REGARDING

SUGGESTED NANOMATERIAL PRODUCTION VOLUMES

Introduction:

Production volumes are a starting point for life cycle analyses and other risk assessment methodologies. This information is difficult to obtain as it involves issues of definitions, anti-trust, confidential business information and traceability. The following table is a listing of suggested nanomaterial production volumes in metric tons/year (t/a). Background explanations for the preferred values ("this work") and a commentary on applying market research to life cycle analyses are also provided.

Suggested Nanomaterial Production Volumes

MATERIAL	HENDREN 2011 US ONLY	PICCINNO 2012	EUR. COM. 2012 (2010 SRI)	KELLER 2012 (2010 FUTURE MARKETS)	THIS WORK	GROWTH TREND
Carbon Black	No Estimate	No Estimate	9,600,000	No Estimate	≥ 10,000,000	GDP
Silicon Dioxide	No Estimate	5,500	1,500,000	95,000	> 2,400,000	GDP
Al2O3	No Estimate	55	200,000	35,000	>> 200,000	GDP
Titanium Dioxide	7,800 - 38,000	3,000	10,000	88,000	>30,000	>GDP
Cerium Oxide	35- 700	55	10,000	10,000	<1,000	>> GDP
Zinc Oxide	No Estimate	550	8,000	34,000	8,000	GDP
Zirconia	No Estimate	No Estimate	2,500-3,000	No Estimate	3,000	>GDP
Carbon Nanofibers	No Estimate	No Estimate	300-500	No Estimate	>500	>GDP
CNTs	55 - 1,101	300	200-250	3,200	250	Uncertain
Cu(OH)2 and Oxide	No Estimate	No Estimate	No Estimate	200	>>150	GDP
FeOx	No Estimate	55	No Estimate	42,000	>>> 1	Uncertain
Silver	2.8 - 20	55	22	452	>70	Uncertain
References	-1	-2	-3	-4		

The values under "this work" parallel the European Commission's reliance on a 2010 SRI market research report over that of Future Markets as reported in Keller, *et a*l. The latter tends to include textured surface applications in addition to commercially available particles-as-ingredients. Regulatory activities have focused on particles used as ingredients and not products, i.e., nanostructured materials. The following commentary provides interpretive "diagnosticity" (5) for the reader's consideration.

Commentary Supporting the Preferred "This Work" Values:

(1). Carbon black production is also available from IARC (6) based on Auchter (7). Considering time lags surrounding each study and intervening economic events, the IARC's higher value is recommended.

(2). Silicon dioxide has several registered forms (8). SRI reports on volumes for synthetic amorphous silica, not silica fume (900,000 from ref. 9) nor diatomaceous earth. Gaffet and colleagues (10) suggested French "silice naturelle" volumes of 200,000 t/a in 2006, but was not cited by the European Commission (EC). The suggested volume for "this work" may therefore be missing a component, diatomaceous earth, but in all cases, overall market growth should align with GDP economic growth.

(3) Aluminum oxides and precursor hydroxides (Boehmite) have not been discussed extensively. Gaffet (10) suggested 469,000 t/a for France in 2006, while the 2010 SRI value is only 200,000 t/a. Definitional differences are likely. The market should grow with the general economy, but supplier-reported production volumes will track increasing awareness of nanomaterial definitions.

(4). The SRI titanium dioxide production volumes are a known underestimate (page 49 of ref. 3). DuPont, a manufacturer of both pigment and nanoscale TiO_2, suggests 0.25 to 0.6% of global pigment grade volume is nano-TiO_2 (11, 12), leading to 30,000 t/a, but with additional volumes likely to be uncovered in Asia.

(5). Rare earth supply tightened dramatically in 2011. Freight on board (FOB) China pricing for the lower value "bulk" cerium oxide was $4.50/kg in 2008, then $138/kg in 2011 and was $12/kg in 2013. Market retrenchment, unforeseen by SRI and Future Markets in 2010, occurred when customers shifted to alternative materials, e.g., ZnO for UV protection in wood varnishes. Long-term supply contracts and stockpiles would have dampened effects for those markets that are especially reliant on CeO_2 properties, explaining the projected 10% growth rate for glass polishing (13), a category that includes the $120 million CMP market (14). The SRI and Future Markets reports are definitely overestimates until pricing returns to historical levels. Additionally, the retrenchment exposed the almost total reliance on Australian mining companies for market information (13). A bottoms-up analysis for CeO_2 on a particle-as-ingredient basis indicates less than 500 t/a outside of China. The French Registry (15), for example, lists 108 tons for CeO_2, which probably represents Rhodia's (now Solvay) production levels. Doubling to account for the other major, Hitachi, and adding overestimates for CeO_2 as a diesel fuel additive leads to the suggested < 1,000 t/a (16).

