicals sector the ratio of sulfuric acid to caustic soda, in mass units, must be close to 1.22. Since the maximum amount of sulfuric acid "available" for organic synthesis processes (including acid "unaccounted for") was 4.5 MMT, we conclude that not much more than 3.7 MMT of caustic soda could have been used in the same processes. (The remainder of the caustic, about 0.5 MMT, must have been used in the inorganic chemical sector).

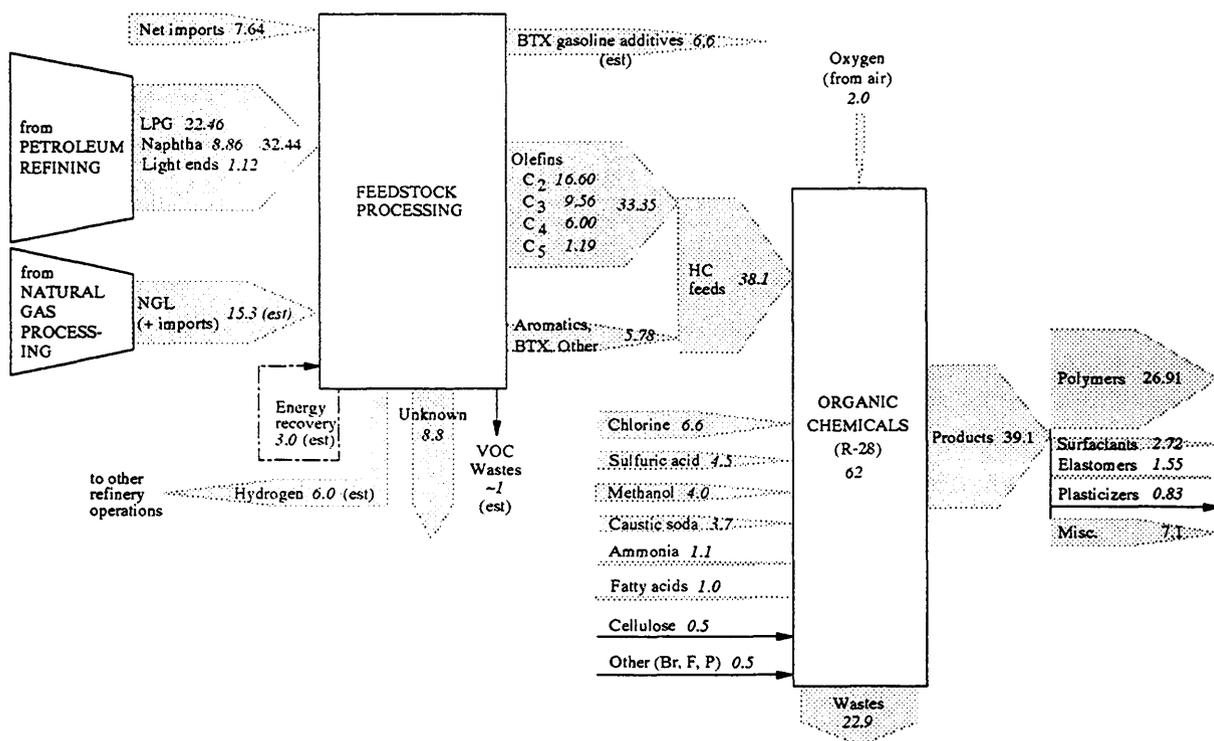


Figure 8: Organic chemicals sector, U.S. 1988 (MMT)

Adding these (as shown in Figure 8), we arrive at a grand total of 60.0 MMT of *produced* chemical inputs to organic synthesis in 1988. Oxygen is needed for a number of downstream oxidation processes, such as production of ethylene and propylene oxides; production of ethanol, iso-propanol and butanol, production of phthalic anhydride; production of terephthalic acid (TPA). Also, oxy-chlorination of ethylene to EDC. A survey of the major tonnage products of the synthetic organic sector (below) indicates that the oxygen content of final product chemicals averages close to 10%, which would amount to a total of just about 4 MMT.

30 Taking account of the availability small amounts of other acids (HCl, HF, HBr, HNO₃, P₂O₅) it might seem at first glance that the need for sulfuric acid would be reduced somewhat. However, to the extent that other acids were used, the neutralization products would be sodium or ammonium salts of chlorine, fluorine, etc. Since these elements are actually embodied in products, they cannot also be a major constituent of the waste stream.

We can account for 1.85 MMT of oxygen embodied in the input methanol. There is also some oxygen in cellulose and fatty acids. Some oxygen is carried into the reactions by the oxidizing agents nitric and sulfuric acid (HNO_3 and H_2SO_4). But nitric acid is itself produced by oxidation of ammonia, and sulfuric acid is the oxidized form of sulfur (dissolved in water). We have estimated (above) that 1.45 MMT (S), or 4.5 MMT of sulfuric acid was utilized in organic synthesis in 1988. This would include 2.9 MMT of oxygen. We must also allow for 3.7 MMT of NaOH used in organic synthesis processes, of which 1.4 MMT was oxygen. Altogether, this adds up to 6.15 MMT (O), which is somewhat more than the amount actually embodied in final products.

**Table 6. End use organic chemical products: U.S. production & sales 1989, 1990
1000 metric tons**

	Production		Sales	
	1989	1990	1989	1990
TOTAL		50338.8		39107.8
Dyes	174	117.0	146	104.0
Organic pigments	50	53.0	43	45.0
Medicinals	130	144.0	204	107.0
Flavor & perfume materials	64	60.0	38	37.0
Rubber processing chemicals	176	179.0	129	136.0
Pesticides	572	557.0	461	442.0
Thermosetting resins		4309.5		3177.0
Thermoplastic resins		25201.3		22093.9
Polymers for fibers		2358.5		1379.1
Polymers, water soluble		309.7		264.7
Elastomers		2233.1		1555.1
Plasticizers		890.7		826.5
Surfactants		5848.7		2718.1
Antifreeze	920	900.9		900.0
CFC's	417	308.3		300.0
Solvents				1200.0
Chelating agents		137.2		101.5
Fuel additives		4224.7		1935.6
Lube oil & grease additives		387.2		343.6
Textile chemicals (ex. surfactants)		22.4		19.8
Miscellaneous chemicals N.E.C.		2096.6		1421.9

Source: [USITC 1992]

In principle, no additional oxygen is needed, except to combine with carbon and/or hydrogen in the feedstock to generate energy to drive the endothermic syntheses. In practice, however, it is probably fair to assume that very little of the oxygen embodied in caustic soda or sulfuric acid ends up in the products. (It ends up as water in the neutralization reaction.) Thus, to arrive at a final oxygen content of 3.9 MMT, as indicated, we must assume that at least 2 MMT must have been extracted from the atmosphere in various processes. This does not include the oxygen needed to oxidize all the missing mass to its final form, however.

Adding these (as shown in *Figure 8*), we arrive at a grand total of 60.0 MMT of *produced* chemicals, plus 2 MMT of oxygen, as inputs to organic synthesis in the U.S. 1988, not including oxygen that is combined with carbonaceous wastes. The major tonnage outputs (sales) of the organic chemicals industry amounted to 39.1 MMT in 1989 (and 39.5 in 1988), not including urea. The categories are listed in *Table 6*.

Subtracting the mass of identified products from the mass of inputs, we find that the *missing mass* was around 225 MMT, plus the mass of any oxygen combined with carbonaceous process wastes. The situation is summarized graphically in *Figure 8*. The approximate composition of the waste stream can be estimated from the composition of the inputs; however, it is clear that water, sodium sulfate and carbon dioxide account for most of it. The remainder consists of various other salts (including some NaCl), and VOC's.

9. Primary Metals Smelting & Refining (SIC 33)³¹

We have conceptually divided the processes of mining, concentration (or winning), reduction or smelting and refining. There are four stages of separation or recombination. The first two, being physical in nature, are assigned to the mining sector (SIC 11) or the quarrying sector (SIC 14). They were discussed previously. The last two, being chemical in nature, are assigned to the primary metals sector (SIC 33). At each separation stage, wastes are left behind and a purified product is sent along to the next stage. In principle, the wastes can be determined by subtracting outputs from inputs.

Unfortunately, from the analytic point of view, published data is rarely available in appropriate forms. There are significant imports and exports of concentrates and crude metals (and even some crude ores) but trade data is often given in terms of metal content, rather than gross weight. Domestic data is also incomplete, due to the large number of data withheld for proprietary reasons. Thus, in a number of cases, we have been forced to work back from smelting or concentration process data to estimate the input quantities of concentrates. Our summary was given in *Table 3*. It excludes ferroalloys, of which U.S. production was about 1 MMT, because of the extreme complexity of the subsector.

Inputs to the U.S. primary metals sector consist of concentrates (produced in the mining sector, or imported), fuels, fluxes, and processing chemicals. We have already discussed fossil fuel combustion above, whence fuel inputs and CO and CO₂ are equally excluded from our materials balance. CO is a major pollutant of smelting processes, but it results from partial oxidation which is later completed in the atmosphere. (Thus, the materials balance approach is not applicable for estimating CO emissions.) Major purchased inputs, other than concentrates, are fluxes. The most important is limestone (and dolomite). In 1988 approximately 9.6 MMT (10.9 million short tons) of limestone and dolomite were used, mostly in blast furnaces. It appears from data published by the U.S. Bureau of Mines that this was actually calcined on site and consumed as lime (4.8 MMT). Other inputs to SIC 33 reported by the Bureau of Mines include salt (0.33 MMT), manganese ore (0.123 MMT) and fluorspar (0.137 MMT).

31 Data mostly from Minerals Yearbook.

The production of primary metals from concentrates is normally accomplished by carbothermic reduction (smelting with coke), or electrolysis. By far the major product, in tonnage terms, is pig iron. U.S. blast furnace output in 1988 was 55.475 tons (49.8 MMT). This material has an iron content of 94%. It is almost entirely used for carbon steel production, via the basic oxygen process. (There was a small amount of open hearth production in 1988, now ended. Electric steel "minimills" use scrap exclusively).

Blast furnace inputs in 1988 included about 3 MMT of scrap iron/steel, while sinter also utilized about 6 MMT of upstream reverts (dust, mill scale). Thus, to account for the virgin ore is somewhat complex. However, the iron content of U.S. ores in 1988 was reported as 57.515 MMT. Blast furnace inputs (pellets) averaged about 63% iron, 5% silica, 2% moisture and 0.35% other minerals (phosphorus, manganese, alumina). The remainder was oxygen.

In the reduction process the oxygen combines with carbon (actually carbon monoxide) from the coke. About 1 metric ton of coke was used per metric ton of pig iron, along with 0.142 metric tons of miscellaneous materials, mostly fluxes (lime and limestone) for the sinter plants and to make the molten slag flow easily. Slag consists of the silica and other non-ferrous minerals in the sinter and pellets, plus the materials in the fluxes. Total iron blast furnace slag production in the U.S. was 14.2 MMT, or 0.35 metric tons of slag per metric ton of pig iron. However, slag is no longer considered a waste, since virtually all slag produced is marketed for a variety of uses. Subsequent refining of pig iron and scrap iron to carbon steel is done in a further refining stage, normally the basic oxygen furnace. Steel furnaces produced an additional 5 MMT of slag in 1988.

As noted, the oxygen in the iron-bearing concentrates reacts in the blast furnace with carbon monoxide. The reduction process requires excess CO, so the emissions ("blast furnace gas", consist mostly of unreacted CO. It is combustible, though of relatively low heating value. Currently most of this is utilized elsewhere in the integrated steel complex as fuel e.g. for preheating blast air. However, the capture of gaseous emissions from blast furnaces is not 100% efficient, so some CO escapes. However, considering the iron/steel process as a whole, all of the carbon (from coke) is eventually oxidized to CO₂. In 1988, the steel industry accounted for 182 MMT of CO₂, from coke, which is included in the grand total from fossil fuel combustion, discussed later. (In addition, some other hydrocarbon fuels were used).