(6). With zinc oxide, Keller, *et al.* (4) report on a wider range of applications than SRI. Weight is given here to the implicit EC *imprimatur*.

(7). Zirconium oxide, optical fiber ferrules should drive growth.

(8). & (9). Carbon nanofibers and carbon nanotubes share markets with carbon black, but respond to different regulatory agency stances regarding chemical registration. Recent SNURs indicate a relatively small U.S. carbon nanotube market, probably 20 t/a (17), which is confirmed by reports of low plant utilization (18) and by market exits (Unidym to Korea and Bayer ceased production). Keller, *et al.* (4) report 800 t/a for CNTs in just composites, a value similar to SRI's total for both CNFs and CNTs in all applications. Keller, *et al.'s* total of 3,200 t/a includes markets that are not prominent in EPA's SNURs. Hence, the preference here for the SRI values.

(10). Copper Hydroxide and Oxide are not in the EC document. Prominent applications in Keller, *et al.* (4) for copper and copper oxides include both particle and textured surface applications. Copper as the carbonate or oxide find use as wood preservatives (19) and along with copper hydroxide as agricultural pesticides (20). In 2011, California reported that 900 tons of Cu(OH)2 and copper oxides were applied to crops and a further 1,880 tons (21) as a fumigant. Combining the particle applications in Keller, *et al.* (70 t/a) with 10% of the crop pesticide volumes yields a suggested >>150 t/a. As with alumina, these volumes may rise dramatically as suppliers become increasingly aware of regulatory definitions.

(11) Iron oxides/hydroxides were reported by manufacturers and importers in the 2013 French Registry (15). As with aluminum oxides and hydroxides, the chemistry of these minerals is complex and include yellow iron oxide, hematite and magnetite. Nanoscale zero valent iron should be considered part of this group due to its reaction products.

(12). Early market estimates for silver (<1 t/a in 2005, a projected 7 t/a for 2010, (22) and 4.7 t/a in 2008 (23) presage the 22 t/a from SRI. Developments in China (recently reported as 45 t/a in 2010 (24)), may be under-reported, leading to the suggested > 70 t/a.

Other materials of note: The French Registry (15) has a extensive listing of materials, perhaps the first where industry responded using a uniform definition of nanomaterial. Calcium carbonate at 34,000 metric tons is a reminder that the Paper Industry is a significant consumer of nanomaterials for coatings and as process additives. There were also a number of organic polymers listed.

Some general comments regarding the production volumes are appropriate. Volume ranking highlights the older, passive fillers that often have mineralogical counterparts. Carbon black, carbon nanofibers and carbon nanotubes share markets for reinforcement, electrical conductivity and thermal conductivity (25). Silicon dioxide has sub-categories (and CASnumbers, (8)): diatomaceous earth, synthetic amorphous silica, silica fume and quartz that also span descriptors such as natural, incidental and engineered. All are "manufactured" when processed into commercial products leading to the combined volumes in the table. (This reflects U.S. practice and differs from Europe where physical processing leaves "natural" as natural.) Adjusting the upper boundary of nanoscale would affect TiO_2 estimates greatly, due to the 5 million t/a of pigment grade TiO_2, where the mean primary particle size is between 250 and 300 nm.

CB, SiO_2, Al_2O_3 and TiO_2 describe a class of "large volume, long-term-use" materials relative to the remaining particles and future novel compositions. Several markets utilize these "large volume, long-term-use" nanomaterials. The tire industry, known for carbon black, is also a significant market for precipitated silica. The cement industry's use of silica fume arose from environmental limits on ferrosilicon plant smokestack emissions. The paper industry utilizes process additives (antifoams, retention aids) and paper fillers (alumina, silica, calcium carbonate) that can be nanoscale, and it is also a source of nanocellulose, which may displace carbon nanotubes and nanofibers in reinforcement. Elastomer & polymer compounders and the paint & coatings industries use fillers extensively.

Applying Market Research Results to Life Cycle Analyses:

At industry meetings, in trade associations, colleagues are reminded of antitrust law requirements such as, "Don't, in fact or appearance, discuss or exchange information on:... company data on costs, production, capacity inventories, sales, etc...." (26), and they further understand that not complying can lead to allegations of price-signaling as in the 2013 pigment TiO_2 suit settled for $163.5 million (27). It is not surprising to them that consolidated nanomaterial production volumes are difficult to obtain or that intermediaries, such as market research firms, provide the estimates. They also recognize that market research is an art form reliant on information gained in interviews, financial reports, trade show handouts, etc., that must be combined with internal market knowledge to be useful.