Coke ovens and steel rolling mills are significant sources of hazardous wastes, even though the coke oven gas is efficiently captured for use as fuel, and about 55 thousand MT of ammonium sulfate (N-content) is produced as a by-product. This material is used as fertilizer. Coke is cooled by rapid quenching with water, and some tars, cyanides and other contaminants are unavoidably produced. Unfortunately, materials balances cannot be used to estimate these wastes. However, they probably constitute a significant fraction of both water and airborne wastes from the primary iron and steel sector.

Also, in the rolling process steel is cleaned by an acid bath ("pickling"), resulting in a flow of dilute wastewater containing ferrous sulfate or ferrous chloride (depending on the acid used). The excess acid is usually neutralized by the addition of lime. In 1988 about 0.215 MMT of 100% sulfuric acid (0.074 MMT S content) were used for this purpose, producing 0.25-0.30 MMT of ferrous sulfate mixed with calcium sulfate. Ferrous sulfate can, in

principle, be recovered for sale. However the market (water treatment) is insufficient to absorb the quantity potentially available, and most is waste.

Light metals, mainly aluminum and phosphorus, are reduced electrolytically. The oxygen in the alumina reacts with a carbon anode, made from petroleum coke. The reaction emits 0.65 metric tons of CO₂ per metric ton of primary aluminum produced. In addition, primary aluminum plants emitted about 0.02 metric tons of fluorine, per metric ton of aluminum, partly as HF and partly as particulates. This is due to the breakdown of cryolite (the electrolyte used in the process, an aluminum-sodium fluoride) at the anode. Total airborne emissions from primary aluminum production in the U.S. (3944 MMT) were, therefore, 2564 MMT of CO₂ (already counted), 0.08 MMT of fluorides and about 0.17 MMT of particulates (Al₂O₃).

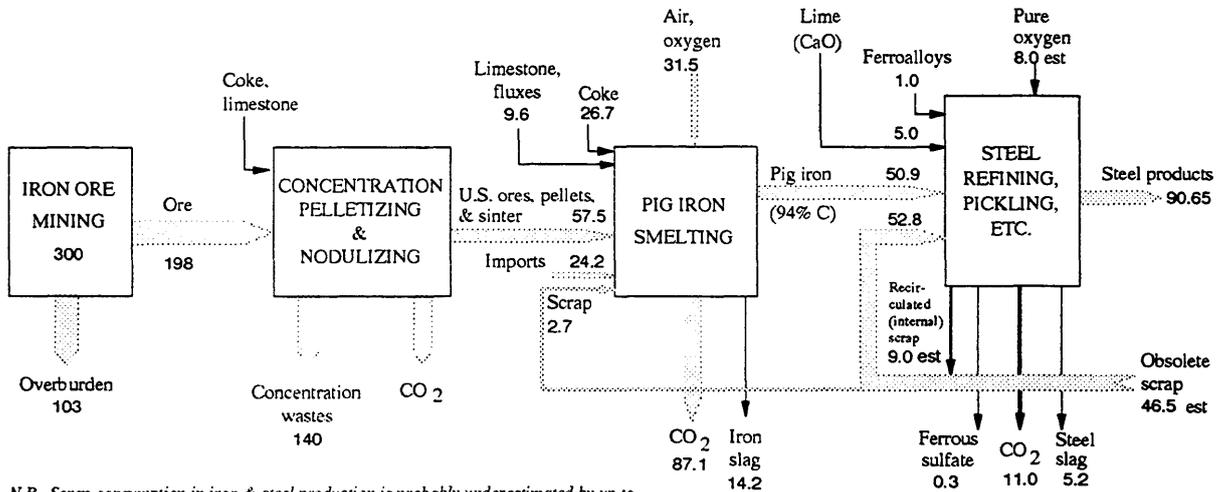
In the case of heavy metals from sulfide ores (copper, lead, zinc, nickel, molybdenum, etc.), the smelting process is preceded by, but integrated with, a roasting process whereby the sulfur is oxidized to SO₂. Roughly 1 metric ton of sulfur is associated with each metric ton of copper smelted, 0.43 metric tons of sulfur per metric ton of zinc, and 0.15 metric tons of sulfur per metric ton of lead. Most of this sulfur (90%) is now captured and immediately converted to sulfuric acid. In 1988 1.125 MMT of by-product sulfuric acid, in terms of sulfur content was produced at U.S. non-ferrous metal refineries, as follows: copper (0.946 MMT), zinc (0.136 MMT), lead/ molybdenum (0.043 MMT). In terms of sulfuric acid (100% H₂SO₄) the quantity of by-product acid produced was 3.54 MMT.

In the case of copper, most of this (1.2 MMT) was used by mines for "heap-leaching" copper. Leaching now accounts for a significant proportion (c. 30%) of copper concentrates produced in the U.S. Leached copper sulfate is subsequently reduced electrolytically, without an intermediate smelting stage. In the case of copper smelting, typical concentrates fed to the roaster/smelter consist of about 35% Cu (23%-45%), 35% S and 30% other minerals. In addition, about 0.25 metric tons of limestone flux is added per ton of blister copper. Thus, slag production amounts to roughly 0.55 metric tons per metric ton of primary copper, or 0.77 MMT in 1988.

In the case of zinc, a typical concentrate would be about 55% Zn (45%-64%), and 27% S, with other minerals accounting for 16%. For lead, the corresponding number appear to be (about) 60% Pb (50%-70%), 9% S, and 21% other. Thus, assuming flux per unit of slag to be the same as for copper (1.2:1), slag output should have been roughly 0.3 metric tons/metric ton for zinc and 0.38 metric tons/metric ton for lead. This implies total slag output of 0.06 MMT for zinc smelting and 0.14 MMT for lead smelting. Total slag production for the three main NF metals was therefore roughly 1 MMT *in toto*. Carbon monoxide and carbon dioxide emissions are not known exactly, but they are quite small in comparison with other sources. The waste numbers for other metals are insignificant.

Altogether, based on mass-balance considerations, we estimate smelting and refining wastes for primary metals, including CO₂, to have been 43.4 MMT in 1988, including the weight of limestone, manganese, calcium fluorite, and other materials used in the blast furnaces and refineries. (This includes about 14.2 MMT of iron (blast furnace) slag, although most of this material is marketed commercially, mainly for road ballast). In addition there was about 5.2 MMT of steel furnace slag, a denser material with a fairly high iron content.

As noted above, much of the sulfur from sulfide copper, lead, zinc and molybdenum ores is also recovered for use, and sold as sulfuric acid (1.125 MMT S content in 1988). Subtracting the B.F. slag, and the by-product sulfuric acid, we get 28.1 MMT as the residual waste. Of this, only about 1 MMT was solid (N.F. slag) and the rest would represent the oxygen content of the original ores — mostly iron — which is released as CO₂³². We have not included the wastes from coking, which we have not estimated. The major airborne emission other than CO₂ is probably CO and particulates. In both cases, blast furnaces are the major sources. The coking quench waters and some spent acids used for pickling constitute the major water-borne wastes.



N.B. Scrap consumption in iron & steel production is probably underestimated by up to 4 million tonnes. Recirculated scrap may be underestimated by a similar amount.

Figure 9: U.S. iron & steel, 1988 (MMT)

Mass flows and wastes for the metallic mineral processing industries and the metallurgical industries, taken together, are summarized in Figure 9 (ferrous) and Figure 10 (non-ferrous). These figures are normalized to U.S. production of the refined metals. Some of the flows are imputed from others. For example, pig iron (94% Fe) contains roughly 6% C, which implies a carbon content of 3 MMT. The oxygen required to burn this carbon away is therefore approximately 8 MMT, implying a carbon dioxide output of 11 MMT for steel production. In the case of iron blast furnaces, we assumed that all of the input coke, less the 3 MMT of C embodied in pig iron, is converted to carbon dioxide. This consumes 63.4 MMT O₂ and yields 87.1 MMT of CO₂. However, some oxygen is captured from the iron oxide in the ore. So, balancing inputs and outputs, we calculate that the additional oxygen taken from the air must have been 31.5 MMT. Scrap flows are very approximate, partly because the statistics of the scrap industry are poor and partly because we have lumped stock adjustments and scrap flows for convenience.

32 Assuming the iron in ore is mostly in the form Fe₂O₃, the 57.5 MMT of iron content in ore (1988) would be combined with 25.55 MMT of oxygen.

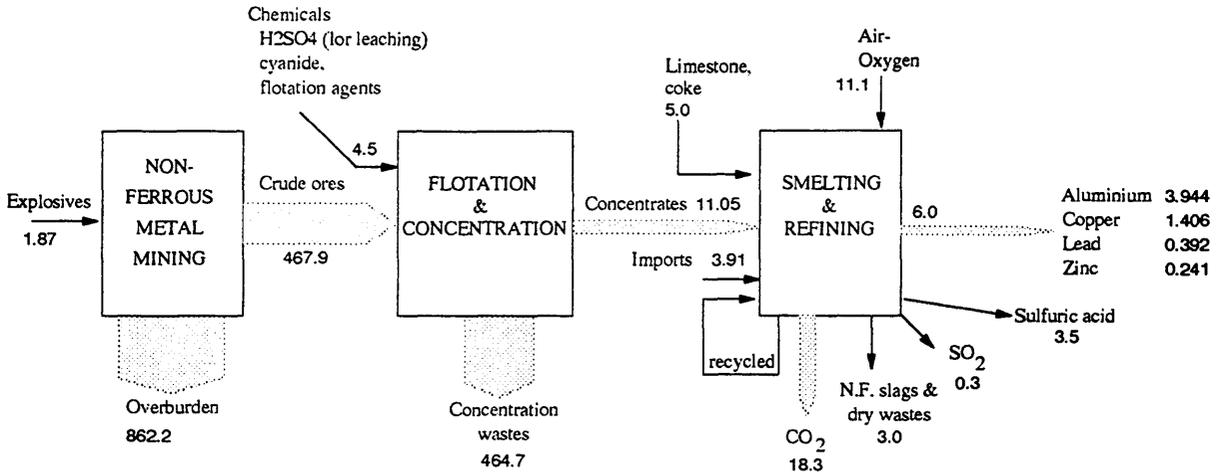


Figure 10: U.S. non-ferrous metals, 1988 (MMT)

For comparison, SAI estimated the 1983 wastes from iron and steel production (probably wet) at 6.0 MMT and from non-ferrous metals at 6.5 MMT [SAI 1985]. Their estimates were not specifically designated as "dry" so some water content can be presumed. EPA estimates airborne emissions from the primary metals sector as a whole to be 2.8 MMT, including particulates and CO, but not including CO₂ [USEPA 1991]. Both sets of estimates are roughly consistent with the above.

10. Stone, Clay & Glass (SIC 32)

Mining of non-metallic minerals has been discussed in Section 4. It will be recalled that overburden and concentration losses for non-metallic minerals other than phosphorus amounted to 47.1 MMT and 36.5 MMT respectively. The outputs of the stone, clay, glass sector include refractories, glass and portland cement. All three are basically durable products used in structures or long-lived products. We do not have detailed quantitative data on glass production. As regards clays, domestic production in 1988 was 43.9 MMT. Production of clay and refractory products (including clay used in Portland cement) was virtually identical. Some of these uses (e.g. fillers, binders, absorbents, drilling mud, filters) are essentially dissipative.