Academic colleagues, desiring realistic volume figures for life cycle analyses, have tended to utilize similar stratagems as market research firms. For silver in the table above, these are: a personal communication (28) for 500 t/a; a trade association analysis (28) for 1230 t/a; a survey of experts (2) for 55 t/a, with a range of 5.5 to 550 t/a; and "creative approaches" combining order inquiries with proxy parameters (1) for a U.S. production figure of 2.8 to 20 t/a. Keller, *et al.* (4) and the European Commission's staff (3) cite market research reports for 450 t/a and 22 t/a, respectively.

Market research practitioners utilize superior access to supply chain resources and a detailed knowledge of end use markets to arrive at self-consistent findings. (For a discussion of financial reporters operating in the nanotechnology environment, see reference 29.) Industrial purchasers of market research reports, unlike academic colleagues, temper any findings with their own market knowledge. These would be sales calls, patents, related product line offerings, collaborations trade conventions and the like.

Considering the almost anecdotal nature of commercial market research reports, one wonders at their value beyond their intended purpose of supporting business decision making. The academic or government scientist does not have internal marketing departments scrutinizing sales revenues, call reports, supplier and customer contracts and collaborations. They are also not actively probing the competitive marketplace through pricing, and they did not participate in the market research firm's interviews. In many respects, the academic efforts responded to questions about consumer and environmental exposures in an uncertain atmosphere regarding nanomaterial governance. Their tools have been computer models for material flows that essentially re-purpose market research.

Silver illustrates a pitfall in that many authors mistook prominence in the PEN listing for large production volumes, even though verifying the products' commercial status has turned out to be very difficult (30). There are additional considerations.

Life cycle analyses track a material from production through to disposal (4 and 28), and production volumes allow for calculating general background exposure levels. Specific production site knowledge is useful for estimating localized environmental exposure such as along a river system, and there are also generic scenarios for point sources (31). Total production volumes also act as surrogates for the frequency of everyday incidents such as spills, broken bags, accidental exposures and their locations, e.g., waste treatment plant excursions. However, anticipated environmental background levels are distinct from the frequency and duration of acute exposures (32).

The investigator interested in establishing a "realistic" or "environmentally relevant" exposure level for nanomaterial testing faces several challenges:

- there are distinctions to draw among environmental concentration, exposure level and dose, with models just calculating concentration;
- there are several assessment methods with accompanying nuances: risk assessment, life cycle analysis (and its sub-category of life cycle impact assessment), comprehensive environmental assessments and multi-criteria decision analysis (33);
- there are simplifications, such as not addressing production discharge permitting, mixing zones and seasonal stream flows, that disconnect the computational models from current regulatory permitting practice; and
- there remain open questions on measuring environmental impacts beyond acute toxicity, e.g., endocrine disruption.

Whether as narratives used to set research priorities (34) or as computer models calculating a predicted environmental concentration (28), these methods establish material flows (mass) passing from production-to-use-to-disposal. Practitioners utilize that mapping to identify life cycle stages or ”hot spots” allowing scenario-specific information to be applied to material flows in order to estimate air or water concentrations. However, estimating environmental exposure is more challenging due to the definition of nanomaterial. Nanoscale materials are defined by size and not by property (35). Without recognized properties or known effects, it becomes difficult to verify life cycle models, leading to over- or underestimates of exposure (36). Recent articles (37, 38, 39) report on nanoscale TiO_2 content in biosolids exceeding nearby production or consumption with paint as an apparent source, i.e., non-nano-pigment grade TiO_2 (36, 37), which has a nanoscale tail in particle size (40).

Additionally, particles respond to environmental conditions, which for silver can entail repeated dissolution and re-precipitation, as well as sulfide formation (41, 42, 43). While silver sulfide does not readily re-oxidize, other metals and metal oxides do (43). Effectively, non-nano sources, sinks, changes in surface chemistry and chemical transformations that also meet the definition of nanomaterial are possible at each environmentally relevant stage of the life cycle and are not necessarily included in the mass balance assumptions of many life cycle models.

Concluding Remarks:

By attributing the difficulties encountered in obtaining production information to industry reluctance, workers in this field overlook the elastic nature of the definitions. A simple change from <100 nm to <300 nm brings in 5 million t/a for just TiO_2. The arguments surrounding “realistic” start with a narrow definitions that leads to small volumes, which when regionalized by rainfall or river flow, lead to insignificant concentrations.

Yet, formulated household products lead to immediate human exposure and, for silver, there is past medical experience to consider (44). Lorenz, *et al*. (45) and the Magic Nano incident (46) demonstrate the very real exposure potential with aerosol sprays. These, however, are set aside using terms such incidental. Spills and everyday discharge into ponds, seasonal flow rivers, and estuaries are invariably viewed beyond the scope of models.

Overall, a false sense of acceptable environmental relevance stops further inquiry that might identify unsuspected concentration cycles or adverse effects of sub-micron particles, not just nanoscale ones.

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