Portland cement manufacture is an important industry. Total tonnage produced in the U.S. in 1988 was 66.5 MMT. Most of the input materials were natural minerals already discussed (limestone being by far the most important, 73 MMT) but small quantities of fly ash and blast furnace slag were utilized. Total non-fuel inputs were 111 MMT, whence the mass lost in cement manufacturing was 44.5 MT. The major fuel consumed was coal (9.5 MMT), though some plants used oil or gas. Emissions are primarily carbon dioxide and particulates. Total weight of emissions from fuel are already counted above. However, based on CO₂ emissions from limestone calcination amount to an additional 35 MMT (or about 10 MMT carbon content). This still leaves nearly 10 MMT of missing mass unaccounted for. It is likely that much of this consists of particulate emissions from cement kilns.

Lime (CaO) is made by calcining limestone. In 1988 U.S. production was 13.2 MMT (consuming 29.5 MMT of limestone and releasing 16.3 MMT of CO₂ to the atmosphere).

Uses are extremely diverse, and not well documented. Use for stack gas treatment has been mentioned already. Many uses are substitutable by limestone (e.g. for glass manufacturing, soil stabilization, desulfurization, etc.) It must be emphasized that calcination of limestone releases CO_2 in a ratio of 1.1 metric tons per metric ton of CaO .

It appears that the major waste emissions from this sector (exclusive of losses in quarrying and concentration) are primarily related to combustion of fossil fuels and calcination of limestone and gypsum, which yields CO_2 . However SAI estimated dry wastes from the sector to be more than 18 MMT, for 1983 [SAI 1985]. EPA's latest estimate of airborne emissions (particulates and CO , primarily) is about 1.0 MMT [USEPA 1991].

We have no estimate of water use by the stone, clay and glass sector. However EPA estimated total (wet) wastes from the sector to be 560 MMT [USEPA 1986]. This seems quite high, given that most processes in the sector are dry.

11. Fossil Fuel Consumption

It should be noted that when fossil fuels are burned there are combustion products that must be counted as wastes. This is particularly true for coal. On the average, U.S. coal has a sulfur content of 1.9%; coal burned by electric utilities averages 2.3% sulfur, while coking coal is 1% sulfur. The latter is mostly recovered as ammonium sulfate. In principle, coal burned in the U.S. emits about 16 MMT of sulfur (32.1 MMT of SO_2). Most of this sulfur dioxide is released to the atmosphere.

In 1988 1.24 MMT of lime (CaO) and 1.035 MMT of limestone (CaCO_3) were sold for purposes of sulfur removal from furnace stack gases. The limestone was equivalent to 0.495 MMT of lime. Since CaO has a molecular weight of 56 and SO_2 has a molecular weight of 64, the total amount of limestone and lime used in scrubbers accounted for only 1.96 MMT of sulfur dioxide, or about 6% of the total emitted. None of the sulfur from coal burning was recovered for use. (It is disposed of in landfills as a mixture of wet calcium sulfite CaCO_3 and calcium sulfate CaCO_4). EPA estimated that flue gas desulfurization (FGD) by utilities produced 16 million tons (14.4 MMT) of solid wastes in 1984 [USEPA 1988, 1991]. The mineral content of these wastes (even in 1988) was evidently no more than 3.7 MMT. The remainder was presumably water of hydration. (The mineral gypsum has the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

If all the sulfur in U.S. coal were to be captured by wet scrubbers using lime, total U.S. lime production would have to be increased by 26 MMT (i.e. trebled), which would require an additional 55 MMT of limestone to be quarried. All of it would, of course, be converted almost directly into a waste stream.

Coal contains a small but significant percentage of "fuel bound" nitrogen (about 1 unit per 68 units of carbon). Most of this is emitted as nitric oxide (NO) but some may be emitted as nitrous oxide, N_2O , one of the "greenhouse" gases. However, figures on this are disputed. More important, coal combustion in high temperature boilers, for electric power generation, produces a significant quantity of NO_x emissions, about 10 MMT/yr [USEPA 1986].

However, virtually all anthropogenic NO_x (about 20 MMT/yr in 1980, and probably a similar amount in 1988) is attributable to fossil fuel burning.

Coal also contains significant quantities of mineral ash (equivalent to the mineral shale). The average ash content of U.S. coal, as burned, is approximately 10% [Torrey 1978], although other estimates put the figure higher. Actually, utilities alone seem to have collected and disposed of 69 million short tons — 62 MMT — of ash in 1983. Assuming constant proportions of ash in coal used, and complete ash recovery, this would have risen to 76 MMT by 1988, which would account for almost all of the ash in the utility coal. However, while recovery of fly ash from electrostatic precipitators is in the neighborhood of 99.8% for the most modern units, some utilities are not so well equipped. Fly ash not captured in 1988 probably amounted to at least 1 MMT. The ash content of coking coal (which is selected in part for its low ash content) ends up in metallurgical slag. The ash content of coal used as a fuel in the cement industry ends up as part of the cement itself. (In fact, the cement industry also uses some fly ash as a raw material, though the percentage is small).

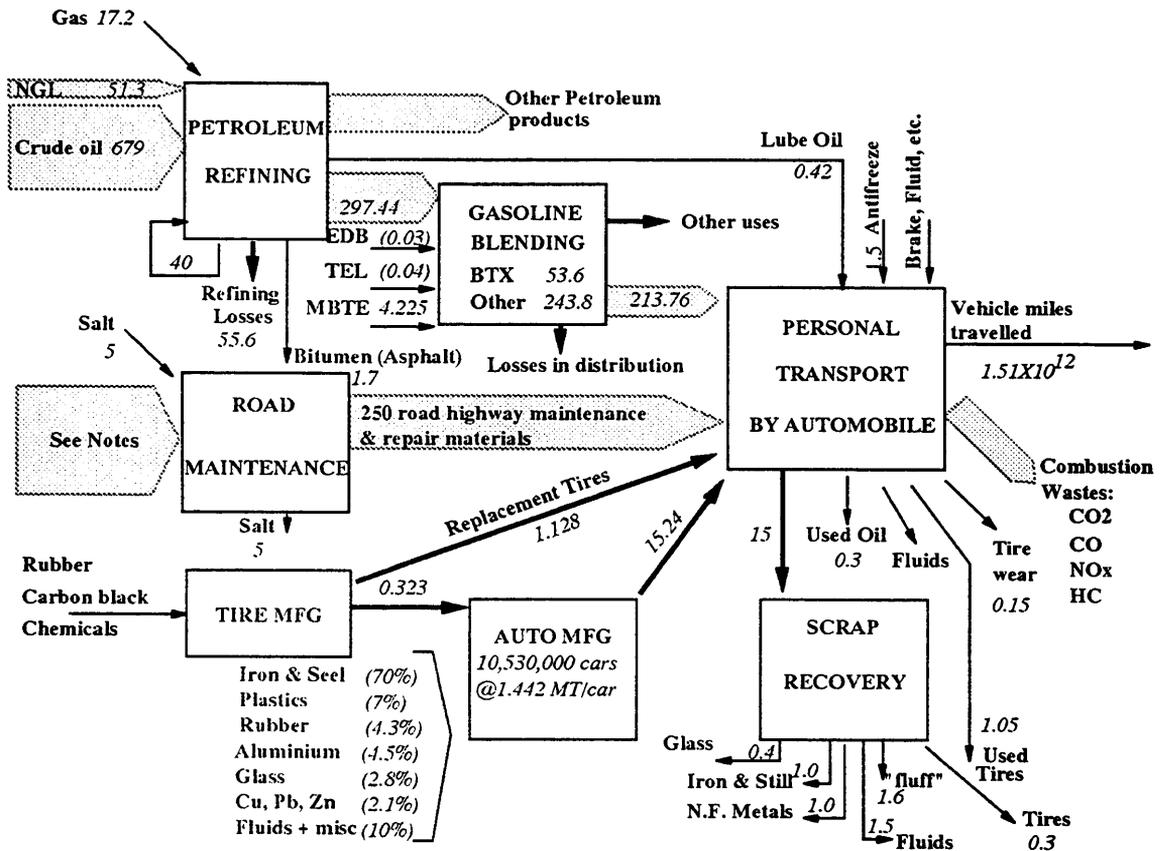
Coal ash contains significant quantities of heavy metals. While most fly ash is captured, the waste ash must be disposed of somehow. Moreover, the more volatile trace metals like arsenic and mercury, still escape as vapor and re-condense downwind of the stack.³³

Finally, the carbon in coal (along with the carbon in other fuels) is converted by combustion into carbon dioxide. The Carbon Dioxide Information Analysis Center at Oak Ridge National Laboratory estimated that the carbon content of this fuel was 1288.6 MMT, or 84.7% of this, 493 MMT (C) was from solid fuels (coal), generating 1810 MMT of CO_2 . This includes the CO_2 from carbothermic reduction processes using coke.

Apart from electric power generation, most fuels are petroleum products or natural gas. The gas is mostly used for domestic purposes and space heating, though some is used in industry. Petroleum products are mainly used for transportation, although some heavy oils are used for industrial boilers or electric power production. The transportation system is of interest because there are so many complex mass flows involved other than the straightforward fuel consumption aspect. We summarize this system (as regards private automobiles only) in *Figure 11*.

The sum total of all fossil fuels consumed in the U.S. in 1988 was 1521.149 MMT (*Table 5*). We can assume that all of the fossil fuel carbon is converted to CO_2 (4726 MMT in 1988), not including calcination processes (lime and cement manufacturing) which are counted separately.

33 U.S. coal is unusually low in ash, most of which is recovered. By contrast, most other countries burn coal that has a much higher ash content — 15% to 25% or more — very little of which is recovered. Thus the problem of heavy metal pollution from coal burning will be far more serious in eastern Europe, the former Soviet Union, China and India.



- Refinery input & output data from International Energy Agency (OECD)
- Fuel Consumption by automobiles in the U.S. from Federal Highway Administration, Energy Information Agency (or World Almanac)
- TEL and EDB inputs estimates from USBM Minerals Yearbook (1988) chapter "Bromine" and using 1975 ratio between bromine consumption (110,400 s.t.) and lead consumption (209,000 s.t.).
- BTX content of gasoline (20%) from [IEI 1991] sections on toluene and xylene
- Lube Oil data (1983) based on [Franklin 1984, section 3-1]; assumes 50% MBTE consumption from [US Tariff Commission 1992] Ethylene glycol (antifreeze) consumption from the same source, assuming 50% is consumed by private cars.
- Tire data from Ecoplan
- Materials content of automobile (1987) from MVMA "Facts and Figures", 1988
- Materials consumed in road maintenance and repair are estimated as follows:
 - (i) 33% of total road/highway expenditure is for maintenance and repair
 - (ii) Materials use per \$ is equal for new construction and for M&R
 - (iii) 50% of all 'road/highway' depreciation is attributable to automobile use
- Materials used for road/highway purposes (total, estimated)

Bitumen (asphalt) , 2.7 % of product	16 MMT
Portland cement (50% of total)	10 MMT
Steel (15% of total)	35 MMT
Slag (70% of total)	15 MMT
Sand & gravel (70%)	600 MMT
Crashed stone (70% is "mostly" for roads)	840 MMT

Figure 11: Mass flows for private automobiles, U.S. 1988 (MMT)

Combustion processes also result in some releases of methane to the atmosphere. One recent estimate, albeit less than production and transmission. One recent study allocates 11.86 MMT of methane releases to all of these activities together, for the U.S. in 1988 [Subak *et al* 1992]. The breakdown between production, transport and combustion is not given in that source for the U.S. alone. However, for the world as a whole, the breakdown was: coal mining (62%), oil and gas extraction (14.8%), gas distribution (17%), firewood combustion (4%) and other fossil fuel combustion (2.3%). For the U.S. firewood would be a negligible source, while coal would be less important than the global average and gas more important than the global average. However, it must be said that we think Subak *et al* sharply underestimated gas transmission losses, both in the U.S. and globally. Using the OECD/IEA estimate of 17.15 MMT, cited above, for transmission losses, we assume 83% of their estimate of 11.86 MMT will cover the other energy-related sources of methane. This yields a total of $0.83 \times 11.86 = 9.85$ MMT for methane from coal, oil & gas extraction and combustion. The grand total, including transmission losses, is 27 MMT.

12. Summary

It may be interesting to summarize our results by waste category, as well as by industry. Overburden moved by mining — mostly stripping — amounts to over 6.8 billion MT. By contrast, topsoil loss in agriculture was 1.5 billion MT. (In addition, the construction industry probably moves comparable amounts). Waste from mineral concentration activities, mostly by froth flotation, produce waste (tailings) of the order of 1.37 billion MT, dry weight. In addition, about 3.6 billion MT of water was used for flotation. Most of this was evaporated in ponds, leaving semi-solid sludges. Wastewater discharged into rivers and streams by the mining industry amounted to 2840 mgd or 3.9 billion MT per year.

By contrast, the weight of solid wastes from metallurgical conversion and fossil fuel combustion processes, including metallurgical reduction (smelting), amounted to only about 122 MMT. We have included in this category 76 MMT of fly ash and bottom ash from thermal power generators and 14.4 MMT of FGD waste, but excluded 14.4 MMT of iron/steel slag that has commercial uses.

Organic wastes prior to combustion for waste reduction or energy recovery purposes are estimated to be 165 MMT for agriculture and food processing. Most of the non-farm biomass was burned for energy recovery. Post treatment wastes (mostly waterborne) cannot be estimated from available data. In addition, the pulp & paper sector burned 73 MMT (dry equivalent) of organic materials in spent "black liquor". The pulp and paper industry withdrew and discharged about 3500 mgd (4.8 billion MT) or process water, while the food industry added another 1850 mgd (2.55 billion MT).

Gaseous combustion products constituted another very large waste stream. We estimate a total of 5.046 billion MT of CO₂ (of which 4.726 was from fossil fuel combustion), 32 MMT of SO₂ from coal, plus EPA's estimate of 20 MMT of NO_x from fossil fuel combustion. Our methodology is not well-suited to estimating fugitive emissions, or particulate emissions. However we note that petroleum refineries may be emitting around 4.3 MMT of hydrocarbons, which are not accounted for anywhere else.

Process water contaminated by acids or other wastes was also emitted in significant quantities by the petroleum refining and metallurgical sectors. The quantitative values discussed above can be summarized as follows:

Table 7. SUMMARY OF ESTIMATED U.S. 1988 DRY-WASTE STREAMS EXCLUDING WATER (MMT)

SECTOR	LOST MASS				PROCESS WASTES (ash, slag, etc.)	EMISSIONS TO AIR				N,S
	Dry Organic		Dry Inorganic			H ₂ O	CO ₂	O ₂	CH ₄ , VOC	
	Combustible	Non-combustible	Soil overburden	Concentration wastes						
Agriculture SIC 01-02	+360 (a) +155 (b)	25	1500	—	—	202	-890 +213	-156 +608	0.68	12 (N)
Food Processing SIC 26	34.5 (c)	18.7	—	—	—	66 (+19)	6.8 (+29,4)	(-21.3)		
Forestry, Pulp, Paper SIC 081, 26	6	—	—	8.6	1.0	-374.5 +269.5	-433 +233.5	-170 +314.5		
Mining SIC 10,14 SIC 11-13	—	—	965 (d) 275.7 (e) 5600 (f) 6 - 7 (g)	600.6 (d) 197.9 (e) 125 (f) 57 (g)					9.8	
Petroleum Refining SIC 29	56	—	—	—		(+76.5)	(+165)	(-120)	17.2 2.0	
Chemicals SIC 281 SIC 282-289	— —	— —	— —	— —	57.2 22.9 (i)					1.0
Primary Metals SIC 33					0.3 (j) 3.0 (k)					0.3 (S)
Stone, Clay, Glass SIC 32					10		51.3	—		
Fossil Fuel + Electric Power	—				90	-2088	-4726	-5393		10 (N) 14 (S)
TOTALS	605.5	43.7	7478.7	969.1	184.4	2251	4072.6	-4796.5	28.68	36.3
						Not including (..)				
(a) Crop residues, normally recycled to land					(h) Including natural gas processing & transmission. H ₂ O, CO ₂ and O ₂ emissions (consumption) based on combustion of process wastes for energy.					
(b) Animal manure, normally recycled to land. Not including emissions from free-ranging animals.					(i) Process wastes of the organic chemical sector are partly combustible and partly incombustible. Detailed breakdown not available.					
(c) Probably burned for energy recovery. H ₂ O, CO ₂ and O ₂ emissions (consumption) are shown in parentheses.					(j) Iron & steel slag are by-products with many uses. Concentration wastes are included with mining sector. CO ₂ emissions are included with combustion.					
(d) Metal ore mining in U.S.					(k) CO ₂ emissions are included with fuel combustion.					
(e) Non-metallic mineral mining in U.S. including alumina and phosphate concentration wastes.										
(f) Coal mining, not including coke oven emissions.										
(g) Petroleum & gas drilling.										

References

- [Brown & Wolf 1984] Brown, Lester R. & Edward C. Wolf, *Soil Erosion: Quiet Crisis in the World Economy*, Worldwatch Paper (60), Worldwatch Institute, Washington DC, September 1984.
- [Deevey 1970] Deevey, E.C., "Mineral Cycles", *Scientific American* **223**, 1970 :148-158.
- [ECOPLAN 1992] Ecoplan International, *New Developments in Tire Technology: Technological Change & Intermaterials Competition in the 90s & Beyond*, Multi-client Industry Report, Ecoplan International, Paris, 1992.
- [Gaines & Wolsky 1981] Gaines, L.L. & A.M. Wolsky, *Energy & Materials Flows in Petroleum Refining*, Technical Report (ANL/CNSV-10), Argonne National Laboratory, Argonne IL, February 1981.
- [Holmbom 1991] Holmbom, Bjarne, *Chlorine Bleaching of Pulp: Technology & Chemistry, Environmental & Health Effects, Regulations & Communication*, Case Study (ISBN 952-9596-00-6), Abo Akademi, Turku/Abo Finland, April 1991.
- [IBRD 1980] International Bank for Reconstruction & Development, *Environmental Considerations in the Pulp & Paper Industry*, IBRD, Washington DC, December 1980.
- [LeBel 1982] LeBel, Phillip G., *Energy Economics & Technology* (ISBN 0-8018-2773-6), The Johns Hopkins University Press, Baltimore, 1982.
- [Lowenheim & Moran 1975] Lowenheim, Frederick A. & Marguerite K. Moran, *Faith, Keyes, & Clark's "Industrial Chemicals"*, Wiley-Interscience, New York, 1975. 4th edition.
- [Manzone 1993] Manzone, R., *PVC: Life Cycle & Perspectives*, Commett Advanced Course, Urbino, Italy, 1993.
- [MIT 1993] Technology Business & Environment Program, Center for Technology Policy & Industrial Development. *Dimensions of Managing Chlorine in the Environment: Report of the MIT/Norwegian Chlorine Policy Study* Massachusetts Institute of Technology, Cambridge MA, March 1993.
- [Obernberger 1994] Obernberger, Ingwald, *Characterization & Utilization of Wood Ashes*, Technical Paper, Institute of Chemical Engineering, Technical University, Graz, Austria, 1994.
- [OECD/IEA 1991] International Energy Agency, *Energy Statistics of OECD Countries 1980-1989*, OECD, Paris, 1991.
- [Rogich 1994] Rogich, Donald G., *Personal Communication*, January 1994.
- [SAI 1985] Science Applications International Corporation, *Summary of Data on Industrial Nonhazardous Waste Disposal Practices*, EPA Contract (68-01-7050), Science Applications International Corporation, Washington DC, 1985.
- [Smil 1993] Smil, Vaclav, *Nutrient Flows in Agriculture: Notes on the Complexity of Biogeochemical Cycles & Tools for Modeling Nitrogen & Phosphorus Flows in Agroecosystems*, unpublished working paper, 1993.
- [STATAB 1991] United States Bureau of the Census, *Statistical Abstract of the United States: 1991*, United States Government Printing Office, Washington DC, 1991. 111 edition.

- [Subak et al 1992] Subak, Susan, Paul Raskin & David von Hippel, *National Greenhouse Gas Accounts: Current Anthropogenic Sources & Sinks*, Report, Stockholm Environmental Institute, 89 Broad St. Boston MA, January 1992.
- [Torrey 1978] Torrey, S. (ed), *Coal Ash Utilization: Fly Ash, Bottom Ash & Slag* [Series: Pollution Technology Review #48], Noyes Data Corporation, Park Ridge NJ, 1978.
- [Ulrich 1990] Ulrich, Alice H., *U.S. Timber Production, Trade, Consumption & Price Statistics 1960-88*, Miscellaneous Publication (1486), Forest Service, United States Department of Agriculture, Washington DC, December 1990.
- [UNIS 1988] United Nations Statistical Office, *Industrial Statistics Yearbook: Commodity Production Statistics 1988 II* (ISBN 92-1-061137-3), United Nations, New York, 1988.
- [USBuMines 1987] United States Bureau of Mines, *Minerals Yearbook*, United States Government Printing Office, Washington DC, 1987.
- [USBuMines 1988] United States Bureau of Mines, *Minerals Yearbook*, United States Government Printing Office, Washington DC, 1988.
- [USBuMines 1989] United States Bureau of Mines, *Minerals Yearbook*, United States Government Printing Office, Washington DC, 1989.
- [USDA 1991] United States Department of Agriculture, *Agricultural Statistics*, United States Government Printing Office, Washington DC, 1991.
- [USDA 1992] United States Department of Agriculture, *Agricultural Statistics* (ISBN 0-16-041621-3), United States Government Printing Office, Washington DC, 1992.
- [USDOC-a 1992] United States Department of Commerce, *Current Industrial Reports: Inorganic Chemicals*, United States Department of Commerce, Washington DC, 1992.
- [USDOE 1980] United States Department of Energy, *Technology Characterizations*, Technical Report (DOE/EV-0061/1), United States Department of Energy, Washington DC, January 1980.
- [USEPA 1986] United States Environmental Protection Agency Office of Solid Waste, *Waste Minimization Issues & Options*, NTIS PB-87-114369 (EPA-530-SW-86-041), United States Environmental Protection Agency Office of Solid Waste, Washington DC, October 1986.
- [USEPA 1988] United States Environmental Protection Agency, *Solid Waste Disposal in the United States*, Report to Congress (EPA-530-SW-88-011), United States Environmental Protection Agency, Washington DC, 1988.
- [USEPA 1991] United States Environmental Protection Agency Office of Solid Waste, *1987 National Biennial Report of Hazardous Waste Treatment, Storage & Disposal Facilities Regulated Under RCRA*, NTIS PB-87-114369 (EPA-530-SW-91-061), United States Environmental Protection Agency Office of Solid Waste, Washington DC, 1991.
- [USITC 1991] United States International Trade Commission, *Synthetic Organic Chemicals 1991*, United States Government Printing Office, Washington DC, 1991.
- [USITC 1992] United States International Trade Commission, *Synthetic Organic Chemicals 1992*, United States Government Printing Office, Washington DC, 1992.

[USOTA 1984] United States Congress Office of Technology Assessment, *Wood Use: U.S. Competitiveness & Technology; Vol II - Technical Report*, Report (OTA-M-224), United States Congress Office of Technology Assessment, Washington DC, November 1984.

[USOTA 1992] United States Congress Office of Technology Assessment, *Managing Industrial Solid Wastes from Manufacturing, Mining, Oil & Gas Production, & Utility Coal Combustion*, Background Paper (OTA-BP-O-82), United States Congress Office of Technology Assessment, Washington DC, February 1992. [ISBN 0-16-036116-8]

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